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Zinc Oxide and Nitride Nanowire Based Light Emitting Diodes

by

Elaine Michelle Lai

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requirements for the degree of
Doctor of Philosophy
in
Mechanical Engineering
in the
Graduate Division
of the
University of California, Berkeley

Committee in charge:

Professor Peidong Yang, Co-Chair
Professor Xiang Zhang, Co-Chair
Professor Liwei Lin
Professor Ming Wu

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Zinc Oxide and Nitride Nanowire Based Light Emitting Diodes

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Abstract

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Doctor of Philosophy in Mechanical Engineering
University of California, Berkeley

Professor Peidong Yang, Co-Chair
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Light emitting diodes are robust and high efficiency light sources that have the potential to replace all lighting applications in the future. Some hindrances to ubiquitous adoption of LEDs though are cost per lumen and lack of high quality materials for green emission or tunable emission. Innovations are needed to continue improving overall efficiency of light emitting diodes as well as finding suitable materials to achieve complete visible tunability. Novel light emitting diodes are made from nanoscale materials to explore potential advantages over conventional thin film approaches. These atomic-scale structures have unique electrical and optical properties that could potentially lead to increased efficiencies.

Three platforms for improved light emitting diodes were designed, fabricated, and characterized. The first consisted of an n-type ZnO vertical nanowire array grown epitaxially from a p-type GaN thin film. The resulting device showed an increase of 13% in light output in the vertical direction as compared to a thin film LED due to waveguiding of light in the vertically oriented nanowires. The second device took advantage of the ability to synthesize In_{x}Ga_{1-x}N materials in nanowire form with x greater than 30%, which would otherwise be unstable in thin film form due to phase segregation. Nanowire arrays were grown on top of conventional InGaN QW LEDs. Resulting light emission was a combination of transmitted QW blue electroluminescence and color converted photoluminescence from the array. Colors achieved ranged from blue, to blue-green, and red-orange. The final platform explored enhancement of electroluminescence by metal coating of nanopillar LEDs. The metal layer is proposed to confine light along the nanopillar and enhance radiative emission due to surface plasmons. Preliminary results suggest some extent of enhanced electroluminescence. However, fidelity of these results needs to be further explored due to concerns of light leakage through cracks in the metal layer.

Nanowire based light emitting diodes were fabricated and shown to offer advantages over thin film LEDs due to waveguiding of light in the nanowire, full-spectrum tunability, and surface plasmon electroluminescent enhancement.
I dedicate this dissertation

to my husband and to my parents.
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Thank you!
Chapter 1. Introduction

Two exciting research fields come together in this dissertation: nanoscale science and light emitting diodes. Light emitting diodes have always gained high interest to their potential for high efficiency lighting. And with the fairly recent invention of the blue light emitting diode (LED) in the early nineties, the visible spectrum has been completed, therefore driving research interest even further (1). In a parallel movement, nanoscale science promises to create new materials and devices for enhancements and innovations in many different applications, including electronics, medicine, and energy production. The idea is that these atomic-scale materials have special properties and characteristics that can be exploited, including high surface area to volume ratio and unique electrical, optical, and thermal properties.

This dissertation concerns itself with the potential advantages that nanoscale science can offer to light emitting diodes. Three avenues are explored. First, the waveguiding nature of nanowires is considered as a mechanism for improving extraction efficiency of a light emitting diode. The architecture consists of an n-type ZnO nanowire array grown atop a p-type GaN thin film. In the second avenue, nanowire morphologies allow for creation of stable In$_x$Ga$_{1-x}$N materials with $x>0.3$ (compositions that are typically unachievable in thin film state). Since the InGaN compositional family encompasses the entire visible spectrum, this nanoscale advantage can offer huge potential in the area of light emitting diodes. The second design consists of InGaN nanowires of varying composition grown atop a conventional multiple quantum well (MQW) InGaN based thin film LED. The MQW LED provides enough electroluminescence to photoluminesce the InGaN nanowires, creating a dual wavelength emission that is tunable by varying the composition of the nanowires. Finally, the third nanoscale LED design explores the effects of metal-coated emission. The large surface area to volume ratio of the nanoscale dimension allows the metal coating to exhibit substantial effects on the emission properties, either due to mode confinement and/or plasmonic enhancement of the emission material.

In this chapter, the field of nanowire photonics will be briefly discussed. Following will be an introduction to the light emitting diode, including physics, material requirements, and efficiency. Then, the potential advantages of nanoscale light emitting diodes will be explored. Finally, some applications of light emitting diodes are mentioned.

1.1 Nanowire Photonics

The area of photonics includes the generation, emission, transmission, modulation, signal processing, switching, amplification, detection, and sensing of light. The use of nanoscale materials in the area of photonics opens up endless possibilities for improvement and innovation and is undoubtedly a very current and exciting field.

