

**A**  
**Dissertation Report**  
**On**  
**Enhancing Light Extraction Efficiency of GaN/InGaN Light**  
**Emitting Diode by using Nano Structures**  
*Submitted to*  
*Malaviya National Institute of Technology, Jaipur*  
*in the partial fulfilment of the requirements for the award of the degree*  
*of*  
**Master of Technology**  
**in Electronics & Communication Engineering with Specialization**  
**in “Wireless & Optical Communication”**

*by*  
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**July 2017**

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**DEPARTMENT OF ELECTRONICS AND  
COMMUNICATION ENGINEERING  
MALAVIYA NATIONAL INSTITUTE OF TECHNOLOGY  
JAIPUR- 302017, RAJASTHAN, INDIA**

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**CERTIFICATE**

This is to certify that the dissertation report entitled “**Enhancing Light Extraction Efficiency of GaN/InGaN Light Emitting Diodes by using Nanostructures**” being submitted by **ALKA JAKHAR (2015PWC5135)**, in partial fulfillment of the requirement for the award of the degree of **Master of Technology** in **Wireless & optical Communication Engineering** of Malaviya National Institute of Technology, Jaipur is a record of bonafide research work carried out by him under my supervision. The contents of this dissertation work in full or in parts have not been submitted to any other institute or university for the award of any degree or diploma.

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I **Alka Jakhar**, declare that the dissertation report entitled “**Enhancing Light Extraction Efficiency of GaN/InGaN Light Emitting Diodes by using Nanostructures**” being submitted by me in partial fulfillment of the degree of **M.Tech (Wireless & Optical Communication)** is a research work carried out by me under the supervision of **Dr Vijay Janyani** and the contents of this dissertation report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma. I also certify that no part of this seminar report has been copied or borrowed from anyone else. In case any type of plagiarism is found out, I will be solely and completely responsible for it.

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## **ACKNOWLEDGMENT**

My deepest gratitude goes to my guide Dr. Vijay Janyani, Associate Professor, Department of Electronics and Communication Engineering, MNIT Jaipur and Dr. Manish Mathew, Senior Scientist, CSIR-CEERI Pilani. This work would not have been successful done without their guidance. I wish to express my sincere gratitude to Dr. Vijay Janyani for providing me an opportunity to do my project work in “CSIR-Central Electronics Engineering Research Institute, Pilani, Rajasthan”. His encouraging attitude has been immensely valuable in keeping me motivated and helping me surmounting all obstacles in my work. He has been a great support for me.

I would like to thank Dr. Manish Mathew for his extraordinary guidance and support throughout the project work. He has been a great teacher, a great guide and above all, a great human being. It is always my pleasure to interact with him on any topic. I sincerely thank scientists and other staff members of CSIR-CEERI who rendered their help during the time of my project work.

I would also like to thank Mr. Nikhil Deep Gupta, based on whose work I could get the idea to start my project. In addition, I feel a deep sense of gratitude to my parents for their encouragement and support. Finally, I would like to give my soul respect to all my mates of the specialization of Wireless & Optical Communication for their constant support and encouragement.

I thank all my colleagues and the technical and non-technical staff of Department of Electronics and Communication Engineering, MNIT Jaipur for supporting and encouraging me throughout this work

ALKA JAKHAR

## **ABSTRACT**

Recently, III-V nitrides and their alloys have emerged as promising semiconductor materials for optoelectronic applications such as full colour LCD displays, biomedical sensors, optical data storage, electronics for aerospace and automobiles. Among these nitrides, GaN have attracted much interest because of its wide band gap 3.4eV and ability to form alloys with other group III elements aluminum and indium which have band gaps of 6.2eV and 0.7eV respectively with spanning of almost ultraviolet to blue, green, yellow wavelengths.

One of the main difficulties associated with these devices is lack of suitable substrate and large lattice mismatch occurs between different hetero layers, which results in strain induced piezoelectric and spontaneous polarization which limits the efficiency of these devices. One of the experimental methods to reduce polarization is to fabricate nanostructures leading to strain relief and quantum confinement due to high Surface to Volume Ratio, hence increase in radiative recombination efficiency of LEDs and LASERS. We demonstrate a simple “top-down” patterning fabrication process of GaN nanorods using nano mask of silver and nickel during Reactive Ion Etching (RIE). The shape and morphology of GaN nanorods was studied using Scanning Electron Microscopy (SEM). We obtained nanorods with diameter varying from 90 nm- 200 nm in case of samples in which Ni was used as a nanomask. While the diameter varying from 80nm – 390nm in case of Silver nanomask.

In addition, the performance of GaN based LEDs is hindered mainly because of total internal reflection phenomenon which prevents light to escape out completely from the device. In order to enhance light extraction efficiency, nano roughening the top p-GaN layer of LED were used in this thesis. The nano-roughened surface improves the escape probability of charge carriers inside the LED structure. Nano-roughening the top p-GaN surface using Ag nanomask increased the output light power of the conventional GaN-based LEDs by a factor of 1.70. While nanoroughened LED using ITO nanomask have shown 1.39 times more efficiency as compared to other conventional LEDs with enhanced light extraction efficiency.

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## ACRONYMS

The following acronyms are used in this work-

LED	Light Emitting Diode
GaN	Gallium Nitride
InN	Indium Nitride
AlN	Aluminum Nitride
MQW	Multi Quantum Well
QCSE	Quantum Confined Stark Effect
UV	Ultra- Violet
Ag	Silver
ITO	Indium Tin Oxide
Ni	Nickel
CCFL	Cold Cathode Fluorescent Lamp
SiC	Silicon Carbide
GaAs	Gallium Arsenide
Al <sub>2</sub> O <sub>3</sub>	Sapphire
LD	Laser Diode
VPE	Vapor Phase Epitaxy
MBE	Molecular Beam Epitaxy
MOCVD	Metal Organic Chemical Vapor Deposition
ODG	Opto-Electronic Group
CEERI	Central Electronic Engineering Research Institute
TS-CCS	Thomas Swan Close Coupled Showerhead

TMGA	Trimethylgallium
TMIn	Trimethylindium
NH <sub>3</sub>	Ammonia
TMA	Trimethylaluminium
Cp <sub>2</sub> Mg	Biscyclopenta-dienyl-magnesium
Si <sub>2</sub> H <sub>6</sub>	Disilane
EBL	Electron Blocking Layer
RGB	Red- Green-Blue
LLO	Laser Lift Off
QWB	Quantum Well Barrier
RIE	Reactive Ion Etching
SEM	Scanning Electron Microscopy
TCO	Transparent Conducting Oxides
TCE	Trichloroethylene
C <sub>3</sub> H <sub>2</sub> O	Acetone
CH <sub>3</sub> OH	Methanol
RTA	Rapid Thermal Annealing
PECVD	Plasma Enhanced Chemical Vapor Deposition
EL	Electro-luminescence

## Chapter 1 Introduction

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The direct and wide band gap semiconductor members of group III- nitride family includes Gallium nitride (GaN), Aluminum nitride (AlN), Indium Nitride (InN) have emerged as the leading materials for optoelectronic devices. Recently, they may be emerged as the suitable material for devices such as UV detectors [1,2], UV and visible light emitting diode [3,4,5], laser diodes (LD) [6], surface acoustic wave devices and high power electronic devices such as power amplifiers [7]. Among these semiconductor group III nitrides, gallium nitride is the widely used material because GaN is a large and direct band gap (3.4 eV) material with high chemical and mechanical stability exhibiting significant hardness. It is useful to use large band gap semiconductors because radiative recombination efficiency is directly related to band gap. Because of wide band gap, these materials are less sensitive to temperature variations.

The applications of GaN are not only limited to light emitting sources but also for high frequency and high power applications. It can easily form alloys with other group III elements such as aluminum (Al) and indium (In), which is helpful in fabricating of hetero structured devices. The band gap of GaN, InN, and AlN is 3.4 eV, 0.7 eV, and 6.2 eV respectively. By varying the amount of elements in an alloy, and thus from tunable bandgap of these materials, one can obtain almost electromagnetic frequency range starting wavelength from 300nm up to 1500nm which almost covers the entire optical spectrum including the near infrared, the entire visible, and the near and deep ultraviolet portion. Figure 1.1 shows variation of band gap with lattice parameter of GaN and its alloys.

The unique properties of III-V nitrides such as thermodynamically stable Wurtzite structure, low dielectric constant with high thermal conductivity, high dielectric breakdown field, high reliability as operated under harsh environment makes them adequate for solid state lightening applications include outdoor TV, traffics signals, flashlights and high density optical storage systems.

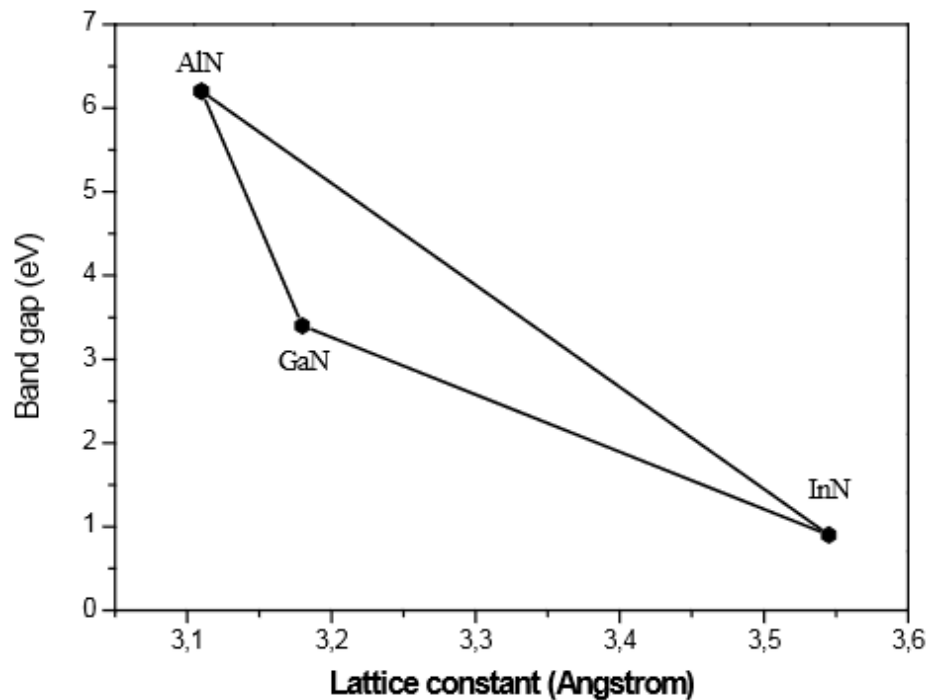


Figure 1.1 Band gap energy versus lattice constant for nitride materials

The existing traditional lightening system of fluorescent lamps and incandescent bulbs can be significantly replaced by light emitting diodes (LEDs) because of their high efficiency. LEDs are widely used sources of illumination because of small size, low energy consumption, high durability and high luminescence efficiency. In LEDs, there is radiative recombination of electrons and holes at the junction in order to generate light. The III-Nitride semiconductors emerge as a promising candidate to obtain light emitting diodes to produce blue and green colour light due to its high brightness efficiency. GaN LED was invented by Shuji Nakamura et.al. in 1993. Invention of GaN based blue LED has become revolutionize in the field of solid state lighting technology. GaN LEDs have wide range of applications in the field of illuminations like display information, sensing system, flashlights, backlights in screen for mobile and television, digital watches, calculators, solid state lighting industry, to enhance photosynthesis in plants as a grow light and high power and UV LEDs for sterilization of water etc.

In order to produce white light from LEDs, the oldest method is mixing of fundamental red, green and blue colour. But this method has not been proved to be

efficient because this requires an individual driver control circuitry for each LED, and additional processing steps for chip integration and also different voltage supply must be provided to each LED chip. This results in increase in overall cost of the system to generate white light. Now days, this technique is often used. The second technique which is commercially employed is the use of GaN/InGaN-based blue-emitting LED coated with yellow phosphor to convert part of the blue emission to longer wavelength ( $\lambda$ ) for white light generation.

However, the light extraction efficiency of LEDs are not high and it is depend on the geometry of the device. Most of the light emitted after recombination in quantum wells cannot emitted into free space. The reason is reflection of light back again and again from the top surface of LEDs. This reflected light is absorbed by metal n and p electrodes, defects and quantum wells which cause extra heat in the device that is harmful for life of LEDs. More ever, the responsivity of human eyes is also very low for high wavelength of blue and green that means blue LEDs should have high extraction efficiency.

Main aim of this thesis is to improve the light extraction efficiency of LEDs by using nanostructuring. There are several ways to increase output light power which includes increase in internal quantum efficiency or light extraction efficiency. These two efficiencies are inter independent from each other. Internal quantum efficiency can be improved by increasing carrier confinement in active region for higher radiative recombination. It can be improved during the growth of layered structure such as optimized use of In content in quantum wells, proper choice of thickness of quantum well layers, incorporating electron blocking layers and current spreading layer etc. on the other hand, light extraction efficiency can be improved by extracting most of the photons from active region into free space. Because of total internal reflection phenomenon at GaN air interface, most of the photons reflected back into the device. Thus proper designing of the top layers may solve this problem by trapping most of the trapped light in the device can escape into free space.

## **1.1 Organization of Thesis**

This thesis is mainly concentrated on improvement of optical properties of LEDs. In this chapter, a brief idea of aim of this work is given.

**Chapter 2** consists of information about GaN, material properties, polarization and lattice mismatch issues. The steps of growth of GaN based LED wafer by using MOCVD system used in this thesis are given.

**Chapter 3** presents working principle and optical parameters of light emitting diodes (LEDs). The introduction of InGaN/GaN based multiple quantum well (MQW) LEDs are given.

**Chapter 4** gives details of first part of this thesis. In the first part, nanorods on LED were fabricated in order to reduce lattice mismatch between hetero layers. In the second part, nano-rough LED was fabricated in order to enhance light extraction efficiency. This chapter deals with first part mainly. The need of nanostructures for optical devices and methods of fabrication of nanostructures are described. We have shown top- down approach of fabrication of nanorods on GaN based LEDs. In this approach, Nickel and Silver metal were used as a nanomask and then Reactive Ion Etching was performed. This is an easy approach as compared to other lithography techniques for fabrication of nanorods. By nanostructuring, the lattice mismatch occurs between hetero layers of LEDs get reduced and hence reduction in QCSE. By reducing QCSE, there is blue shift in wavelength and we can obtain desirable wavelengths in visible light region. Scanning Electron Microscopy (SEM) results of these nanorods LED are given in chapter fourth.

**Chapter 5** deals with second part. For roughening the top p-GaN layer of LED, we have used Silver and ITO as a nanomask. The steps of fabrication of LED wafer are discussed in this chapter. The details of system such as RTA system, Evaporation Beam system, Photolithography, Electroluminescence etc used for fabrication at CSIR-CEERI, Pilani are given.

**Chapter 6** describes the measurement about I-V Curves and wavelength v/s Intensity Curves for these LEDs. An increase in the Electroluminescence intensity of the nanoroughened LED with Ag and ITO nanomask by 1.7 and 1.39 times as compared to as-grown LED is observed. The details of Hall measurement which provides information about carrier concentration, carrier mobility are also given.

**Chapter 7** concludes the work.



## Chapter 2 Gallium Nitride properties

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### 2.1 Introduction

Semiconductor group III-Nitrides emerge as promising candidate for optoelectronics because of their wide and direct band gap properties which almost covers entire full visible range, IR and most of ultra violet region. They can be used in high frequency and high temperature optoelectronic devices such as LEDs, lasers photo detectors, high power transistors, high density electronic devices, sensors etc. under harsh environmental conditions. In recent years, LEDs are dominating lightening market by replacing CCFL and incandescent bulbs. LED usages such as backlights in flat panel displays, traffic lights, sensing systems, digital watches, street lights etc. have been increasing continuously day by day.