Nanoscale materials can offer certain advantages over their macro counterparts. First, nanowires form a natural optical cavity. In the application of LEDs, the cavity can help to guide
the light in a certain direction and therefore improve extraction efficiency (2) (3). These natural optical cavities and naturally faceted ends can also be sufficient to sustain a lasing mode resonance and result in very tiny lasers (4) (5).

The high aspect ratio of nanowires can have benefits for solar cells and many research groups are actively pursuing this area. The large surface area to volume ratio could potentially remedy the issue of absorption versus carrier collection in solar cells. In solar cells, a large absorption area is desired to absorb as much light as possible but this creates a problem because carriers have a greater chance of recombining before they are collected as usable energy. With a nanowire structure, groups have demonstrated that a nanowire device can be designed to have both large absorption volume while maintaining a shorter carrier pathway (6) (7).

The dimensionality of nanowires could also be the ideal platform for a photonic bandgap device. A periodic array of nanowires with spacings comparable to the wavelengths of visible light will act as a physical filter of light passing perpendicular to the array (8) (9). There are currently efforts to create these perfectly aligned arrays of nanowires (10).

The small dimension of nanowires can provide tools for probing other nanoscale entities such as cells. Efforts are being made to use nanowires to interrogate cells (11).

Finally, the morphology of nanowires can offer solutions to problems that exist at the macro-level. InGaN alloys could be very advantageous to the photonic world because their range of compositions from GaN to InN span the entire visible spectrum in terms of their emission properties as related to their bandgap. However, this advantage has not been utilized because InGaN alloys suffer from phase segregation issues at compositions of above 30% InN. Recent work though has showed that these compositions can stably exist in the nanowire morphology (12).

There are many avenues to explore in the area of nano-photonics and the rest of this dissertation will focus on the area of light emitting diodes.

1.2 Light Emitting Diodes

A light emitting diode (LED) is a semiconductor diode that emits incoherent narrow-spectrum light when forward biased. An LED is a device that falls under a larger umbrella of devices that can undergo electroluminescence (EL) which is loosely defined as generation of light by an electric current passing through a material under an applied electric field (13). There are four general forms of electroluminescence (13). Intrinsic electroluminescence occurs when a semiconductor subjected to an alternating electric field can exhibit electroluminescence due to impact ionization of accelerated electrons. Avalanche electroluminescence can occur in a PN junction or metal-semiconductor barrier that has been reverse biased to the point that avalanche breakdown occurs and the resulting interband transitions emit light. Tunneling
electroluminescence also occurs in a PN junction or metal-semiconductor that has been reversed biased to the point that carriers tunnel into the active material from the metal contacts and the resulting interband transitions result in emitted light. Finally, *injection* electroluminescence occurs when a PN junction is forward biased and the movement of minority carriers across the junction leads to radiative recombination of carriers and the emission of light. Specifically, LEDs fall into this category of injection electroluminescence.

### 1.2.1 Physics

A light emitting diode is based on a PN junction diode. This diode consists of a p-type semiconductor material in direct junction with an n-type semiconductor material. When the two materials are joined together the excess carriers on either side (electrons on the n-side and holes on the p-side) will begin to diffuse across the junction. As the minority carriers cross the junction and recombine with the majority carriers already present, they leave behind ionized acceptor and donor atoms of the opposite charge in what is known as the space-charge region surrounding the junction. A negatively charged region exists on the p-side and a positively charged region exists on the n-side. This creates a “built-in” electric field across the junction. The presence of this electric field creates a drift current that occurs in the opposite direction of the diffusion current. When these two currents balance out, a state of thermal equilibrium is reached.

![Band Diagram of a PN Junction at Thermal Equilibrium](image)

*Figure 1: Band Diagram of a PN Junction at Thermal Equilibrium*

If an external applied voltage is applied to the PN junction, there will be a net current flow across the junction. The junction is considered forward biased when a positive voltage is applied to the p-side. This bias will lower the bands on the p-side with respect to the n-side, thus lowering the potential energy barrier. Therefore, more majority carriers will have enough
thermal energy to diffuse across the junction. A positive current is achieved. In a reverse bias scenario, a negative voltage is applied to the p-side, thus raising the bands on the p-side with respect to the n-side. The bands in this configuration create an energy barrier for diffusion to occur. The only current that can exist is a drift current due to the influence of the electric field on the minority carriers. This results in a negative current in the reverse bias.

![Band Diagram of a PN Junction](image)

**Figure 2:** Forward Bias and Reverse Bias Band Diagram of a PN Junction

The current-voltage characteristics of a PN junction can be described by Shockley’s Ideal Diode Equation, with some non-idealities. The generalities of this relationship are an exponentially increasing positive current in the forward bias regime and a constant negative saturation current in the reverse bias regime ($I_o$). In the following equations, $I$ is current, $q$ is elementary charge, $V_a$ is applied voltage, $k$ is Boltzmann’s constant, $T$ is temperature, $A$ is cross-sectional area, $n_i$ is intrinsic carrier concentration, $D$ is diffusion coefficient, $L$ is diffusion length, and $N$ is dopant concentration. The subscripts of P and N refer to the p-type material and n-type material, respectively. The subscripts of D and A refer to the donor and acceptors, respectively.

$$I = I_o \left( e^{qV_a/kT} - 1 \right) \quad \text{Eq. 1}$$

$$I_o = Aq n_i^2 \left( \frac{D_p}{L_p N_D} + \frac{D_N}{L_N N_A} \right) \quad \text{Eq. 2}$$

In forward bias, the current increases exponentially because as the applied bias is increased and the potential barrier between the p and n sides of the junction are lowered, there is an exponential increase in the number of carriers that have enough thermal energy to cross the junction. This is governed by the well established Fermi-Dirac theory for distribution of carriers in a semiconductor. In the following equations, $n$ and $p$ are the electron and hole concentrations, $N_c$ and $N_v$ are the effective density of states in the conduction band and valence band, $E_c$ is the
conduction band energy level, $E_c$ is the valence band energy level, $E_F$ is the Fermi level, $k$ is Boltzmann’s constant, and $T$ is temperature.

\[
n = N_c e^{-(E_c - E_F)/kT} \quad \text{Eq. 3}
\]

\[
p = N_v e^{-(E_F - E_v)/kT} \quad \text{Eq. 4}
\]

In reverse bias, there is a constant saturation current. The magnitude of this current is determined not by the magnitude of the applied reverse bias, but rather how many carriers are generated within a diffusion length of the electric field at the junction. These carriers can make it to the electric field region and drift through the region to contribute to the saturation current.

**Figure 3:** Ideal and Non-Ideal Current-Voltage Characteristics of a PN Junction Diode

There are usually non-idealities of a PN junction diode current that deviate from the ideal Shockley’s diode equation. In forward bias, overall carrier recombination can lower net current levels in the low forward bias regime. At higher levels, high level injection occurs where the concentration of minority carriers in either side of the junction begins to reach or even exceed the majority carrier concentration. At this stage, the assumptions made for the minority carrier diffusion equations no longer hold. Finally, at higher bias voltages, the series resistances in the rest of the device begin to have a significant contribution, most notably the metal-semiconductor contacts.
In reverse bias, carrier generation can contribute to the negative current in low bias regimes. At high reverse bias regimes, the device often undergoes some form of breakdown, avalanche breakdown, tunneling breakdown, or a combination of both. Avalanche breakdown often dominates in lightly doped diodes and occurs when the electric field is so large that the energy released in thermal interband transitions is enough to trigger an electron-hole pair generation event. This new electron can also undergo the same process and result in another electron-hole pair generation event. This domino effect creates an avalanche of new mobile carriers and therefore a sudden large increase in reverse bias current. Tunneling breakdown dominates in highly doped semiconductors, where depletion widths are very narrow so that in high reverse bias conditions, electrons can suddenly tunnel through the junction and result in high reverse bias current.

1.2.2 Material Requirements

A PN junction can function as a light emitting diode when the recombination of the minority carriers with the majority carriers results in an emission of a photon. This can only occur if there is a significant amount of radiative recombination, as opposed to non-radiative recombination.
This necessitates a direct bandgap material. In a direct bandgap material, such as gallium nitride, the minimum of the conduction band and the maximum of the valence band are aligned in k-space. Therefore direct transitions can occur at the same k-number when the electron recombines with the hole and a photon can be emitted. In indirect bandgap materials, such as silicon, the conduction band minima and valence band maxima are not aligned so that there cannot be a direct transition. It must be a three particle process where the electron releases some energy in the form of a phonon in order to transition in k-space to recombine with the hole. But even in a direct bandgap material, non-radiative transitions can take place through deep level traps, usually caused by defects in the material. Radiative recombination must dominate in order to have a functioning light emitting diode.

The wavelength of emission (i.e. color of the light) of a light emitting diode is determined by the bandgap of the semiconductor since the amount of energy released in the form of a photon is equal to the amount of energy lost when the electron transitions from the conduction band minima to the valence band maxima. Since the energy of a photon is equal to Planck’s constant (h) multiplied by the frequency of the photon (ν), the equation can be rearranged to show that the wavelength of the emitted light (λ) in nanometers is equal to 1240 divided by the bandgap (Eg) of the material in electron-Volts.

\[ E_g = E_{\text{photon}} = h \nu_{\text{photon}} \]  \hspace{1cm} \text{Eq. 5}

\[ \lambda_{\text{photon}} (\text{nm}) \approx \frac{1240}{E_g (eV)} \]  \hspace{1cm} \text{Eq. 6}

1.2.3 Efficiency

The efficiency of a light emitting diode can be separated into three groups. First the extraction efficiency (ηext) describes the fraction of photons generated that actually get out of the device. This can be referred to as the packaging challenge. Once photons are generated, losses can occur due to total internal reflection, internal reabsorption, and contact blocking. Another issue in extraction efficiency is desired radiation pattern.