The Group- III nitrides show several remarkable properties which makes them attractive for solid state device applications. These are different from conventional semiconductor materials as they exist in thermodynamically stable Wurtzite structure. Gallium Nitride semiconductor provides high breakdown voltage operation and thermal conductivity which leads to faster operating speed. GaN's wide direct band gap, high dielectric breakdown field, good electron and hole transport properties [8,9] (an electron mobility possibly in excess of  $2000 \text{ cm}^2/\text{V}^{-1}/\text{sec}^{-1}$ ), and favorable high electrical and thermal conductivity make these materials suitable for high power and high temperature electrical and electronic devices [10]. It is also an important characteristic of III-nitrides that they are very robust materials with high melting points and favorably high mechanical strength with large withstand capability at high temperature.

### 2.2 General properties

#### 2.2.1 Crystal Structure

Semiconductor group third nitride materials exist in three crystalline form i.e. wurtzite, zinc blende and rock-salt structures. Among these, the most

thermodynamically stable structure is Wurtzite. The zinc blende structure for GaN and InN has been made stable by epitaxial growth of thin films of these materials on  $\{0\ 1\ 1\}$  crystal planes of cubic substrates such as SiC [11], Si [12] and GaAs [13]. The rock salt structure exists only under high pressures and, therefore, is a laboratory form of exercise. The wurtzite structure has a hexagonal unit cell and thus two lattice constants,  $c$  and  $a$ . It contains six atoms of each type. The lattice parameter  $a$  gives the distance between atoms at different axes in the hexagonal plane. The lattice constant  $c$  describes the spacing of identical hexagonal planes [14].

Three common types of crystal planes are usually used in a wurtzite system. The  $c$  plane that is perpendicular to the  $[0001]$  direction is called polar. Crystal planes that are parallel to the  $c$ -axis are called non-polar planes i.e.  $a$  and  $m$  planes as shown in Figure 2.2. The planes that make an angle different from  $0^\circ$  and  $90^\circ$  with the  $c$ -axis are called semi polar ( $r$ -plane).

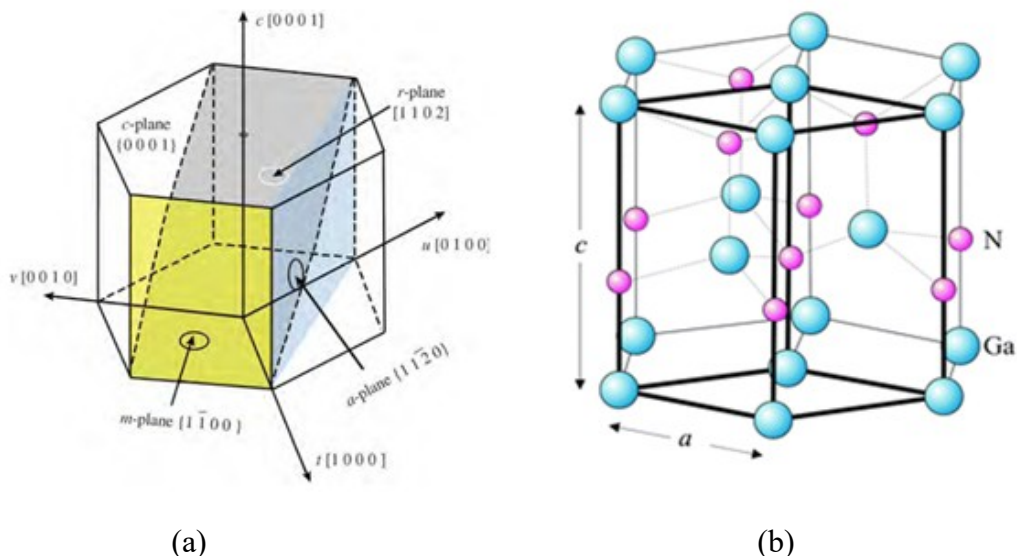


Figure 2.1a) Atoms position in Wurtzite Structure with indication of lattice parameters  $a$  and  $c$ ; b) Main Atomic Planes [14]

### 2.2.2 Spontaneous and Piezoelectric Polarization

Wurtzite structured III- nitrides possess polarization properties in the absence of external electric field which distorts band diagram of quantum wells and hence reduction in radiation efficiency. The total polarization field is the combination of spontaneous and piezoelectric polarization components [15]. Wurtzite structures show central symmetry to  $m$  and  $a$  plane but there is no central symmetry with respect to  $c$ -plane. GaN LEDs are generally grown on (0001) sapphire and (0001) SiC along the

polar c-axis of the wurtzite crystal. Thus semiconductor nitrides exhibit spontaneous polarization due to the lack of inversion symmetry. This spontaneous polarization is an important parameter in case of structures involving heterointerfaces with varying electro negativity. As nitrogen is the most electronegative and smallest group V element, resulting in highly ionic metal-nitrogen bonds. When multiple nitride materials are placed in layered fashion, the individual dipole moments no longer cancel along c-axis, results in induced charges at the interface.

Another component is piezoelectric polarization which occurs due to lattice mismatch. As different materials have different lattice parameters, due to which lattice mismatch occurs between different nitride layers of hetero structures results in development of strain [16]. Because of this induced strain, piezoelectric polarization develops in hetero structured devices.

As a result of these polarization effects, the InGaN/ GaN quantum wells get distorted due to altered band diagram and results in reduction of radiation recombination efficiency [17].

### **2.2.3 Lattice Mismatch**

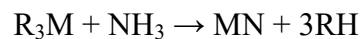
One of the particular difficulties in the growth of nitrides is lack of sufficient large crystals used as substrate material. There are different parameters which must be satisfied while choosing proper substrate with large lattice matching with GaN. The most important is that substrate should be stable at high temperature around  $1000^{\circ}\text{C}$ – $1500^{\circ}\text{C}$  since growth of GaN around this temperature is carried in MOCVD. Also the crystal structure of substrate should be almost similar to that of GaN with large lattice matching. In addition, large thermal match between substrate and GaN should present in order to prevent crack and defect generation while the film cools down to room temperature from high growth temperature. The substrate should have high thermal conductivity coefficient so that heat generated in the high powered devices can easily radiated out in the space. Under these presuppositions, the various available substrates are Silicon Carbide (SiC), Sapphire ( $\text{Al}_2\text{O}_3$ ), and Silicon (Si). The Sapphire is the most widely used substrate due to several reasons such as wide availability, ease of handling, low cost and stability at high temperature [18]. After all these limitations, GaN LEDs grown on sapphire substrate still performs very well.

### 2.3 Growth of GaN LEDs

Many techniques have been used for the epitaxially growth of III-V nitrides since last few years such as Hydride Vapor Phase Epitaxy, Organometallic liquid Phase Epitaxy (VPE)[19], Molecular Beam Epitaxy (MBE). Recently, the most frequent widely used methods are the VPE methods. The most suitable and economical technique among these VPE methods is the metal organic chemical vapor deposition (MOCVD) because high-quality nitride thin films are grown by using this technique [20]. MOCVD has higher growth rate and it is suitable for the large-scale production. It has flexibility in growing precision controlled layers and has the capability to grow complex structures.

MOCVD was first given by Manasevit et. al in late 1960s [21]. MOCVD is non-equilibrium growth technique, in which the growth of the crystal is done by chemical reaction and not by physical deposition. The vapor phase of precursors of required compounds are sent to surface of the substrate. In MOCVD, metal organic (MO) precursors for growth are sent to the heated substrate. These MO precursors are carried out by hydrogen and nitrogen gases in this system. The wafer is placed on heater and radio frequency (RF) are provided to heat wafer in the quartz chamber. Then the chemical surface reactions take place at elevated temperature in which these precursors decomposed into smaller molecules and then diffuse and adsorb onto the surface. These precursors react with each-other onto the substrate to form an epitaxial layer and the by-products are pumped away through the scrubber. The growth rate of these epitaxial layers depends on various parameters such as temperature of substrate, gas flow, vapor pressure of gases etc. in the chamber during growth. A buffer layer of AlN is grown between sapphire and GaN in order to decrease defects caused by lattice mismatch and thermal strain.

General chemical reaction of this process can be expressed as:



Where, R – Alkyl groups such as CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>

M – Group III element,

And N – Group V element.

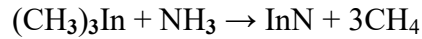
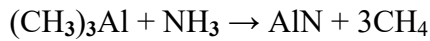
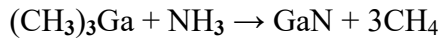


Table 2.1 Precursors used in MOCVD

Precursor	Symbol	Element
Group III Metal Organic Precursors		
TrimethylGallium(TMGa)	(CH3)3Ga	Ga
Triethyl Gallium (TEGA)	(C2H5)3Ga	Ga
Trimethyl Indium(TMIn)	(CH3)3In	In
TrimethylAluminium(TMAI)	(CH3)3Al	Al
Group V Precursors		
Ammonia	NH	N
Dimethyl-hydrazine	DMHZ	H
Dopant Precursors		
Silane (n-dopant)	SiH4	Si
Disilane (n-dopant)	Si2H6	Si
Bis(cyclopentadienyl) Mg(p)	Cp2Mg	Mg

Growth of GaN on sapphire substrate was a three step process involves:

1. High temperature cleaning and Nitridation
2. Low temperature nucleation layer growth
3. High temperature GaN layer growth

### 1. High temperature cleaning and Nitridation:

Before starting growth of samples initially sapphire substrates were cleaned to improve surface quality. Since, the surface of substrate may contain dust particles, polishing residues and may get oxidized with atmospheric oxygen so it is essential to clean the substrate to obtain improved quality of surface of the samples. Initially, samples were loaded into reactor chamber through load-lock and baked at 1020 °C for

10 min in hydrogen ambient.

**Nitridation:** Nitridation is a procedure for improving epitaxial growth quality of GaN films. Ammonia (NH<sub>3</sub>) gas is employed for nitridation and this process takes place at 585 °C. Surface of sapphire substrate reacts with NH<sub>3</sub> and form a thin layer of AlN which improves adhesion and also electrical and optical properties of the device. In MOCVD, AlN layer is used between the GaN film and substrate are meant to minimize the considerable mismatch between film and substrate.

## **2. Low temperature nucleation layer growth:**

A nucleation layer of 30 nm was grown at 585 °C to accommodate dislocation density caused due to huge lattice mismatch and a large difference in thermal expansion coefficient between GaN and sapphire due to which obtained layer was poor quality polycrystalline layer.

## **3. High temperature GaN layer growth:**

After growth of nucleation layer temperature was raised from 585 to 1180 °C. Annealing of nucleation layer converts poor crystalline nucleation layer into islands of GaN. Then these islands were grown over until they form a flat surface. Initially a thin undoped GaN layer was grown then n-type layer was grown with Si doping using SiH<sub>4</sub> precursor with the thickness of 4µm.

Figure 2.5 shows temperature variation for growth of different layers of LED. The Fabry Perot interferometry system is used to analyze and monitor the MOCVD growth of thin films materials. A 635 nm laser source is equipped with it. Laser beam passes through a beam splitter and incidents on the substrate through one of the optical ports. Then the reflected beam incidents on the photodiode. Laser light are reflected at two boundaries, one at the air-film interface and the other at the film-substrate interface as shown in figure2.5.

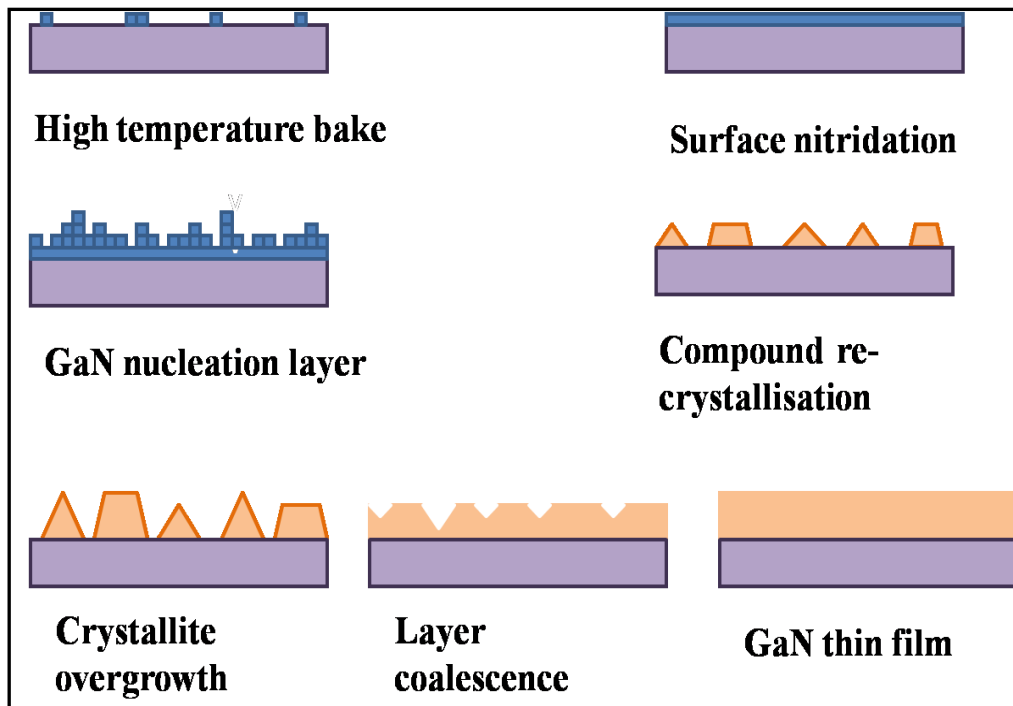


Figure 2.2 MOCVD Growth Steps

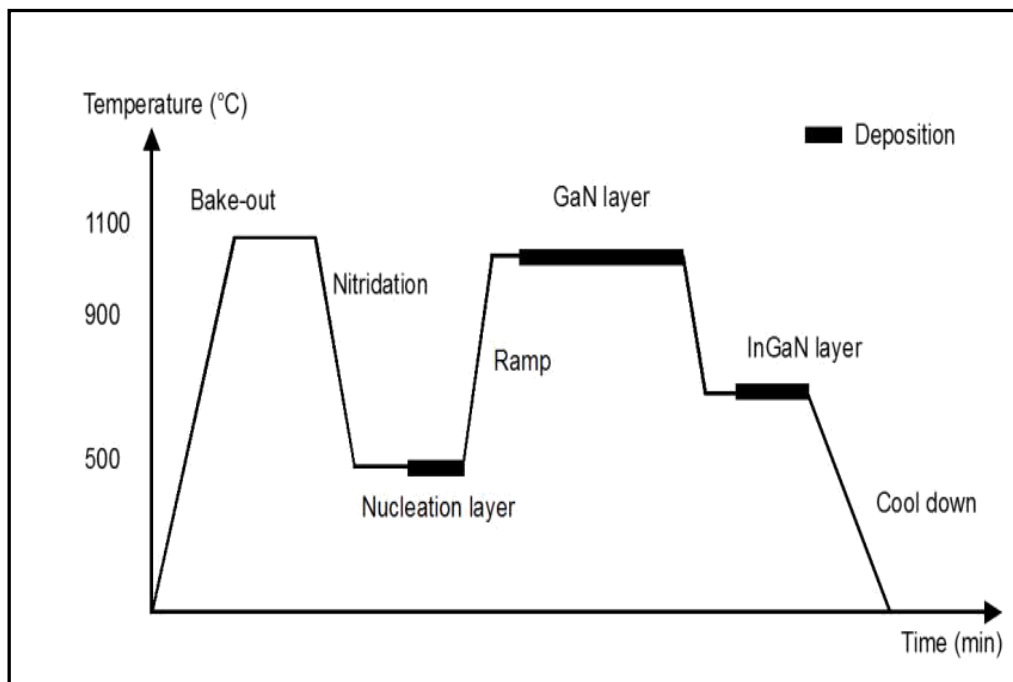


Figure 2.3 Temperature parameter variation during MOCVD

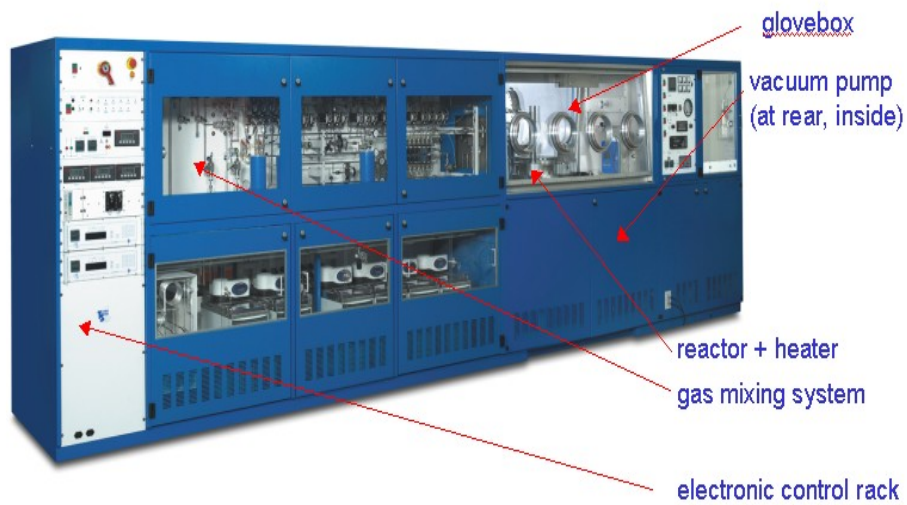


Figure 2.4 Thomas Swan Close Coupled Showerhead (TS-CCS) MOCVD system at ODG, CEERI

The reflections from bottom substrate are negligible as polished sapphire is used in this growth process. As the light is partly reflected at the surface, another part is transmitted to film- substrate interface. This process of partly reflected and partly transmitted light will be repeated inside the sample. The process of intensity modulation will occur because of phase difference between different light beams due to multiple reflections. For constructive interference, the path difference between two beams is equal to an even number of the half wavelength:

$$2nd = m\lambda$$

For destructive interference, the path difference is equal to an odd number of half wavelengths:

$$2nd = (m + \frac{1}{2}) \lambda$$

Where  $m$  = integer number

$d$  = thickness of the layer

$n$  = refractive index of material

Thus, the layer thickness can be derived from the intensity modulation of the reflected light beams.



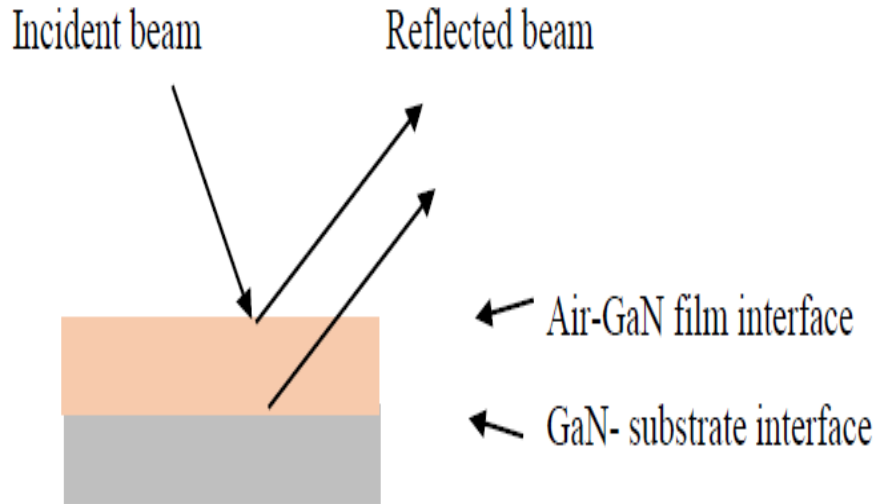


Figure 2.5 Multiple reflection during measurement of thickness in Fabry Perot interferometry system

### 2.3.1 Layered structure of LED used in this thesis

The GaN based LED wafers used in this thesis were grown at CSIR-CEERI, Pilani. These LED wafers used were grown by MOCVD on the c-plane sapphire substrate. In MOCVD, Trimethylgallium (TMGa), Trimethylindium (TMIn), Ammonia (NH<sub>3</sub>), Trimethylaluminium (TMA) were used as sources of Ga, In, N, Al respectively. Biscyclopenta-dienyl-magnesium (Cp<sub>2</sub>Mg) and Disilane (Si<sub>2</sub>H<sub>6</sub>) were used as p and n dopant respectively. The details of MOCVD have been given in section 2.3. The LED structure consist of a nucleation layer of 30nm followed by Si doped n-type GaN layer of 4 $\mu$ m. Above the n- GaN layer, five pairs of GaN/InGaN Quantum Wells with a well width of 2nm and GaN barrier width of 13nm to achieve higher quantum confinement were deposited. Then, 20nm p-AlGaN layer as an electron blocking layer (EBL) was deposited. This was followed by Mg-doped p-type GaN layer of 100nm. In the subsequent chapters, this top p-GaN layer was nanoroughened in order to improve light extraction efficiency. The details of different processes used in fabrication such as photolithography, metallization, RTA etc are discussed in chapter 5. Figure 2.6 shows layered structure of GaN/InGaN MWQ LED used in this thesis, which was grown at CSIR-CEERI, Pilani.

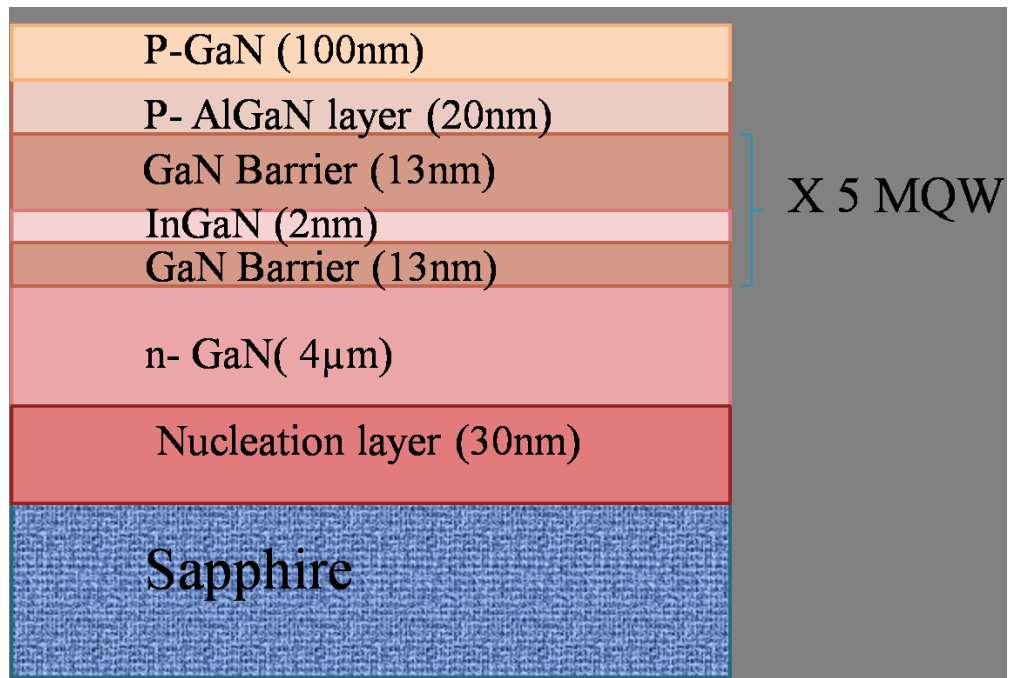


Figure 2.6 InGaN/GaN MQW LED structure grown at CSIR-CEERI, Pilani

## Chapter 3 Basics of Light Emitting Diodes

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### 3.1 Introduction

The solid-state lighting device LED is one of the most widely used device for lighting than the conventional incandescent and florescent lamps because of its higher efficiency. The LEDs based lightening system is estimated to have high reliability, long lifetime and environment friendly as they are mercury free systems [22, 23]. They offer benefits of small size, low power consume, high durability and low heat output.

LED is an optoelectronic device which works on the principle of electroluminescence, i.e. when current is passed through device, it generates light. It is a direct band gap semiconductor material p-n junction device in which n-layer with excess of electrons and p-layer with excess of holes. In simple LED, the electrons and holes recombine radiatively at the junction to generate photons. When no biasing is applied, net current through the device is zero. When forward biasing is provided, by getting energy electrons and holes from their respective sides crosses the junction and reaches to other side as excess minority carriers. The wavelength of the light emitted depends on the energy bad gap of the materials used for the device. In order to improve efficiency of LEDs, the distance covered by charge carriers before diffusion known as diffusion length should be minimum so that carrier life time of charge carriers is small and charge carrier recombine rapidly instead of being trapped by impurities or dislocations.

### 3.2 Direct and Indirect Band Gap Structures

The structure of band gaps of materials characterizes the optical properties of the material. The electrons present in the valence band can be excited to the conduction band either by thermal excitation or by optical absorption. During recombination of electrons and holes, the energy can be released either in the form of photos or phonons. Semiconductors can be classified into two groups based on the band structure i.e. direct and indirect band gap materials.

In a direct band gap material, the maxima of valence band and minima of conduction band lies on the same value of propagation constant,  $k$ . During transition of electron from conduction band to valence band for recombination, the energy is released in the form of light (photons) which is used for optoelectronic devices. Examples of direct band gap materials such as GaAs, GaN, InN.

On the other hand, in an indirect band gap material, the maxima of valence band and minima of conduction band occur for same value of  $k$ . During recombination, the energy is released in the form of heat (phonons) given to the lattice. Examples of indirect band gap materials such as Silicon, Germanium.

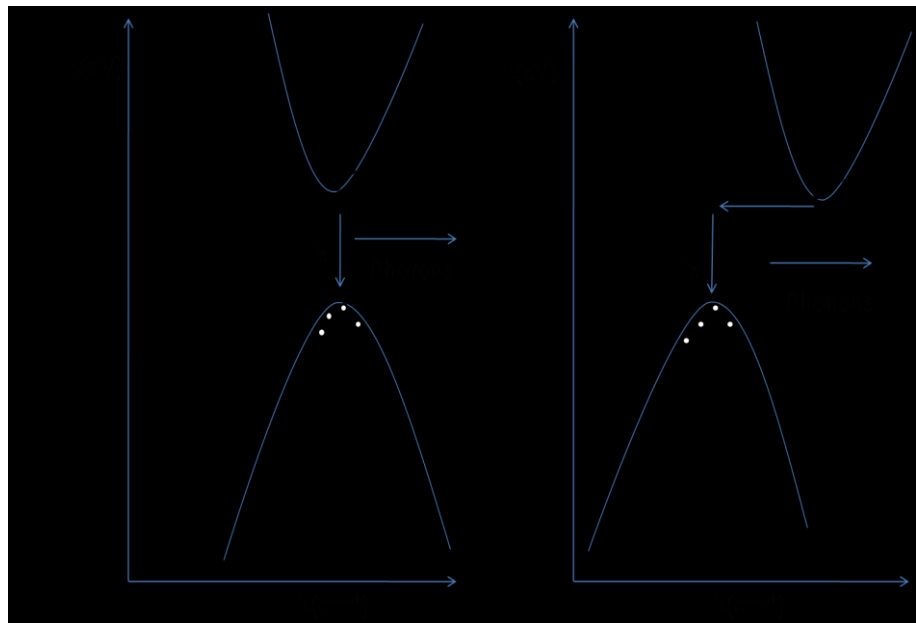


Figure 3.1 Direct and indirect band gap materials

### 3.3 Background of LEDs and III Nitride LEDs

In recent years LEDs have become the most significant optoelectronics device because it has a huge impact on day to day life of every human being. Research work on LEDs has been started before 1907 and first direct semiconductor based p-n junction LED was fabricated by Nathan in 1962 [24]. By now, various advancements have been made regarding to improvement in material quality, epitaxial growth systems and formation of p and n contact with minimum resistance in LED systems for the last 50 years. Higher than 100 m/W efficiency has been achieved by using red, amber, yellow and orange LEDs that use AlGaInP chips. In 1993, first GaN based

high brightness blue LED was invented by Shuji Nakamura and it became revolutionary solid state lighting device in the field of illumination [25]. He was awarded by the Nobel Prize in Physics for his great invention. After invention of high brightness GaN LEDs it become possible to achieve white light either using phosphor coating on blue LED or Red, Green, Blue (RGB) colour mixing. The first GaN/InGaN based Double Hetero structure blue LED was designed by Nakamura in 1993 in order to increase carrier confinement in active region. By varying the composition of indium in InGaN one can obtain the desired emission wavelength and also obtain a strong band-to-band emission by incorporating In with GaN at room temperature. Although the improved growth LED technology has led to great advancement in short wavelength LEDs, but the high refractive index difference between the semiconductor and air remains a problem, which results in low light extraction efficiency.

In 2006, O. B. Shchekin et al. demonstrated the thin film LED structure to enhance light extraction efficiency of GaN on sapphire substrate [26]. To create the thin film LED structure sapphire is removed using Laser Lift-Off (LLO). N-contact metals are formed on the exposed n-type GaN layer after metalized or bonded with another semiconductor substrate on p-type GaN. This structure reduced the problem of current crowding near mesa edge. [26]

### **3.4 Parameters of LED**

LEDs work on the principle of electroluminescence in which electronic excitation is created by an applied electric field. During recombination of electrons and holes, the energy of charge carriers converted into optical energy. Thus conservation of energy requires that forward voltage of LEDs must be equal to or larger than the band gap divided by an electronic charge. The diode voltage is given as-

$$V = E_g / e$$

There is an additional voltage drop occurs due to contact resistance, resistance caused by abrupt hetero structure, bulk resistance in materials with low carrier concentration.

#### **Internal quantum efficiency:**

It is defined as number of photons emitted from active region with respect to the number of electrons injected into LED.

$$\eta_{\text{int}} = \frac{P_{\text{int}} / h\nu}{I/e}$$

Where  $P_{\text{int}}$  is the power emitted from active region and  $I$  is injected current at the junction.

$$\eta_{\text{int}} = \frac{R_r}{R_r + R_{\text{nr}}}$$

Where  $R_r$  and  $R_{\text{nr}}$  are termed as radiative and non-radiative recombination rates.

**External quantum efficiency:**

It is defined as the ratio of photons emitted to free space to the number of electrons injected into LED structure per second.

$$\eta_{\text{ext}} = \frac{P/h\nu}{I/e}$$

Where  $P$  is termed as optical power emitted into free space.

**Extraction efficiency:**

Extraction efficiency is defined as the ratio of number of photons emitted to free space to the number of photons emitted from active region.

$$\eta_{\text{extraction}} = \frac{P/h\nu}{P_{\text{int}}/h\nu}$$

$$\eta_{\text{ext}} = \eta_{\text{int}} \eta_{\text{extraction}}$$

In case of ideal LED, the extraction efficiency is unity as all the photons from active region of LED is emitted into free space. However, in case of real LEDs, it is not possible to take out all the light generated into active region due to several loss mechanisms. For example, light emitted from active region may be absorbed by substrate or it may get reflected by metallic contacts on the top surface of LEDs. In addition, the phenomenon of total internal reflection does not allow light to completely escape from semiconductor surface. Because of large difference in refractive index of GaN ( $n=2.7$ ) and air ( $n=1$ ), light coming out of active region is internally reflected back when angle of incidence is greater than critical angle and hence reduces external quantum efficiency significantly. Using Snell's law, the

critical angle  $\Phi$  is given as:

$$\Phi = \arcsine (n_{\text{air}} / n_s)$$

where  $n_s$  is refractive index of semiconductor.