Second, the internal quantum efficiency (ηi) describes the fraction of electrical current that contributes to excited carriers that recombine before reaching the contacts. Materials are desired that have short radiative recombination lifetimes and the diodes must be long enough to sustain these lifetimes and encourage recombination. Creative structures such as quantum wells aid in improving this efficiency by providing an energy trap where carriers do not have energy to escape once they are within the wells. Since they are trapped, they will surely recombine.
Efforts should be made to reduce contact resistance and bulk resistance so most or all of the voltage drop occurs at the PN junction. This insures minimal electrical power loss. Device engineering and design are crucial in improving this efficiency.

Finally, radiative efficiency ($\eta_{\text{rad}}$) describes the fraction of excited carriers that recombine radiatively, as opposed to non-radiatively. This efficiency relies on material selection and quality of material. Foremost, an LED requires a direct bandgap semiconductor to have any significant radiative recombination at all. However even direct bandgap semiconductors can have deep level traps which lead to non-radiative recombination. Care must be taken to grow materials of very high quality with few defects to ensure higher radiative efficiency. Smaller radiative recombination lifetimes and larger non-radiative recombination lifetimes are desired. Furthermore, surface traps and interface traps between the p and n semiconductors can also lead to increased non-radiative recombinations.

The external quantum efficiency (EQE) of the entire light emitting diode is merely a product of the three different efficiencies described here. This EQE relates the final power output of the photons to the input electrical power.

1.3 The Motivation behind Nanoscale Light Emitting Diodes

The research area of nanoscale light emitting diodes is fairly new and therefore nano-LEDs haven’t made it to the commercial realm yet. However, there are attributes of the nanowire, both physical and inherent, that could quite possibly lead to huge improvements and breakthroughs in the light emitting diode world.

1.3.1 Optical Advantages

The 2D nanoscale dimension of nanowires makes them natural optical cavities. This allows light to be guided along the long axis of the nanowire and therefore could mean improvements in extraction efficiency. Currently, conventional LEDs are made of thin film materials. Photons are most commonly emitted in all spatial directions. In LEDs that incorporate quantum wells (or thin films that are generally below 10 nanometers in thickness) can confine light within the thin film plane, thus leading to edge-emitting light emitting diodes. These quantum wells, though, are specially fabricated. Nanowires naturally have a 2D confined quantum space which can lead to a one-directional output of light. This waveguiding phenomenon has already been shown with optical excitation and electrical excitation (14). A
nanowire will function as a single-mode optical waveguide when the following equation is met (15).

\[ 1 \approx (\pi D/\lambda)\left(n_1^2 - n_0^2\right)^{0.5} \ll 2.4 \]

**Eq. 7**

![Figure 6: Schematic of waveguiding modes in a nanowire cavity](image)

The high surface area to volume ratio could have two advantages. First a metal coated nanopillar LED could be a good platform for plasmonic enhancement of electroluminescence. It has already been shown that optically excited luminescent material showed enhanced photoluminescence with a metal layer in close proximity (16). They explained that the surface plasmons increase the spontaneous emission rate in the semiconductor, leading to the enhancement of light emission. In a nanopillar configuration, there could be more metal-semiconductor interface to achieve even higher enhancements. It has been shown that a metal coated nanopillar has enhanced the electroluminescence to the point of lasing in the nanopillar (17).

The increased surface area to volume ratio also means that the light has a greater chance to escape to the outside world rather than get reabsorbed in the semiconductor material. There is calculated to be about two times more surface area for light to escape in a nanowire platform versus a dimensionally comparable thin film platform.

![Figure 7: Schematic of light emission in a thin film device versus a nanowire device](image)

1.3.2 Electrical Advantages
Nanowire light emitting diodes could help to increase radiative efficiency. Nanowires are grown in a bottom up approach and most often epitaxial growth from a lattice matched substrate is involved. This commonly leads to a highly defect free material growth. None of the dislocations associated with thin film strain are apparent in nanowire growth. Therefore, if a p-type material is grown from an n-type material or vice versa, there are potentially less interface traps and higher material quality (less defect states) in the materials in general. This will decrease non-radiative recombination in the light emitting diode. However nanowires do have increased surface states which can lead to an increase in non-radiative recombination.

The size of the nanowire LED could also be advantageous for integration with the integrated circuit world. Fiber optic communications could benefit from high efficiency nanoscale light sources and optical/electrical equipment can benefit from light emitting diodes that can be integrated into the tiny platforms of existing circuitry.

1.4 Applications

The applications for light emitting diodes are plentiful. In general, they can be useful in all lighting applications. This can include general lighting, displays such as televisions and cell phones, signaling, signage, and more currently automotive lighting.

A breakdown of the LED market is shown on the left and a breakdown of energy consumption in the US by lighting technology is shown on the right. These graphs are represent the year 2002. Clearly, LEDs have a long way to go in terms of penetration into the market. There are still challenges in terms of output power, efficiency, and cost and will be discussed in the next chapter.