### **3.5 InGaN/GaN Multi Quantum Well (MQW) LEDs**

In the starting years of LED development, homo junction LEDs were used which consist of simple p-n junction. After that Hetero junctions are used instead of homo junctions. Hetero structure LEDs usually consists of a smaller band gap material which acts as active region and a higher band gap material which acts as barrier material. Double hetero structures are used for bulk as well as quantum well active regions. In hetero structures, the charge carriers are confined in the intermediate layer which acts as active layer instead of going into nearby layer hence improvement in carrier confinement which increases radiative recombination efficiency.

In InGaN/GaN multi quantum well LEDs, InGaN behaves as active region to confine carriers and GaN is the barrier layer. For example, Nichia Corporation shows that violet blue GaN/InGaN LED which has 405 nm peak produced 5.6mW power at 20 mA direct current with an external quantum efficiency of 9.2 % [27]. Multiple quantum well (MQW) structure is widely used for high intensity LEDs, but there is tradeoff between number of quantum wells and efficiency of LEDs. Experimental results of an LED structure with different number of quantum wells (QWs) shows that as the number of quantum wells increases, uniformity between top and bottom quantum wells decreases which causes broadening of gain spectrum [27]. Thickness of quantum wells is also a critical parameter. InGaN/GaN multi quantum well layers are kept thin in order to reduce electron and hole wave function separation because of effect of polarization. In this structure, radiative recombination occurs in InGaN active layer. Therefore, wavelength of the emitted light depends on energy band gap of InGaN layer which can be altered by variation in concentration of In in InGaN quantum well layer. As the concentration of In increases, wavelength of emitted light increases. Thus all these parameters need to be optimized for getting appropriate results.

## Chapter 4 Nanorods characterization and fabrication

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### 4.1 Issues related to Polarization and Quantum Confined Stark Effect (QCSE)

The semiconductor group III-Nitrides are considered as important materials which show different optical and electrical properties from other semi-conductors because of the presence of an in-built electric field which originates from spontaneous and piezoelectric polarization. Because of these polarization fields, the band gap diagram of InGaN-GaN quantum wells gets distorted due to which the electron and hole wave functions move apart from each other. The overlapping between electron and hole wave functions reduces which results in a reduction of recombination rates. Because of distortions, the confined carriers in the active layer move into barrier layers which reduces the confinement of charge carriers and causes absorption spectra to broaden [28]. These in-built polarization fields result in the splitting of the valence band, red or blue shifting of emission wavelength, polarized emission from the active layer and a decrease in intensity of light output from devices. [29].

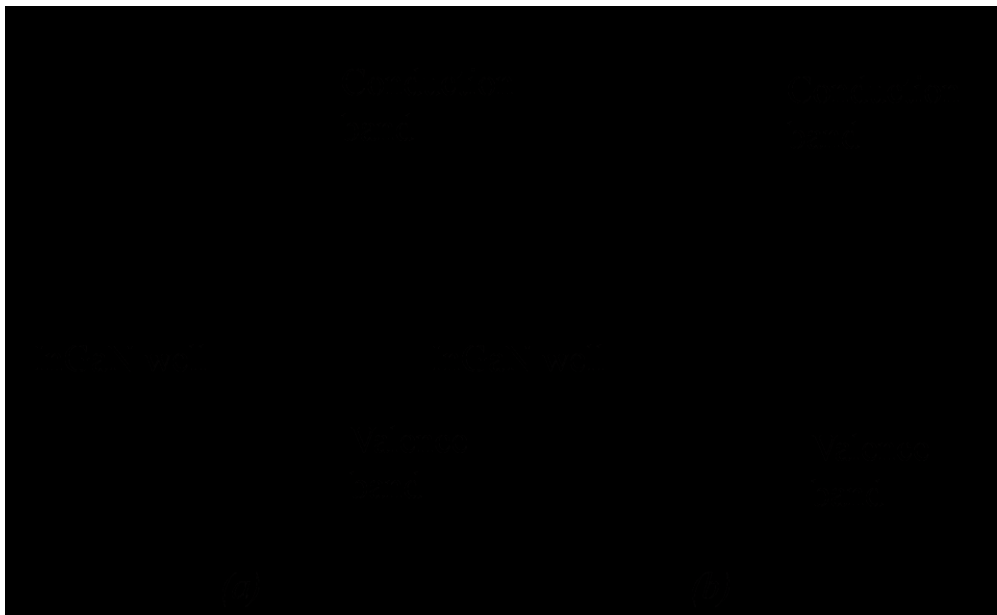


Figure 4.1 Separation of electron hole wave function (a) No bias (b) Forward bias

The control of in-built polarization and QCSE effect is one of the critical



issues for improvement of efficiencies of visible LEDs. In order to mitigate these effects, there have been various methods found out to improve quantum efficiency of LEDs which makes them dominant source for next- generation solid state lighting.

- The QCSE effect can be minimized by introducing extra free charged carriers in the device structure. The electrons and holes into the quantum wells can be provides by photo excitation, carrier injection in p and n side structures under forward-bias condition. Ryouet *al.* reported the change in electrical and optical properties of LEDs by Silicon doping in the quantum well barrier layers. [30]. As the Si doping concentration in the QWBs increases from, the EL intensity peak decreases significantly and the turn-ON voltage decreases slightly, which shows that doping of Si is done in order to screen the QCSE must be carefully done to optimize design of visible LEDs for the improvement of internal quantum efficiency.
- The epitaxial growth of group III-Nitride films on substrate has been done generally on the polar (0 0 0 1)  $c^+$ -plane because it is easy to obtain better surface morphology and reduced threading dislocation densities in the epitaxial layer. The a, r, and m planes are non polar and semi polar planes. In order to mitigate the effect of polarization, the growth of nitride material has been done on non polar and semi polar planes such as (1 1  $-2$  0) a-plane GaN on a-plane SiC [4] and on (1 0  $-1$  1) r-plane sapphire [31], a-plane MQWs [6] and LEDs [32] on epitaxially overgrown  $a$ -plane GaN. However, the growth of GaN and InGaN on non polar substrate materials by using strained heteroepitaxy results in a poor crystalline growth quality with layers containing a high density of threading dislocations and stacking faults and rough surface morphologies.
- An extra InGan/GaN quantum well with lower In content was employed in the GaN LED structure in between the n GaN layer and active layer and this proved reduction in QCSE by reduced blue shift [33].
- A p-InGaN layer was employed as a hole injection layer in the LED structure in place of top p GaN layer of GaN LEDs which results in reduction of pre strain between different layers of the QWs, which proved to be one method for mitigation of QCSE [34].

It has been widely proposed that nanostructures on the LEDs such as nanorods, branched nano wires, nano cylinders, nano tetra pods, nano tubes etc. can enhance the efficiency of the optoelectronic devices because of reduction of QCSE leading to strain relief and carrier confinement [35].

## **4.2 Introduction of Nanostructures**

The nanostructures such as nano wires, nanorods, and nano pillars have diameter lies in the range of several nanometers with high aspect ratio. The length of these nanostructures varied from hundreds of nanometers to hundreds of micrometers. These exhibits different optical and electrical properties because of their nano geometry, large charge carrier confinement, reduction in strain and high surface-to-volume ratio.

### **4.2.1 Methods of fabrication of Nanorods**

GaN based nano scale structures can be fabricated by two methods i.e. bottom-top approach and top-down approach.

#### **Bottom-top Approach:**

This approach involves complex mechanisms and expensive technologies to built atomic or molecular components into complicated nano dimension assemblies. This method involves controlled assembly of atoms and molecules to generate multi-component devices without making or eliminating parts of the final system. The bottom-up technique, in that the formation of nanorods is carried out stepwise from atoms or molecules, includes Vapor Liquid Solid (VLS) growth, Molecular Self Assembly, Sol-gel nanofabrication, Molecular Beam Epitaxy [36].The scalable Molecular Self Assembly allows self assembly of molecular nano structures of width less than 20 nm with the large pattern stretches, [37]. The Chemical Vapor Deposition technique is a flexible nanofabrication tool for fabrication of nano structures including complex multi component nano composites. It allows controlled simultaneous deposition of several materials including metal, ceramics, semiconductors, insulators and polymers, with high purity nano films on the substrate material [39, 40]. However these methods are relatively complicated due to lack of control of doping profile, size and site control, non favorable material quality and less versatility and scalability in

material design such as hetero structures. Usually these are slow and expensive processes, due to deposition of vacuum components. It is difficult to deposit certain metals, oxides, certain important semiconductors such as silicon, germanium etc with minimum number of defects.

### **Top-Down Approach:**

A top-down approach involves fabrication of nano scaled devices with desired dimensions and shape by using nano fabrication tools which depends on experimental external parameters. This method involves fabrication of nano structures which starts from larger dimensions and reducing them to the desired dimension and shape [41]. In this the constituent elements are eliminated from an original object and reducing them to required dimensions, includes conventional photolithography, electron beam lithography, nano imprint lithography, stamp technology, self assembled nano masking and nano sphere lithography etc. The E-beam lithography is able to make periodic nano scale features easily by using diffraction limit of light [42]. The optical lithography is generally used for chip production with high level of resolution and desirable throughputs. The soft and nano imprint lithography is pattern transfer based simple and most effective tool for fabricating ultra small features with high resolution [90, 91]. However, lithography is expensive, complex and slow process for production of large scale dense nanostructures [43, 44]. It is difficult to make self-assembled nano structures with periodic variations required for many applications as high defect densities are developed in nano structures [45].

In our work, we demonstrate a simple “top-down” patterning and large scale fabrication process of GaN based nanorods using self assembled Ni islands and Reactive Ion Etching. Self-assembled Ni nano-clusters were used as an etching mask during etching process. Ni acts as a nano-mask since it shows good selective etching rate to GaN material [46]. The dimension and density of GaN nanorods depends on Ni layer thickness, annealing time and annealing temperature [47].

#### **4.2.2 Need of nanorods on LEDs**

Recently, GaN based blue light emitting diodes (LEDs) have been emerge as the most useful application in the development of optoelectronic devices. However, InGaN/GaN materials still have inherent difficulties and further improvement in optical performance is still required to meet the essential needs for replacement of

conventional lighting source. One of the considerable difficulties is internal developed built in electrical fields in InGaN/GaN MQWs induced by the large lattice mismatch and strain developed in hetero layers. Another problem is the high dislocation density ( $10^9-10^{11}\text{cm}^{-2}$ ) of the epitaxial layer grown on the hetero substrate, leading to detrimental effect on the performance of the device [48]. While most commercial LEDs were fabricated based on planar structure, it have been demonstrated that nanorods based LEDs have proved as attractive method for higher light extraction efficiency due to the increase of surface area provided by side walls of nano wires or nanorods and higher radiation directionality. The advantages of GaN nanorods based devices as compared to bulk GaN based devices are-

- High surface to volume ratio results in increase in active area for LEDs and solar cells.
- Reduction of compressive stress developed because of lattice mismatch in GaN layer grown over sapphire.
- Increase in radiative recombination efficiency in multiple quantum wells (MQWs) due to reduction of effect of in built polarization field.
- The GaN based nanostructures can be used in high temperature and high power electronic devices because of direct and wide band gap of GaN [49].

Thus fabrication of nano rod arrays on optical devices in a nanometer size is another suitable approach to further improve quantum efficiency of InGaN/GaN-based optical devices.

#### **4.2.3 Parameters that determines dimensions and density of Nanorods**

It was found after a series of experiments that the annealing temperature, annealing time and Ni layer thickness were the most effective parameters to decide dimensions and density of nanorods. The variation of dimension and density with Ni layer thickness and RTA temperature is shown in figure 4.2 and 4.3 respectively.

##### **Effect of temperature:**

The RTA temperature need to be chosen above  $700\text{ }^\circ\text{C}$  to form the Ni self assemble nano-masks. The Ni nano-masks formed under RTA temperature condition at  $850\text{ }^\circ\text{C}$  for 1 min showed more uniform distributed dimension with smaller standard deviation error bar.

### Effect of Ni thickness :

As the Ni thickness increases, Ni clusters dimension size became smaller and denser at the same annealed condition.

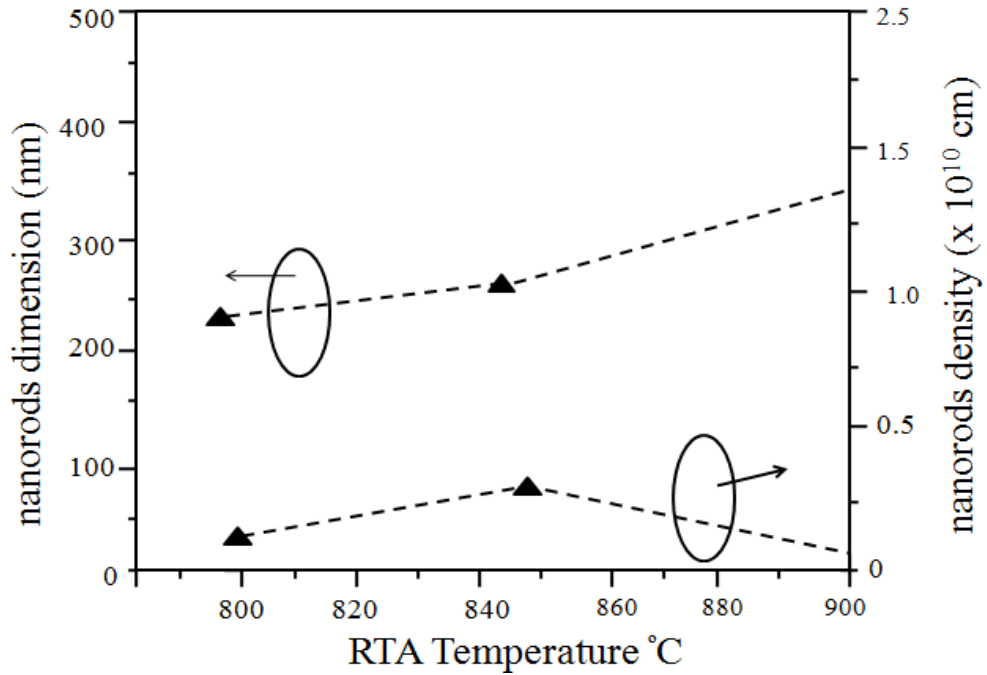


Figure 4.2 Variation of mean dimension and density of GaN based nanorods as a function of the RTA temperature varies from 800 to 900 °C

## 4.3 Fabrication of Nanorods

### 4.3.1 Using Ni as a nanomask during Reactive Ion Etching (RIE)

The GaN LED wafer processed in our work is grown by the MOCVD on the c-plane sapphire substrate, as details given in chapter 3. On this GaN LED, a 100nm thin SiO<sub>2</sub> layer was deposited by using Plasma Enhanced Chemical Vapor Deposition (PECVD) which behaves as an insulating layer. Before the samples were loaded into the furnace, pre-metallization etch process was carried out in HCL and deionized water (DI) in 1:1 ratio and thoroughly rinsed in DI water in order to remove native oxides from the sample surface. In order to fabricate nanorods, first a 10nm thick nickel (Ni) layer was deposited by using E-beam evaporation system. After this, the samples were undergone to Rapid Thermal Annealing (RTA) at 850°C for 1 minute

under nitrogen ambient in order to form Ni nanoislands on the top surface of LED sample which acts as masking for RIE. In the next step, RIE of SiO<sub>2</sub> was performed under the gas mixture of CF<sub>4</sub>/O<sub>2</sub> = 35/2 sccm for 2 minutes. Finally, the etching of GaN was carried out with reactant gases BCl<sub>3</sub>, Cl<sub>2</sub>, Ar of 10 sccm, 3 sccm, 2sccm respectively.

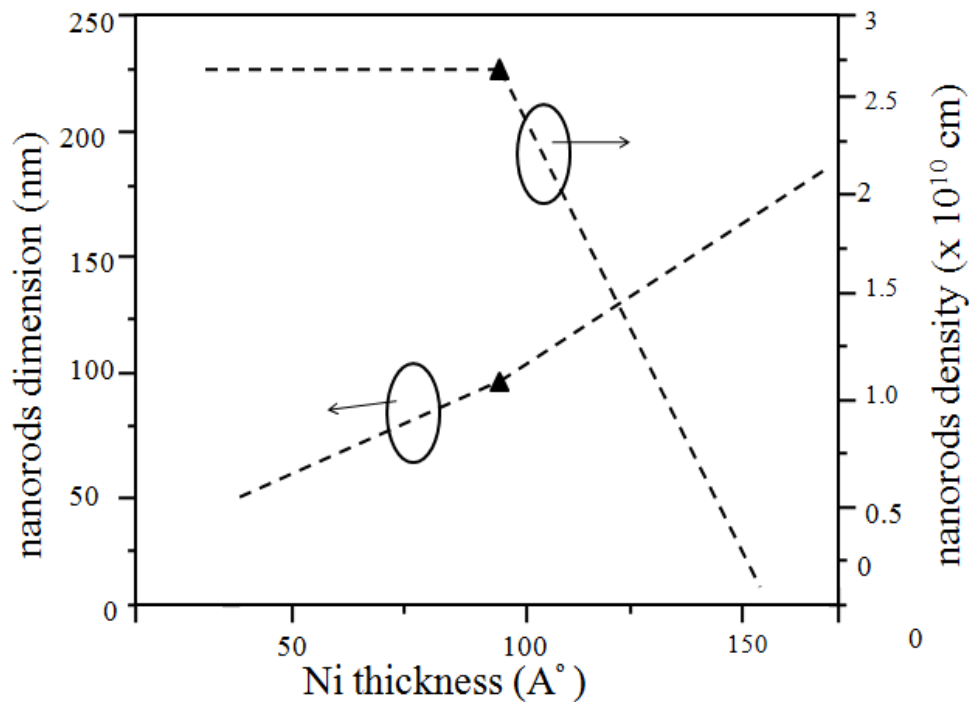


Figure 4.3 The mean dimension and density of GaN-based nanorods as a function of the Ni film thickness varies from 50 to 150 Å at the same RTA 850 °C for 1 min

The etching rate was about 80 nm/min and bias power was 75W with RF frequency of 13.56 MHz. Finally SiO<sub>2</sub> and Ni were etched using HF to fabricate GaN nanorods. The process for fabrication of GaN nanorods is shown in figure 4.4. After that the dimensions and density of nanorods were examined by Scanning Electron Microscopy (SEM). It is possible to obtain nanometer sized nickel islands by proper selection of Ni metal thickness, annealing temperature and annealing time. The details of systems used in our work are given in next chapter.

We performed another experiment in which Silver (Ag) was used as a nanomask during Reactive Ion Etching (RIE) to fabricate nanorods on GaN based LED. Silver is the only metal that has highest efficiency of Surface Plasmon resonance among three metals (Au, Ag, and Cu) by which light interacts with matter

[50]. Silver has the ability to capture more light by interacting with light more efficiently as compared to particles of same dimension and size [51, 52].

#### **4.3.2 Fabrication of Nanorods using Silver as a nanomask during Reactive Ion Etching (RIE)**

The same grown GaN/InGaN LED wafer as discussed previously in chapter 3 was used here also. On this LED wafer, a 100nm thin SiO<sub>2</sub> layer was deposited by using PECVD which behaves as an insulating layer. In order to fabricate nanorods, first a 1nm thick Silver (Ag) layer was deposited by using E-beam evaporation system. After this, the samples were undergone to Rapid Thermal Annealing (RTA) at 550°C for 1 minute under nitrogen ambient in order to form Ag nanoislands on the top surface of LED sample which acts as masking for RIE. In the next steps, RIE of SiO<sub>2</sub>, GaN was done to fabricate GaN nanorods. After that the dimensions and density of nanorods were examined by Scanning Electron Microscopy (SEM).

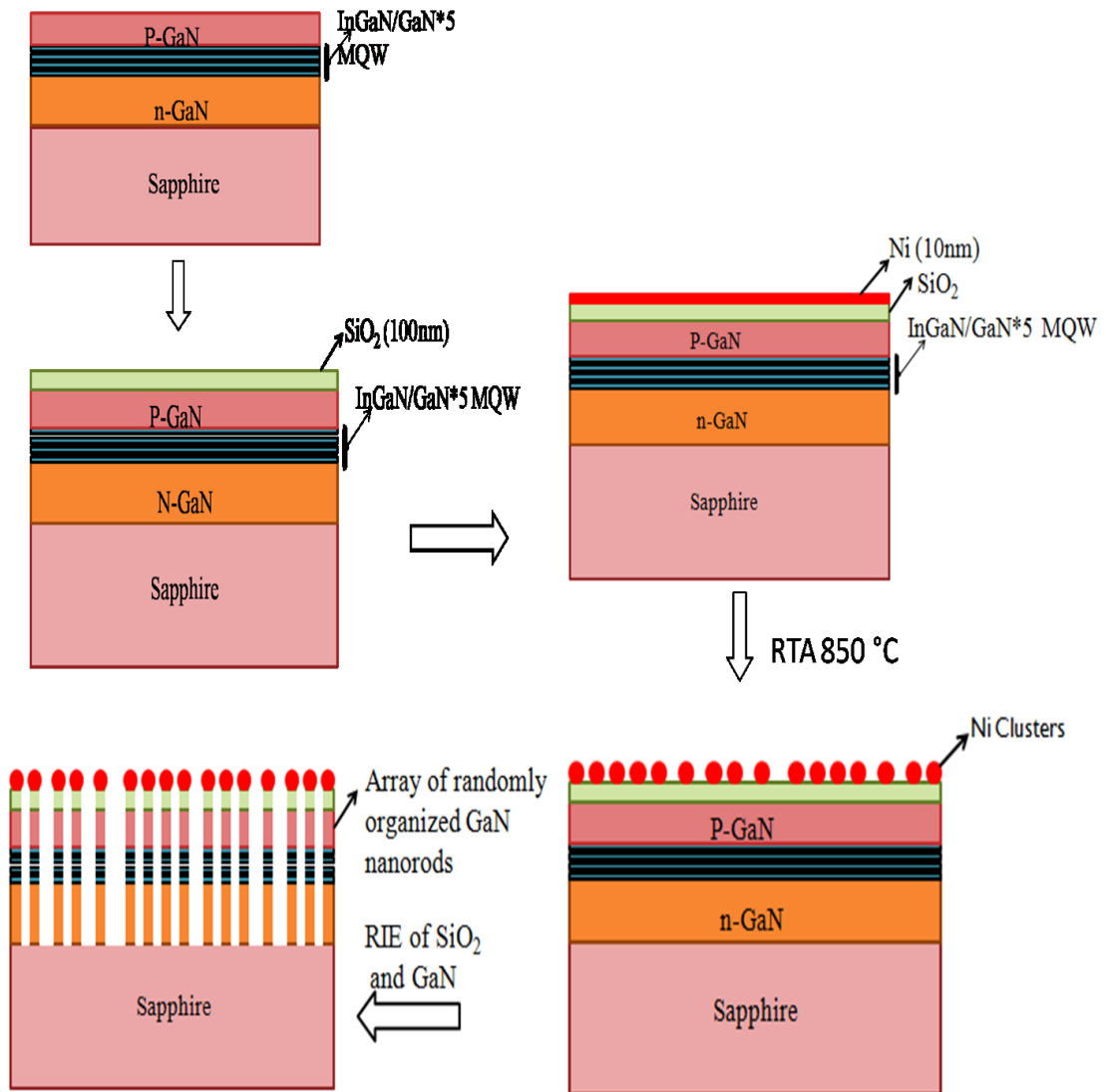


Figure 4.4 Schematic diagram showing fabrication steps of GaN nanorods

#### 4.4 Scanning Electron Microscopy (SEM) Result

The shape and morphology of the GaN based nanorods was observed using Scanning Electron Microscopy (SEM). Scanning electron microscope technique is employed for imaging of surface of the patterned LED sample. This technique is used over light microscope because it has high magnification and resolution capability. In SEM, a focused beam of electron is used to generate an image of sample. The electron beam is further focused with the help of a series of electromagnetic lenses. Incident beam scans in raster pattern to create an image of the sample. This high energy electron beam is incident on the surface of sample where it knocks electron from sample surface, called secondary electrons. This secondary electron emission is collected by a secondary electron detector. An image of the sample is formed by



scanning of the electron beam back and forth across the entire surface of the sample. Secondary electron detector collects number of secondary emitted electrons from each point of the sample surface. A fluorescent material is coated on either side of detector which is connected by a high supply voltage of 10 kV to attract the secondary electrons. Then amplifier amplifies the output signal obtain by secondary electron detector and transfer it to a display unit.

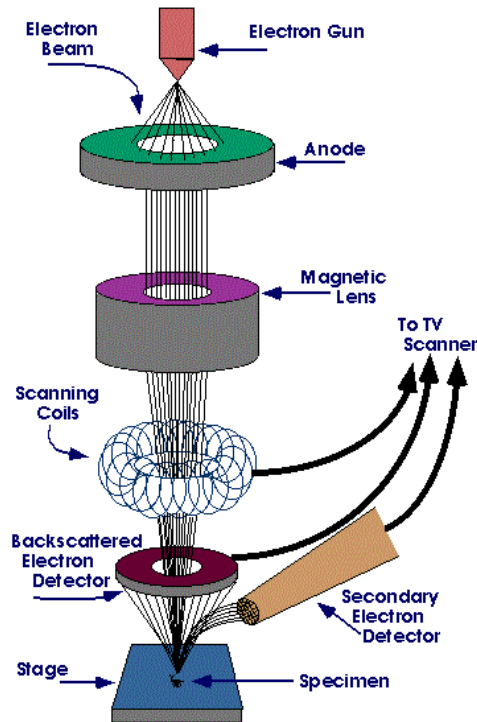


Figure 4.5 Working principle of Scanning Electron Microscopy

The top view image of the GaN nanorods for Ni and Ag nanomask for different magnification ( $\times 50,000$  and  $\times 20,000$ ) at 30Kv high voltage was shown in figure 4.6 and 4.7 respectively. From the images, it was found that not only isolated nanoislands but cluster of nanorods were also formed. We obtained nanorods with diameter varying from 90 nm- 200 nm in case of samples in which Ni was used as a nanomask. While the diameter varying from 80nm – 390nm in case of Silver nanomask.

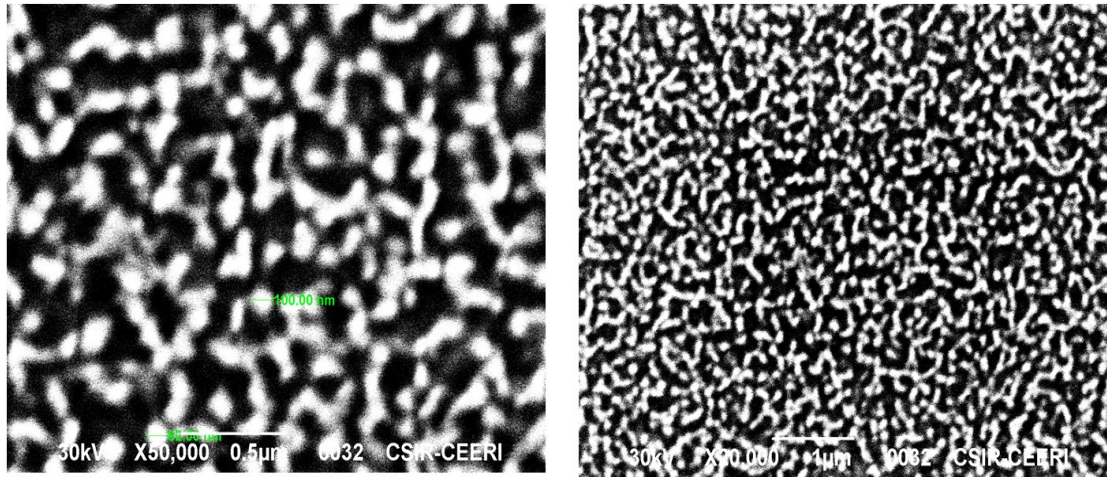


Figure 4.6 SEM images of GaN nanorods fabricated by using Ni as a nanomask during RIE at two different magnification ( $\times 50,000$  and  $\times 20,000$ )

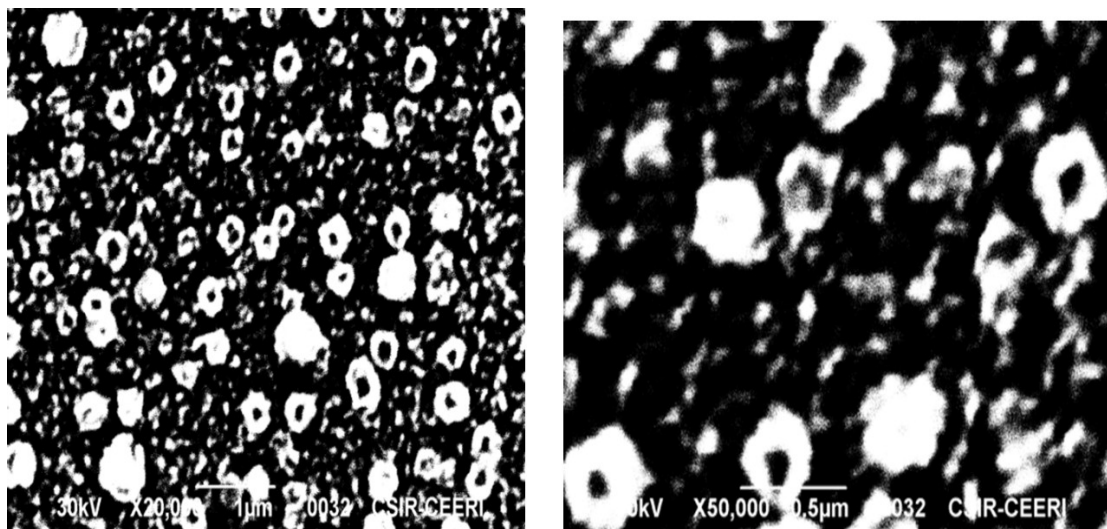


Figure 4.7 SEM images of GaN nanorods in which Silver was used as nanomask at two different magnification ( $\times 50,000$  and  $\times 20,000$ )

#### 4.5 Issues related to fabrication of nanorods based LEDs

The nanostructures on GaN based LED can enhance the efficiency because of strain relaxation effect and quantum confinement which reduces Quantum Confined Stark Effect. Thus, GaN based nano rod LEDs with higher radiation efficiency are expected to be a good candidate for future solid state lighting devices development. However, there are some problems associated with fabrication of nano rod LEDs such as-

- There is large leakage current from rough unprotected sidewalls of nanorods fabricated in quantum wells resulting in poor electrical properties.

- It is quite difficult to establish p-type ohmic contacts for each individual nano rods as nanorods fabricated by these methods are non-uniformly distributed over the entire surface.
- Since RIE is an isotropic process, nanorods formed after RIE could not get separated completely from nearby rods up to n-GaN, resulting in short circuit during contact formation.
- During RIE, the mole fraction ratio of Indium in multiple quantum wells may get altered, resulting in wavelength shifting effect.

Hence, we proceeded with another approach to fabricate top-Surface Nano-Roughened LEDs using self assembly nano masks of Silver (Ag) and Indium Tin Oxide (ITO) and Reactive Ion Etching (RIE) in order to improve light extraction efficiency. The results show that by adding a rough top surface, the extraction efficiency could be enhanced because of reduction in internal reflections.