![Figure 8: a) 2002 LED market by application and b) 2002 breakdown of energy consumption for lighting in the US taken from Pelka (18)]

The US Department of Energy set a roadmap for solid-state lighting. Their predictions are that light emitting diodes can lead to a savings of $100 billion dollars a year and an annual reduction in carbon emissions of about 200M tons if all light sources were replaced (19).
Chapter 2. Literature Review

In the previous chapter, the science behind a light emitting diode was explained and the potential for improvements utilizing nanoscale science was introduced. In the following sections, the current state of LEDs will be discussed, including current materials used and the currently achievable efficiencies. Then, methods for achieving white light emitting diodes are shown, including commercially available white LEDs and research level novel approaches. Finally, some examples of current research efforts in nanowire light emitting diodes are explored.

2.1 The Current State of LEDs

Light emitting diodes have a fairly short history. The first infrared LEDs were discovered in the 1950’s by Braunstein (20). The discovery of the first visible LED in the red region is credited to Holonyak in 1962 (21). From there red, yellow, and green LEDs were made and began to gain popularity and were used mostly as indicators for industrial and research equipment. In order for LEDs to truly gain popularity and ubiquity however, one of the challenges to overcome was to complete the visible spectrum with a blue LED. The aluminum gallium indium phosphide family covered the most of the spectrum from red to yellow-green, however a new material needed to be utilized to realize the blue emission (22).

Figure 9: The workhouse materials for LEDs showing bandgap energy versus lattice constants. Taken from Krames (22)
The discovery was slow to come and it wasn’t until the very early 1990’s that the first practical blue LED was created by Nakamura. The reason he was able to achieve this goal was because he discovered a reliable way to make p-type GaN material (1). As will be discussed in the next chapter, GaN is intrinsically n-type. In order to have an LED device, a p-type material needs to be in junction with an n-type material. Researchers knew Mg was the most probably p-type dopant for GaN but had great difficulties in ionizing the dopants and making a p-type material. Nakamura discovered that hydrogen, which became dissociated from ammonia (NH₃) during thermal annealing, would form acceptor-H neutral complexes in the material. The hydrogen essentially provided hole compensation and therefore prevented p-type material to be attained (23). He fixed this problem by simply annealing in N₂ instead of NH₃. The result was the discovery of the p-type GaN material and led to the making of the first blue LED.

Light emitting diodes offer the potential for highly efficient and low cost lighting solutions. The reason for its high efficiency is that there is a direct electrical to light conversion and the emission spectrum from a light emitting diode is narrow where the wavelength of emission is dictated by the material’s bandgap. Other common lighting sources, in contrast have a broad emission spectra. The incandescent light bulb for example works under the mechanism of incandescence, or heat-driven light emission. Simply put, an electric current is passed through a thin filament until it is hot enough to produce light (24). The more efficient fluorescent lamp is a gas-discharge lamp. It uses electricity to excite mercury vapor that is encapsulated in the bulb, producing ultraviolet light. The UV light in turn excites phosphors that emit visible light (25). Both of these light sources have wasted emission and energy as can be seen in the spectra below. Furthermore, fluorescent lamps are environmentally unfriendly due to the presence of mercury. Light emitting diodes have robust solid-state components and don’t result in wasted emission. Their mechanism of light emission also allows for a long life span. LEDs operate at low powers and heat generation and dissipation are not nearly as critical as in the more commonly known light sources.

![Output spectra of incandescent light bulb, fluorescent lamp, and blue light emitting diode. (24) (25)](figure10.png)
2.2 LED Efficiencies

As described in Chapter 1, the total efficiency of an LED, or external quantum efficiency, is made up of its extraction efficiency, internal quantum efficiency, and radiative efficiency. Innovative engineering has increased external quantum efficiency quite a bit as shown in the figure below. The highest efficiencies are on the order of 50%. However it is clear that not all wavelengths are created equal. Efficiency drops off in the longer wavelengths for the nitride regime and in the shorter wavelengths for the phosphide regime. The reason for the dropoff in the nitrides relates to the difficulties in producing high indium nitride concentration compounds due to the miscibility gap as well as the compressive strain in the high indium nitride concentration compounds atop the conventional GaN/sapphire base layers. The dropoff in the phosphides has to do with a shift from direct to indirect bandgap in going from red to yellow wavelengths (22).

![Figure 11](image_url)

**Figure 11:** a) External quantum efficiencies for LEDs of various emission wavelengths and b) external quantum efficiency and light output for blue and green LEDs as a function of forward current (22)

These external quantum efficiencies seem fairly high, however, these are values rated for the maximum performance of an LED at a specific input current. These optimal levels are generally low-levels for LEDs, around the order of 10s of mA. Once current levels are increased, as seen in the graph on the right, a phenomenon known as droop occurs. Droop is defined as the decrease in external quantum efficiency of LEDs as injection current increases. The causes of droop are increased forward voltage, leading to an increase in series resistance contribution, heating of the chip, and also a decrease in internal quantum efficiency. In fact, the decrease in internal quantum efficiency plays the most dominant role. The reason for the
decrease in internal quantum efficiency is still not completely understood however some mechanisms include electron leakage into p-layers, Auger recombination, and de-localized recombination in quantum dot like InGaN compositional fluctuations (22).