# Chapter 5 Light extraction efficiency enhancement of Nano-rough LEDs

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## 5.1 Introduction

The light extraction efficiency of an ideal LED is considered as unity since all the photons from active region after radiative recombination are emitted into free space from LED device. However, in case of real LED, it is not possible that all the photons emitted from active region are emitted into free space. This is because of total internal reflection phenomenon takes place at the semiconductor- air interface. In conventional GaN LED, there is a large difference in refractive index of air and GaN. As the critical angle is inversely depends on refractive index. The higher the refractive index, smaller is the critical angle. Therefore, the critical angle at GaN and air interface is 23.4 is small. Now, when the angle of incidence of light is smaller than critical angle, a large fraction of light is transmitted or we can say that most of the light emitted out from the device into free space. But when angle of incidence is larger than critical most of the light get reflected back or we can say that photons emitted from active region are reflected back into device instead of going into free space. Thus most of the photons get trapped into hetero layers of LED because of total internal reflection. These photons inside the device may get absorbed by metal electrodes i.e. p and n contacts, defects and dislocation densities and quantum wells. By absorbing energy of these photons, heat is produced inside layered structure of LED. This heat may raises the temperature which is responsible for decrease in efficiency of LED. Because of extra heat and higher temperature, there is red shift in emission wavelength which causes low intensity and colour rendering problems. In addition, the responsivity of human eye is very high for short wavelength up to green colour but it drops rapidly as the wavelength goes down to blue colour. Therefore, low human eye responsivity for blue colour is another issue for efficiency droop of blue GaN LED.

In the past few years, several efforts have been made to improve external quantum efficiency of LEDs such as use of anti-reflection coatings [53], photonic

crystals [54], patterned sapphire substrate [55] etc. Surface roughening of the top P-GaN surface is known to be efficient method for improvement of light extraction efficiency [56].

Small (less than the wavelength of light) metal particles whose size even less than wavelength of light i.e. up to nanometers exhibit a phenomenon called “plasma resonance” with many potential applications such as trapping of photons inside layered structure. The optical absorption cross section of molecules is very small as a consequence of their small size. The reason for this is the “Plasmon-polariton” resonance of the free electrons in the metal surface. Thus, a resonant metal particle is able to trap light inside layered structure of optoelectronic devices over a large region with dimensions of many wavelengths although the particle dimension is comparable to wavelength of light. Based on this theory and obtained results, we have been shown that light extraction efficiency can be improved with nano-roughened GaN LEDs.

In our work, we took two samples of GaN based LED grown by MOCVD system as given in chapter 3. In one sample silver as a nanomask while in other sample ITO as a nanomask were used during RIE. Silver exhibits the highest efficiency of Surface Plasmon resonance among three metals (Au, Ag, Cu) by which light interacts with matter. A single Ag nano particle interacts with light more efficiently than a particle of the same dimension which indicates that Ag particles can capture more light. ITO, which is a Transparent Conducting Oxide (TCO), is preferred due to its lower electrical resistivity, higher transparency to visible wavelength region and compatibility with fine patterning processes. ITO films are highly degenerate n-type semiconductor with high intentional Sn doping and oxygen vacancies. TCO films on the top surface of devices not only serves as the transparent electrode but also, acts as antireflection coating to reduce total internal reflection.

## **5.2 LED Processing and Fabrication Steps**

The schematic diagram to achieve the desired structure of LED with nanoroughened top p- layer Lateral is shown below in table 5.1.

Table 5.1 Steps of fabrication of nanoroughened LED

MOCVD Growth
Wafer dicing
Sample cleaning
Nano structure formation on top p-GaN layer
Mesa etch
N- contact metallization
Current spreading layer
P- contact metallization
EL measurement
I-V measurement
Hall measurement

The schematic diagram of nano roughened LED is shown in figure 5.1. The steps of processing of grown LED wafers and incorporation of nanostructures in LEDs as given in table 5.1 is given in detail below-

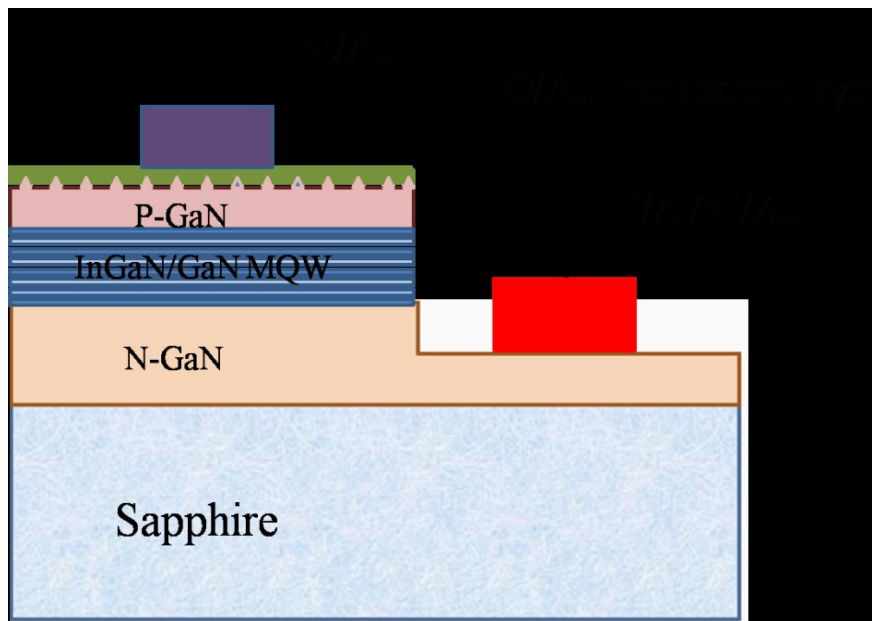


Figure 5.1 Schematic diagram of Nano- roughened LED

### 1. Wafer Dicing

Automatic Dicing Saw (DAD-321, Disco) system was employed to dice the wafer. To dice the wafer firstly it was mounted on dicing tape and diced the wafer in 10 X 10 mm samples.



Figure 5.2 Automatic Dicing Saw (DAD-321) system

Table 5.2 Details of dicing process

Wafer thickness	520 $\mu$ m
Blade height	50 $\mu$ m
Tape thickness	70 $\mu$ m
Spindle rotation	18000rpm
Round work size	55mm
Cut size	15mm

## 2. Wafer Cleaning

The cleaning of samples was carried out before fabrication of LED. The cleaning of samples involved following steps-

1. Place the samples in Trichloroethylene (TCE) and boil them for 5-8 minutes in order to remove greasy particles.
2. Then boil these samples in Acetone ( $C_3H_6O$ ) for 5-8 minutes so that metal particles and residues of TCE were removed from the surface.
3. Then transfer these samples in Methanol ( $CH_3OH$ ) and boil them for 5-8 minutes to remove the traces of Acetones.
4. After this rinsed these samples in DI water properly. Finally, dehumidified these samples with dry Nitrogen.

### **3. Activation of P- GaN**

Before start of fabrication process on the LED wafers, p- layer activation at higher temperature was done. As the temperature is generally high during the growth of LED in MOCVD system, there is formation of bond between magnesium (Mg) which was used as p type dopant and hydrogen (H) which was used as carrier gas in MOCVD form and results in formation of Mg-H complex which causes Mg to be inactive and due to which resistance of p-GaN increases. Thus this bond should be broken which was done by annealing at higher temperature. As the indium present in quantum wells is decomposed at higher temperature, so the temperature of activation must be properly optimized for better results. In our work, p activation of wafer was carried out by annealing the wafer in rapid thermal annealing (RTA) system at 500 °C under N<sub>2</sub> environment for 1 minute. Rapid Thermal Annealing is done using ANNEALSYS As-One system. In this process, Mg-H bond breaks and atoms of hydrogen become free which reacts with nitrogen in the nitrogen ambient. Due to which resistance of p-GaN improves and hole concentration increases.

### **4. Incorporation of Nanostructures on the top p-GaN**

A 100nm thin SiO<sub>2</sub> layer was deposited by using (PECVD) which behaves as an insulating layer. Before the samples were loaded into the Evaporation Beam System furnaces, pre-metallization etch process was carried out in HCL and deionized water (DI).

On sample 1, the nanomask was formed by depositing a thin film of Ag with thickness of 1nm on the p-GaN surface. RTA was then performed at 550° for 60 sec in order to form Ag nano-islands on the p-GaN surface. After this, the etching of p-GaN was carried out with reactant gases BCl<sub>3</sub>, Cl<sub>2</sub>, Ar of 10 sccm, 3 sccm, 2sccm respectively.

On sample 2, a thin film of ITO with a thickness of 5nm was deposited by Electron Beam Evaporation system which works as nanomask layer. After that RTA was performed at 480° for 60 seconds. In order to etch ITO from the top surface of p-GaN, the sample was boiled in HCL for 1minute and then rinse in DI properly and blown off with dry Nitrogen. After this, the etching of p-GaN was carried out with reactant gases BCl<sub>3</sub>, Cl<sub>2</sub>, Ar of 10 sccm, 3 sccm, 2sccm respectively.





Figure 5.3 Rapid Thermal Annealing system at ODG, CEERI, Pilani

## 5. Mask Layout of LED and Photolithography Recipe

Photolithography is a process used to transfer geometric patterns to a film or substrate. Photo resist can be of two types:

A positive resist is a type of photo resist in which the portion of the photo resist that is exposed to light becomes soluble to the photo resist developer.

A negative resist is a type of photo resist in which the portion of the photo resist that is exposed to light becomes insoluble to the photo resist developer.

The resolution of the photolithography is determined by the wavelength of the exposure source. In our case, we have relatively large devices (the size of mesa is  $0.5 \times 0.5 \text{ mm}^2$  and  $1 \times 1 \text{ mm}^2$ ) and we used ultra-violet (UV) light with 365 nm wavelength. When the desired size of the device is smaller, it is necessary to decrease the exposure wavelength. The system used for photolithography was Karluss MJB3 UV 300/400 system with UV 365nm wavelength. Here SU1818G photo resist was used as a resist for photolithography steps, and as a masking layer for RIE dry etching steps.



Figure 5.4 Karluss MJB3 UV 300/400 system for photolithography

In photo resist spin coating, the samples were held on a spinner chuck by vacuum and resist is coated by providing 4000RPM for 40 seconds leading to the 2 $\mu$ m thickness. After that, the samples were prebaked at 90° for 30 minutes in order to remove the excess of solvents, densify the resist film and improve the adhesion of the resist to the wafer. Now the samples were ready for UV exposure. These samples were placed on vacuum chuck in Karluss MJB3 UV 300/400 photolithography system. Mask was held by mask holder with the help of vacuum. Then the mask was properly aligned to transfer the pattern on sample and exposed by UV light for 35 seconds. The final step of photolithography is development. Here the samples were developed in MFCD-26 developer for 70 seconds and rinsed in DI. In order to stabilize and harden the resist for subsequent dry etching process, it is post-baked at 90° for 10 minutes. It also removes any remaining traces of the coating solvent or developer.

Table 5.3 Specification of photolithography process

Photo resist used	SU(1818) Positive photo resist
Spin rotation speed	4000rpm
Spin rotation time	40 sec
Prebake time	30 min
Exposure time	35 sec
Developer used	MF-CD 26
Developing time	70 sec
Post bake time	10 sec

## 6. Mesa Formation

Reactive Ion Etching (RIE) technique using  $\text{BCl}_3$  based chemistry was used to form a mesa up to N-type GaN layer. RIE is used to open area of n-region which is beneath all the layers of LED structure. RIE is a kind of dry etching which has higher etches rate and high directionality compared to wet etching. In this process chemically reactive plasma is used, which is generated under low pressure (vacuum) by using an electromagnetic field. Due to the oscillating electromagnetic field gas molecules are ionized by stripping them of electrons. Electrons are accelerated up and down in the vacuum chamber for every cycle of EM field. And these electrons strike both upper wall of chamber and the wafer. Some of these electrons are absorbed by the walls and they are fed out to ground. The electron deposited on the wafer creates charge due to DC isolation. This charge develops large negative potential field approximately a few hundreds of volts. The plasma itself develops a slightly positive charge because of higher concentration of positive charge as compared to electrons. Due to potential difference the positive ions move towards the wafer and collide with the surface of sample. These ions reacts chemically with material deposited on the surface of sample, etch out the organic matter and it is pulled away by vacuum pump. The ions can also remove some material by transferring their kinetic energy.

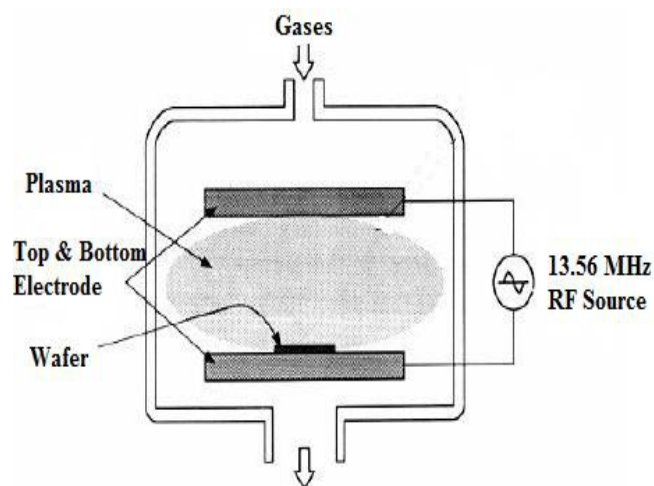


Figure 5.5 Reactive Ion Etching (RIE) system chamber



Figure 5.6 Reactive Ion Etching (RIE) system at ODG-CEERI, Pilani

In our work, RIE was performed by RIE SI 591 system using  $\text{BCl}_3$  and  $\text{Cl}_2$  gases for generation of plasma for 7 minutes. The etching rate of GaN in our set up was about 100nm per minute. After etching process, samples were boiled in Acetone for 10-15 minutes to remove photo resist from etched areas and then rinsed in DI and blown off with dry nitrogen.

Again photolithography process was done to imprint pattern for n- contact. The SU1818G photoresist was spun coated and prebaked at  $90^\circ$  for 30 minutes. After that, UV exposure was provided for 35 seconds and then developed in MFCD-26 developer for 70 seconds.

## 7. Ashing

Ashing is used to remove traces of photo resist if present in the developed area of samples by using oxygen plasma. The Specifications used in plasma ashing are given as:

Plasma Used- Oxygen

Gas Flow- 100sccm

Ashing Time- 2min

Power-200W

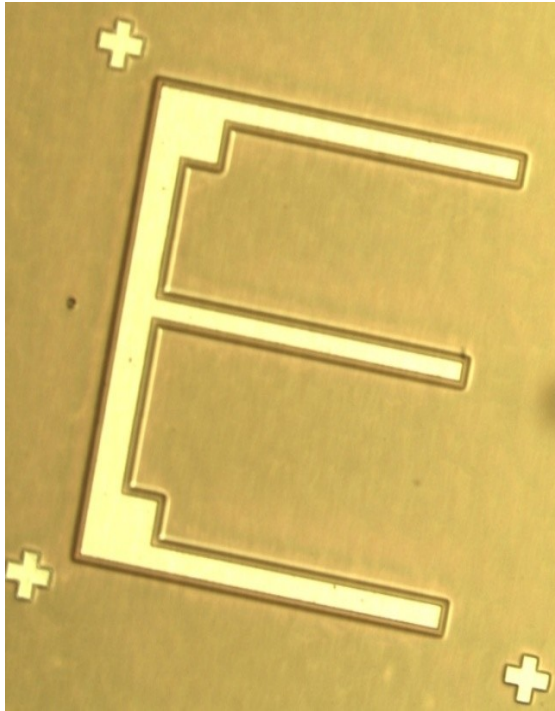


Figure 5.7LED wafer after mesa etch and ashing process

## 8. Metallization

Before metallization, pre-metallization etch process was carried out in order to remove native oxides from contaminated surface. In this process, samples were etched in HCl and DI solution in the ratio of 1:1 for 1 min and then rinsed them properly with DI water.

Metallization is very important process for formation of electrical contacts to the device. There are two techniques of metal deposition- Electron Beam Evaporation and Sputtering. In our work, we used Electron Beam Evaporation. In electron beam evaporation system, the deposition is done under condition of high vacuum so the deposited films are very pure without any extra residual particles or gases in the deposited film. An electron beam which is produced by heating of filament under high vacuum condition is incident on the material that is to be deposited on the samples by passing through focusing magnet and deflecting magnet. Then the material is heated up to its melting point by the electron beam. After reaching melting point, the material is converted into liquid and molecules of liquid will collide with each other, transfer the energy and converted into vapor. The vapor moves towards the sample and condensed on the surface of the sample.

There are two types of metal- semiconductor contacts-

### **Schottky Contact:**

When work function of metal is large as compared to semiconductor, electrons move from semiconductor to metal, leaving behind positive charges. These positive charges create a space charge region appearing as a barrier on a band diagram. If the difference in work function and electron affinity is high, the height of the barrier increases blocking further movement of electrons from semiconductor to metal and from metal to semiconductor. Schottky contact has a rectifying behavior allowing no or very small current to flow through the contact till the critical voltage is reached.

### **Ohmic Contact:**

When work function of semiconductor is large as compared to metal, electrons move from metal to semiconductor side. The height of the barrier created at the metal/semiconductor interface is quite small and electrons freely go from metal to semiconductor and in opposite way depending on applied voltage.

In photovoltaic devices, Ohmic Contact is desirable because charge carriers can easily move between metal and semiconductor. Low contact resistance in case of ohmic contact allows minimizing the power consumption of future device and prevents the internal heating of the contact.



Figure 5.8 The TFDS-462B thin film deposition system

### Ohmic Contact to n-GaN:

Formation of n-contact was done by depositing metal layers of Ti/Al/Ni/Au with thickness 30nm/130nm/20nm/50nm respectively on the exposed n-GaN region. Usually, ohmic contact is achieved by depositing metals with low work-function such as Al ( $\Phi_m = 4.24$  eV) or Ti ( $\Phi_m = 4.33$  eV) [Skriver,1992]. Lin *et al.* showed that the resistivity of Al contact can be significantly improved by insertion of thin Ti layer before Al deposition [Lin, 1993; Luther, 1997]. It was proposed that Ti forms TiN layer on the top of n-GaN resulting in a creation of nitrogen vacancies that act like donors forming highly-doped n-GaN layer on the metal/semiconductor interface. Heavy doping in the semiconductor causes a very thin depletion width, as a consequence of that the depletion layer between metal and semiconductor becomes very thin allowing carriers to tunnel through the barrier. Further the resistivity of ohmic contact was even more improved by inserting Ti/Al/Ni/Au contact [Boudart, 2000; Qin, 2004]. The top Au layer is introduced in order to avoid the oxidation of Al layer and improve the current spreading in the contact. Ni layer between Al and Au was shown to be important to prevent the Au diffusion through Ti/Al layers.

Table 5.4 Specification of n-contact

Metal	Thickness(nm)	Rate(A /sec)
Ti	30	0.2-0.5
Al	130	0.2-1.5
Ni	20	0.2-0.5
Au	50	0.2-1

### 9. Lift-off

Lift-off process is done for the removal of metal from the substrate surface in order to obtain the desired pattern. After standard photolithography process and metallization, the metal is both deposited directly on the top of the substrate and on the top of the resist that was left by photolithography. It is necessary to remove the resist together with the metal to form a final pattern. In this process, samples were placed in Glass vessel with acetone for 3-5minutes and continuously stir it.

Afterwards ultrasonic is provided for 2-3 minutes in order to remove metal completely from the substrate surface. After this, all samples were rinsed in DI Water properly and dehumidified by dry nitrogen.

RTA was performed at 830 for 30 seconds. Rapid thermal annealing provides a way to rapidly heat wafers to an elevated temperature in short time period typically less than 1-2 min long. Heating occurs by optical energy transfer between the radiating lamps that rapidly heat a single wafer resting on sharp pins or on a low-thermal mass holder. RTA system is used for dopant activation, density deposited films, for change in state of grown films and repair of damage from ion implantation.

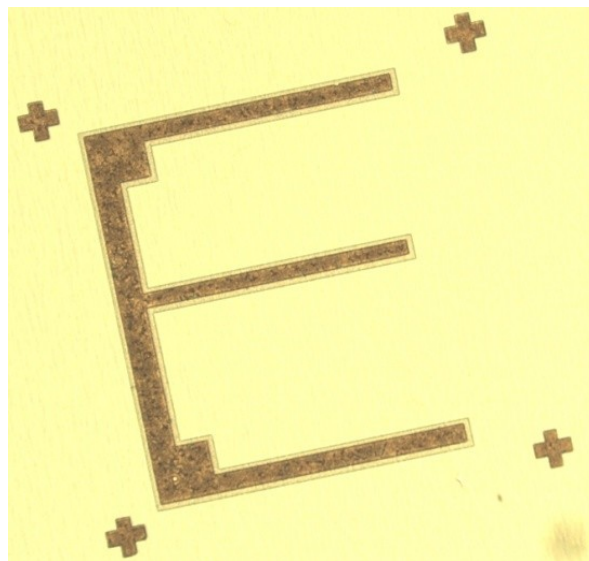


Figure 5.9 LED wafer after n contact formation

## 10. Current spreading Layer

In LEDs, generally the top p layer as a confinement layer for charge carriers is used. More ever there is top p and n metal electrodes at the top of LED structure. The current is provides to the device through these metal electrodes. Thus, most of the current is injected under the top electrode and less amount of current reaches up to active region and most of the light is generated under these metal electrodes which is absorbed by metal electrodes. This is responsible for low light extraction efficiency. In order to solve this problem, current spreading layer is incorporated at the top of LED device. This current spreading layer spreads the injected current to the regions which are not covered by these opaque metal electrodes.



In case of LEDs grown on Sapphire substrate, which behaves as an insulator, both n- contact and p-contact are formed on the top side of the surface of the LED and mesa structure is used for n-contact formation so the current laterally flows between p-electrode and n- electrode that's why most of the carriers concentrated near the mesa edge. Due to increase in current crowding effect efficiency droop also increases at higher current density. Hence current spreading layer is used to spread current more uniformly.

Current spreading layer was deposited by thin film layers of Ni and ITO with thickness of 1.5nm and 50nm respectively. Indium Tin Oxide layer (ITO) was used for current spreading layer because of its high transparency in visible region and low resistivity. But it was not possible to achieve ohmic contact by directly depositing ITO on p-GaN substrate so, Ni intermediate layer was used between ITO and p-GaN to achieve ohmic contact. Ni gets oxidize and forms NiO in the presence of ITO film because it provides oxide source. NiO behaves as p-type semiconductor and provides high hole concentration.

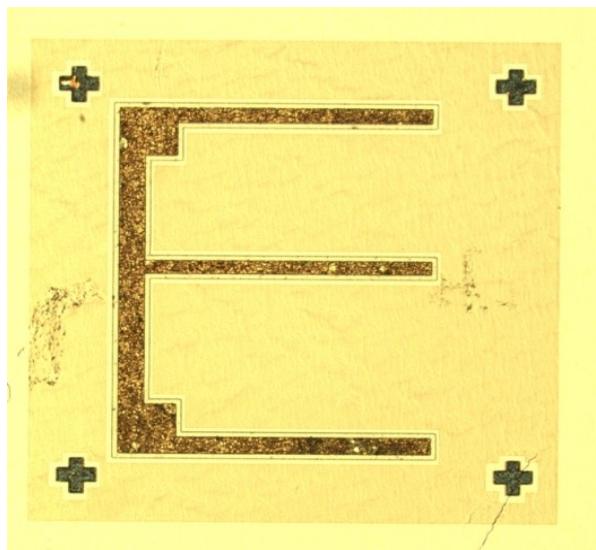


Figure 5.10 LED wafer after current spreading layer

## 11. Ohmic Contact to p-GaN

Unlike to n-contact, ohmic contact to p-GaN is very difficult to achieve. It is related to several factors:

- The lack of appropriate metals (as GaN has a large band gap (3.4 eV). Indeed, materials with very high metal work function (normally more than 5 eV) are

required.

- Quite low hole concentration in p-GaN (because of high activation energy (about 200 meV) of doping Mg atoms.

In our work, Ni/Au with thickness of 20nm/50nm respectively is used as a contact to p-GaN. Ni prevents the Au diffusion to the GaN surface and removes hydrogen from p-GaN surface [Smalc, 2010; Sheu, 1999]. Moreover, Ni has large work function (5.15 eV), is easy to use in device processing, and is low cost.

Table 5.5 Specifications of p-contact

Metal	Thickness(nm)	Rate(Å /sec)
Ni	20	0.2-0.5
Au	50	0.2-1

## 12. Rapid Thermal Annealing

The Ohmic contact has been optimized after annealing the wafers in Rapid Thermal Annealing system. Rapid Thermal Annealing has been done at 830 °C for 30 sec in N<sub>2</sub> ambient.

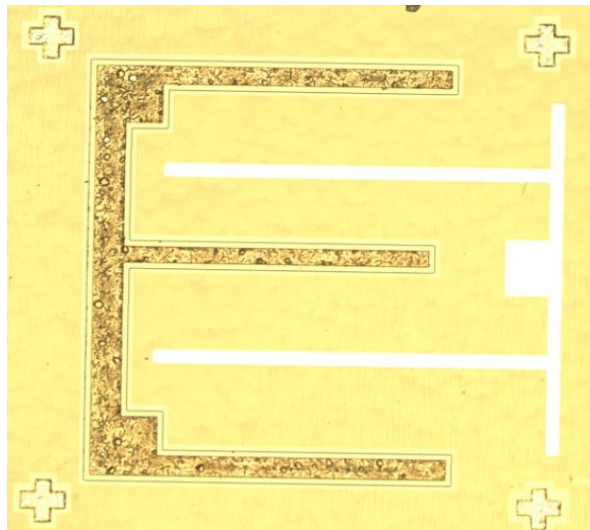


Figure 5.11 LED wafer after n-contact and p-contact

After fabrication of LED, characterization was performed in which we observed I-V characteristics, wavelength vs intensity curve of these LEDs.

## Chapter 6 Measurements and Results

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In this chapter, processed LEDs were studied regarding electroluminescence and I-V measurements. From these graphs, we can say that nanoroughening the top surface of LEDs by using Silver and ITO as nanomask, light extraction efficiency get improved and hence intensity of light. Hall measurement was done to determine mobility, resistivity and concentration of n-type and p-type ohmic contacts on semiconductor.

### 6.1 Electroluminescence (EL) measurement

EL measurement is employed to determine optical and electrical characteristics of LED samples. Electroluminescence is a phenomenon based on emission of light by applying an electrical field. It converts electrical energy into light output power.

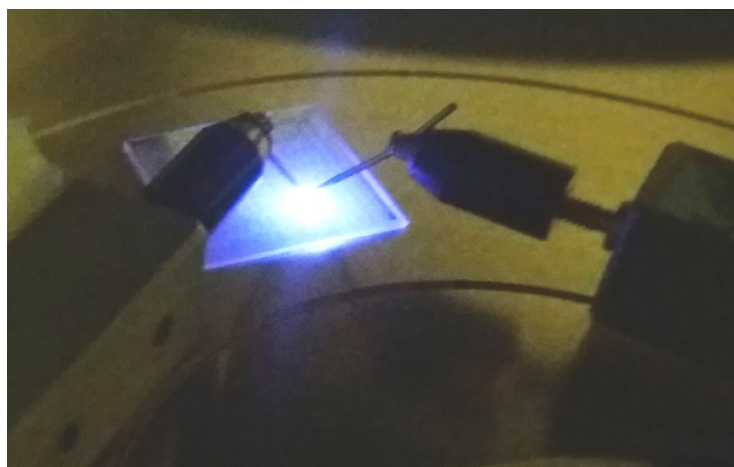


Figure 6.1 Image of blue emission from nanoroughened GaN based LED

The EL properties of the nanoroughened LEDs are measured at the injecting current of 20mA. Figure 6.1 show intensity versus wavelength graph of conventional LED and nano roughened LED. Luminescence peak of the as grown LEDs were at 405.42nm. Nanoroughened LED using Ag as a nanomask and nanoroughened LED using ITO as nanomask had peaks at 406.46nm and 426.19nm respectively. The grown MOCVD LED wafer using ITO as nanomask is different from other grown LED wafers of as grown LED and LED using Ag as nanomask. Because of different growth conditions during MOCVD, there is difference in wavelengths. Nano-

roughening the top p-GaN surface using Ag nanomask increased the output light power of the as grown GaN-based LEDs by a factor of 1.70. While nanoroughened LED using ITO nanomask have shown 1.39 times more efficiency as compared to other conventional LEDs with enhanced light extraction efficiency.

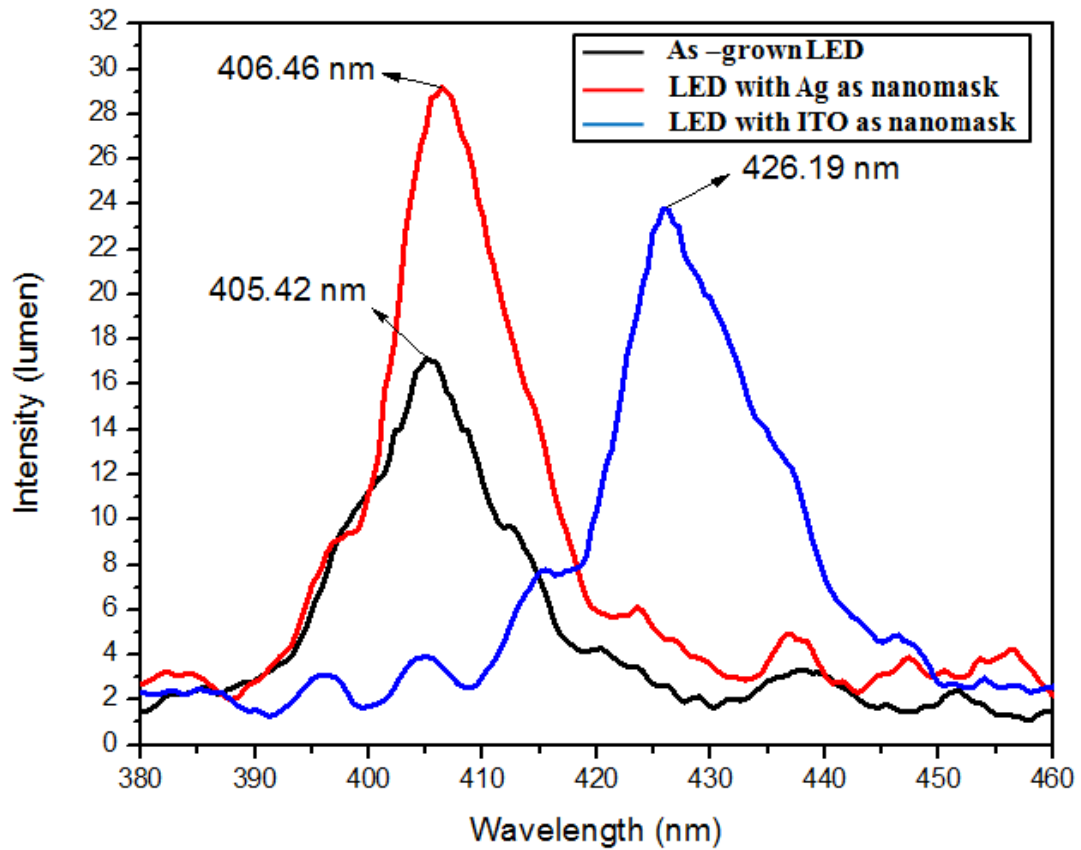


Figure 6.2 EL intensity peak spectra at different wavelengths for as grown LED and nano-roughened LED

## 6.2 I-V measurement

I-V measurement technique was employed to characterize the obtained LEDs structure. The I-V characteristics of as grown LED and nano-roughened LED are shown in Figure 6.3. Because of high resistivity, very high turns on voltages were examined. The forward voltages of the conventional LED and nanoroughened LED using Ag as nanomask and nanoroughened LED using ITO as nanomask were 4.49V and 4.65V and 4.72V at a driving current of 20mA, respectively. The nano-roughened LEDs has higher forward voltage, the reason behind this is that top surface morphology was too rough during nanostructure formation so that it is difficult to form good ohmic contact with low specific resistivity on the top p-GaN layer.