2.3 White Light Emitting Diodes

With the recent advances of the blue LED, the path was paved for realizing a white LED. Since LEDs are many advantages, namely efficiency, over current white light platforms, it would be very useful to create a high intensity true white LED. Two common platforms are used to create the white LED. The **Multichip Method** combines the emission from three separate LED chips combining the colors blue, green and red. The advantage of this method is that you can achieve a full tunable range of color by varying the contributions of each chip. This advantage could be applied to displays. However, a three chip system is a complicated system that needs color feedback circuitry for degradation over time and temperature cycles. It is not a practical or cost-effective method for general lighting applications. The **Color Conversion Method** combines a blue LED with yellow phosphor coatings. The phosphor is excited by the blue emission and the combination of the transmitted blue emission and broad yellow emission from the phosphors results in white light. This method is simple and combined into one chip. One disadvantage though is the reliance on phosphors which are known to gradually lose efficiency over time. Also the Stokes shift, the loss of energy resulting from the absorbed photon relaxing down to the phosphor transition levels, ultimately means the light emitting diode is less efficient.

![Figure 12: Schematic of white LED generation platforms including the a) Multichip Method and the b) Color Conversion Method.](image)

Typical luminescence spectra for color converted white light LEDs are shown below. The spectra on the left is for an InGaN/GaN blue LED with YAG phosphor coating. To get a “white” emission, they tune the relative contributions from the blue LED and emission from the YAG. Typically though, these devices are a “cool” white, with CRI typically below 80 and CCT around 4000K. In order to be appropriate for indoor lighting use, a CRI of above 80 and CCT closer to 3200K are necessary. Therefore, efforts have been made to produce multi-phosphor conversion LEDs which produce a warmer tone can be compared to a black-body radiator as seen in the spectra on the right.
Figure 13: Luminescence spectra for a) blue + YAG LED and b) blue + multi-phosphor LED (22)

With the advances in white conversion LEDs, the output is now comparable to other white light sources as seen in the graph below. In terms of lumens/W, the LED beats the incandescent bulb and is on the same order as fluorescent lamps. The US Department of Energy roadmap for solid state lighting reports that when luminous efficacy reaches 137 lm/W, the worldwide energy savings could be 1000 TW h/year, corresponding to a savings of $100 B/year, if all general lighting was replaced (19).

Figure 14: Luminous efficacy of common white light sources over the years (22)
The most high intensity white LED thus far has been produced by Nichia Corporation and is based on the color conversion platform. These LEDs are bright enough to be used for lighting and are commonly seen on state-of the art car headlights and backlights. They claim that their newest white LED has a luminous efficiency of 150 lm/W (26).

The issue though is still cost per lumen. LEDs still need to improve in terms of overall internal quantum efficiency and the issue of droop. This would in turn improve the cost per lumen. The upfront cost to the consumer is still much higher for an LED as opposed to an incandescent light bulb as shown in the table below. A second issue is reliability at high current levels. Lumen depreciation begins to occur at 3500 hours (22).

Table 1: Luminous Efficacy, Lifetime, and Cost for Common White Light Sources (22)

<table>
<thead>
<tr>
<th>Light Source</th>
<th>Luminous Efficacy (lm/W)</th>
<th>Lifetime (hours)</th>
<th>Upfront Cost for ~1000lm ($)</th>
<th>Operating Cost over 2000 hours ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incandescent</td>
<td>~17</td>
<td>2,000</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>Fluorescent</td>
<td>~80-100</td>
<td>10,000-16,000</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>LED</td>
<td>~70-100</td>
<td>3,500</td>
<td>30</td>
<td>3</td>
</tr>
</tbody>
</table>

Although white conversion LED is currently the accepted model in commercial production, researchers have come up with novel approaches toward white light generation. Researchers at Bilkent University in Turkey hybridize the top surface of a blue LED with various types of CdSe/ZnS core-shell nanocrystals in a UV-curable polymer (27). They can add various layers of nanocrystals with different emission wavelengths to combine and create white light.

Researchers at the Chinese Academy of Sciences in Beijing created a novel white light emitting diode by controlled production of In-rich quantum dots by phase separation of indium from InGaN quantum wells (28). The result is a mixture of blue and yellow lights coming from the InGaN quantum well and In-rich quantum dots, respectively.

2.4 Nanowire Light Emitting Diodes

Although nanowire based LEDs are not in the commercial sector, they are quite a number of research groups in the field to try to utilize the potential advantages of nanowires as described in Chapter 1. The two general approaches to nanowire LEDs are a nanowire array LED or single nanowire LED.