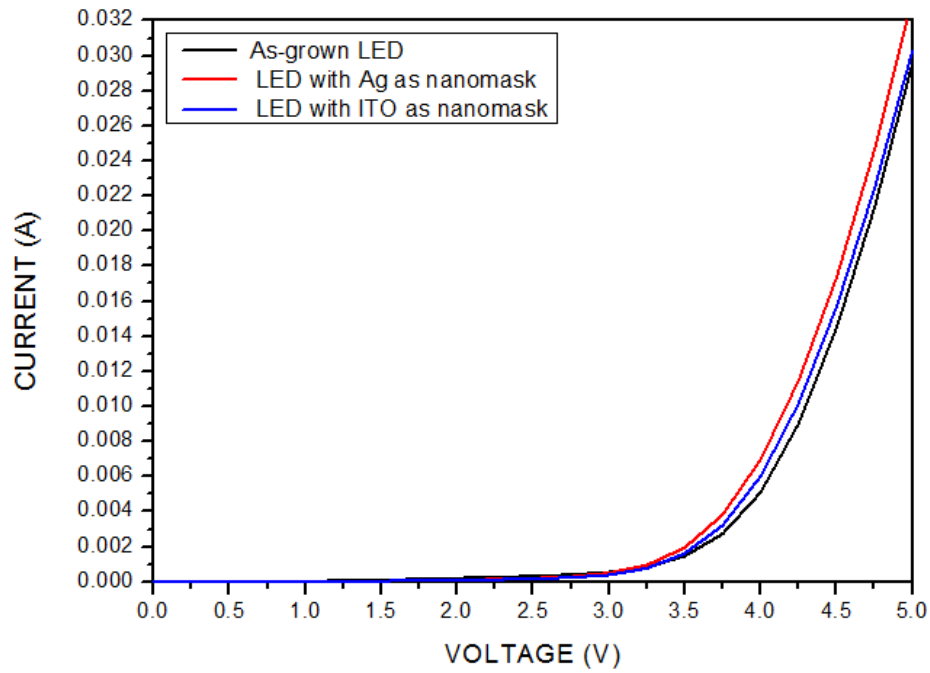


Figure 6.3 I-V Characteristics of conventional LED and nano-roughened LED

### 6.3 Hall Measurement

The Hall effect measurement technique has found wide application in the characterization of semiconductor materials because it gives values of resistivity, the carrier density, concentration and mobility. When mutually perpendicular electric and magnetic fields are impressed on an isotropic solid, the charge carriers are deflected in the third mutually perpendicular direction. If the current in this direction is constrained by the boundary of the solid (to be zero), a transverse voltage is developed to oppose the deflection of the charge carriers.

The mobility of carriers in conventional LED, nanoroughened LED using Ag as nanomask and nanoroughened LED using ITO as nanomask is 4.18cm/V-sec, 4.68cm/V-sec, 9.93cm/V-sec respectively, after performing Hall experiment.



Figure 6.4 Hall Effect Measurement System HL 5500 PC (Nanometrics)

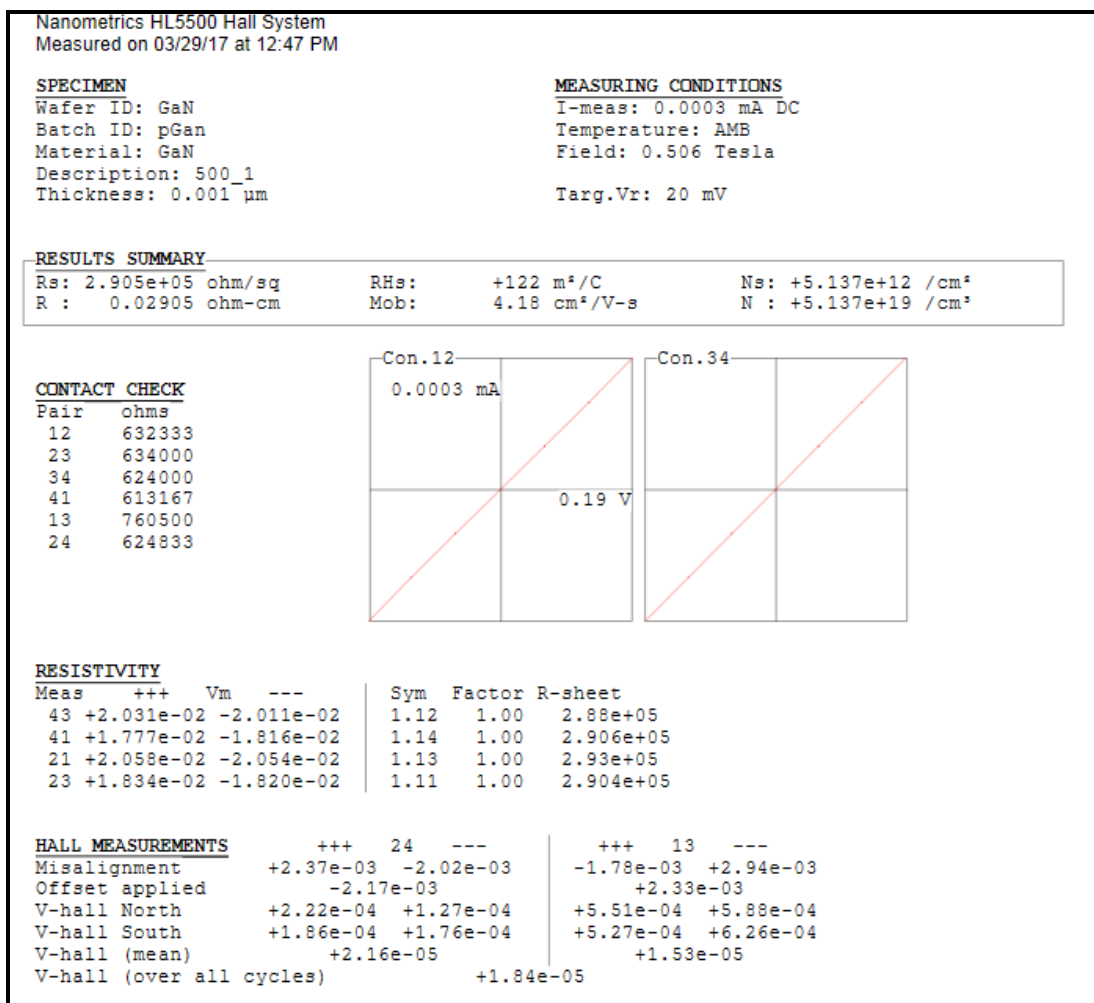


Figure 6.5 Hall measurement data for as grown LED



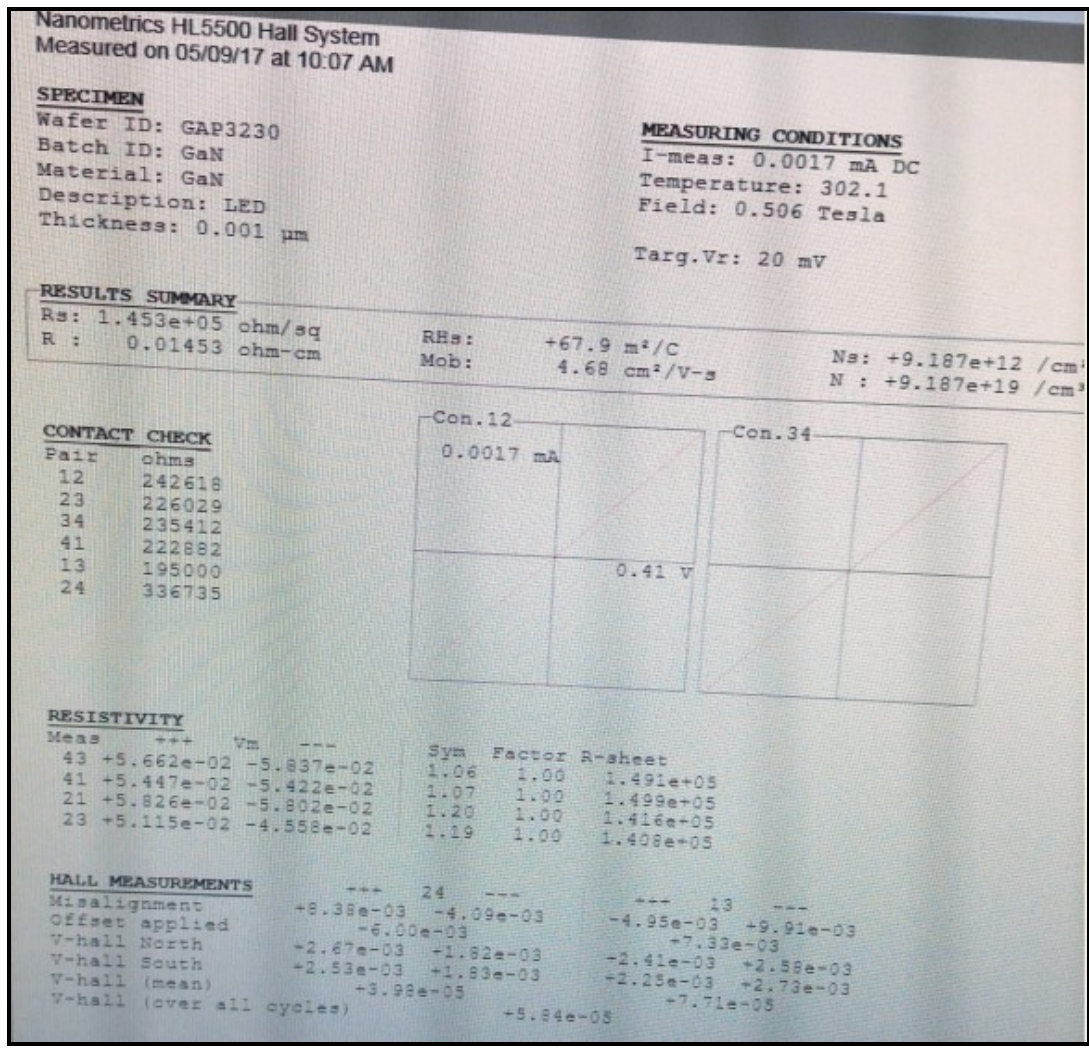


Figure 6.6 Hall measurement data for nanoroughened LED using Ag as nanomask

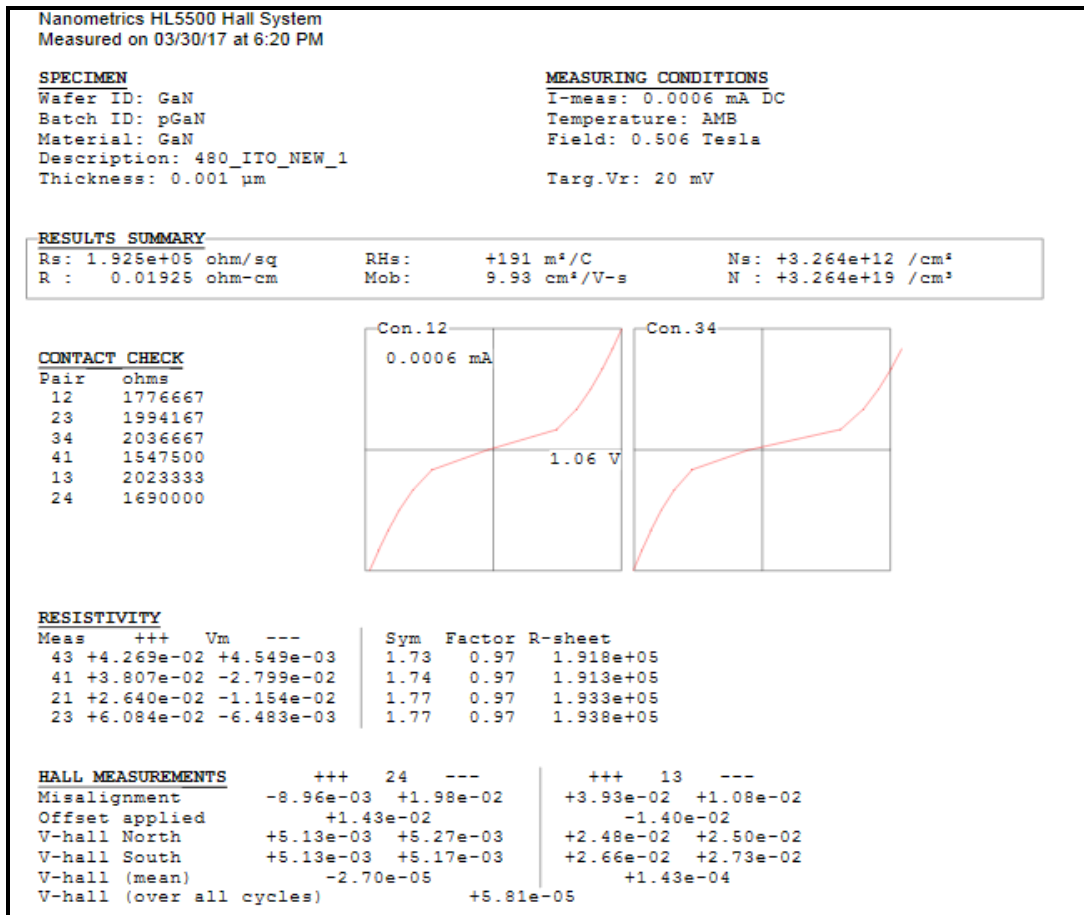


Figure 6.7 Hall measurement data for nanoroughened LED using ITO as nanomask



## Chapter 7 Conclusion

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Semiconductor group III nitride materials have been emerged as promising materials for the development of optoelectronic devices. However, they cover the entire visible and UV region spectrum, the optical problems such as total internal reflection caused by high refractive index difference limits their performance.

This thesis has given details about growth of LED wafer, fabrication steps and characterization of nanoroughened InGaN/GaN LEDs and showed improvement in light extraction efficiency. The nano-masks were successfully applied to GaN-based light-emitting diodes (LEDs) in order to accomplish nano-roughened surface to enhance light output power.

In the first part of thesis, we have shown top- down approach of fabrication of nanorods on LEDs. In this approach, Nickel was used as a nanomask and then Reactive Ion Etching was performed. This is an easy approach as compared to other lithography techniques for fabrication of nanorods. By nanostructuring, the lattice mismatch occurs between hetero layers of LEDs get reduced and hence reduction in QCSE. By reducing QCSE, there is blue shift in wavelength and we can obtain desirable wavelengths in visible light region.

In the second part, we have fabricated nanoroughened LED. In this, we have used Silver and ITO as a nanomask during Reactive Ion Etching (RIE). We have shown fabrication steps of formation of n- contact, current spreading layer and p-contact. By this approach, light extraction efficiency of LEDs increased and hence efficiency of LEDs get increased up to 2 times.

We have shown I-V Curves and wavelength v/s Intensity Curves for these LEDs. An increase in the Electroluminescence intensity of the nanoroughened LED with Ag and ITO nanomask by 1.7 and 1.39 times as compared to as-grown LED is observed.

**Future Aspect :**

Based on the obtained results, further work can be done to improve efficiency of LEDs. By fabricating of nanorods on LED structure with proper mask layout, it is possible to enhance quantum efficiency due to the reduction of lattice mismatch and strain relaxation. We can show that there is no blue shift in wavelength in nanorods based LEDs due to reduction in QCSE by photo luminescence (PL) measurement. Further simulation work can be done for these LED structures.

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## **List of Publications**

1. Alka Jakhar, Manish Mathew, Ashok Chauhan, Kuldip Singh, Vijay Janyani, Nikhil Deep, “A Top-Down Approach for Fabrication of Nanorods on GaN based LEDs using Self Assembled Ni.” International Conference on Optical and Wireless Technologies, Springer, Jaipur, India, March, 2017.