Researchers at Yonsei University in Korea have developed a ZnO nanowire array/p-type GaN thin film LED (29). Both their thin film and nanowires are grown using the metal-organic chemical vapor deposition (MOCVD) approach. Researchers at Portland State University discovered a way to make a flexible nanowire array LED device (30). Their LED is based on a
ZnO nanowire array and p-type polymer called PEDOT/PSS. Synthesis of the nanowire array was by electrodeposition. The entire LED was built on a transparent polyethylene terephthalate (PET) foil, giving it its flexible nature. The resulting maximum radius of curvature was around 10 µm.

Researchers at National Institute of Standards and Technology, in collaboration with Howard University and University of Maryland developed a single nanowire LED (31). Their platform was a n-type GaN nanowire on p-type GaN thin film. The nanowires were assembled by dielectrophoresis (DEP). There were able to detect band emission from the device. Researchers at Peking University grew ZnO wires by chemical vapor transport method (CVT) and dispersed them on p+ silicon substrate (32). Band edge emission was observed in addition a 700 nm peak was observed due to luminescence centers in native Si oxide layer on p+ Si substrate.

In this dissertation, several other novel approaches to nanowire light emitting diodes will be explored. First, an n-ZnO nanowire array on p-type GaN thin film LED will be demonstrated. This work differs from previous work in that the ZnO nanowire array is made by a simple, cost effect hydrothermal method. Second, light emitting diodes based on InGaN nanowire will be explored. InGaN thin films suffer from phase separation at high indium nitride concentrations however a method has been developed to create stable high indium nitride concentration compounds through a nanowire medium (12). Third, metal coated nanopillars for enhanced electroluminescence will be explored.
Chapter 3. GaN, ZnO, and InGaN

Thus far, the physics behind light emitting diodes and the potential advantages of nanoscale concepts has been discussed. The current state of light emitting diodes and nanoscale light emitting diodes has also been reviewed. Before moving on to the actual devices of this dissertation, it is first necessary to include a survey of the materials explored. Namely, background knowledge of the material, electrical, optical, and thermal properties of the semiconductors involved is crucial in understanding the diode characteristics and performance.

The materials studied in the realm of this dissertation include ZnO, GaN, and InGaN. ZnO and GaN are both interesting because they are wide and direct bandgap materials (33) and have the potential to be very useful for short wavelength photonic devices. In addition, ZnO is chemically stable and environmentally friendly (34). GaN is both electrically and thermally robust, a useful characteristic for device performance. The compositional family of InGaN materials is highly interesting due to the fact that their bandgaps, from pure GaN to pure InN, encompass all the visible wavelengths. This can have huge potential in the area of lighting, displays, and communication (35).

First, ZnO and GaN will be explored. Then, the special case of the InGaN family will be examined.

3.1 Structure and Growth

3.1.1 Crystal Structure

ZnO and GaN exist stably in the wurtzite crystal structure. This is a hexagonal structure as shown in the figure below. The smaller atom, i.e. Ga or Zn, are represented by the smaller red spheres and the larger atoms, i.e. O and N, are represented by the larger yellow spheres. Images are courtesy of the US Naval Research Laboratory Website (36).
Figure 15: Schematic of wurtzite hexagonal structure, showing 3D perspective as well as the commonly referred to c-plane, m-plane, and a-planes.

The planes commonly referred to in a wurtzite hexagonal structure are the c-plane, m-plane, and a-plane. There is also a commonly referred to r-plane, not pictured here. Commercially available substrates are offered in these orientations. The bandgap of ZnO and GaN are very similar, 3.36eV and 3.35eV respectively. Furthermore, their lattice constants are also closely matched, with only a maximum lattice mismatch of about 1.9% in the a-plane (37).

Table 2: Bandgap and Crystal Structure of ZnO and GaN

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>3.36</td>
<td>3.35</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Wurtzite Hexagonal</td>
<td>Wurtzite Hexagonal</td>
</tr>
<tr>
<td>Lattice Constants (Å)</td>
<td>a=3.249</td>
<td>a=3.189</td>
</tr>
<tr>
<td></td>
<td>c=5.205</td>
<td>c=5.186</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>2.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>
3.1.2 Growth Substrates

It is still a challenge to grow bulk crystals of GaN or ZnO and therefore substrates of different materials must be utilized for growth (33). The table below summarizes possible growth substrates for GaN. Most commonly, GaN films will be grown on sapphire (Al₂O₃) substrates. This is often the best choice in terms of availability, cost, lattice matching, and thermal expansion. The following table summarizes the properties of available materials.

**Table 3: Material Properties of Possible GaN Growth Substrates, taken from Strite (33)**

<table>
<thead>
<tr>
<th>Material</th>
<th>Symmetry</th>
<th>Lattice parameters</th>
<th>Coefficient of Thermal Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wurtzite GaN</td>
<td>Hexagonal</td>
<td>a = 3.189Å</td>
<td>5.59x10⁻⁶/K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 5.185Å</td>
<td>3.17x10⁻⁶/K</td>
</tr>
<tr>
<td>Wurtzite AlN</td>
<td>Hexagonal</td>
<td>a = 3.112Å</td>
<td>4.2x10⁻⁶/K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 4.982Å</td>
<td>5.3x10⁻⁶/K</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Hexagonal</td>
<td>a = 4.758Å</td>
<td>7.5x10⁻⁶/K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 12.991Å</td>
<td>8.5x10⁻⁶/K</td>
</tr>
<tr>
<td>Si</td>
<td>Cubic</td>
<td>a = 5.4301Å</td>
<td>3.59x10⁻⁶/K</td>
</tr>
<tr>
<td>GaAs</td>
<td>Cubic</td>
<td>a = 5.6533Å</td>
<td>6.5x10⁻⁶/K</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>Hexagonal</td>
<td>a = 3.08Å</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 15.12Å</td>
<td>--</td>
</tr>
<tr>
<td>3C-SiC</td>
<td>Cubic</td>
<td>a = 4.36Å</td>
<td>--</td>
</tr>
<tr>
<td>InP</td>
<td>Cubic</td>
<td>a = 5.8693Å</td>
<td>4.5x10⁻⁶/K</td>
</tr>
<tr>
<td>GaP</td>
<td>Cubic</td>
<td>a = 5.4512Å</td>
<td>4.65x10⁻⁶/K</td>
</tr>
<tr>
<td>MgO</td>
<td>Cubic</td>
<td>a = 4.216Å</td>
<td>10.5x10⁻⁶/K</td>
</tr>
<tr>
<td>ZnO</td>
<td>Hexagonal</td>
<td>a = 3.252Å</td>
<td>2.9x10⁻⁶/K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 5.213Å</td>
<td>4.75x10⁻⁶/K</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>Cubic</td>
<td>a = 8.083Å</td>
<td>7.45x10⁻⁶/K</td>
</tr>
</tbody>
</table>

Sapphire as a growth substrate, however, is far from perfect. A lattice mismatch of 16.1% is obtained when comparing the spacing of oxygen atoms in the (001) plane of sapphire to the spacing of nitrogen atoms also in the (001) plane of GaN. The following figure, taken from Edgar et. al., demonstrates the lattice mismatch schematically (38). The average oxygen spacing in Al₂O₃ is 2.75 Å. The lattice constant “a” of GaN, the spacing between Ga atoms, is 3.18 Å, giving the calculated 16.1% lattice mismatch.
As a result, high amounts of dislocations are a challenge in GaN thin films. The most notable detriment is that the dislocations reduce the internal quantum efficiency of a light emitting diode by increasing the number of non-radiative pathways. Dislocation densities are on the order of $1 \times 10^8 - 1 \times 10^{10}$ cm$^{-2}$ (22).

### 3.2 Electrical Properties

#### 3.2.1 Bandgap

Both GaN and ZnO have a direct bandgap which is essential in photonic devices. A direct bandgap means the maximum of the valence band and minimum of the conduction band are aligned in k-space, allowing for a direct transition during an electron-hole recombination resulting in the emission of a photon with energy equal to the bandgap. They are also both intrinsically n-type in nature. This means both materials, grown naturally will have excess electrons. GaN is intrinsically n-type due to the existence of nitrogen vacancies (33). ZnO is intrinsically n-type due to the existence of zinc interstitials and oxygen vacancies (34).

Two of the most common challenges in ZnO and GaN photonic devices are described in the next two sections, namely the existence of deep level traps and the problems in p-type doping.

#### 3.2.2 Deep Traps

The prevalence of deep traps in GaN and ZnO are a challenge for photonic devices. As described in the previous chapter, the efficiency of an LED relies on the ability for electrons and holes to recombine radiatively. Deep level traps are finite numbers of energy states deep within the bandgap that are caused by impurities and defects. The deep traps can assist in non-radiative recombination.
recombination and lead to a decrease in efficiency of the LED. As stated before, high purity GaN and ZnO materials are still a challenge to create, therefore defects play a substantial role in device performance. Following are diagrams of common deep level traps in GaN and ZnO, taken from Van de Walle et. al. (39) and Djurisic et. al (34).

![GaN Deep Level Traps](image1)

![ZnO Deep Level Traps](image2)

**Figure 17:** Deep Level Traps of GaN and ZnO. Diagrams taken from Van de Walle et. al. (39) and Djurisic et. al. (34)

### 3.2.3 Doping

Doping is one of the biggest problems in using ZnO and GaN materials in photonic devices. The problem is the difficulties in creating stable p-type ZnO and p-type GaN. Only recently has it been shown that p-type GaN can be made reliably (1) and even then, the dopant concentrations have limitations and electrical characteristics are not ideal. P-type ZnO has still to be made reliably but efforts are definitely in process (40).

The difficulties in achieving p-type are similar in the two materials. Specifics will be described in terms of GaN since this field is more understood. The first problem is solubility. There is a maximum concentration that an impurity can attain in a semiconductor. For GaN, the typical p-type dopant is magnesium and the solubility of Mg in GaN is limited by the formation of Mg$_3$N$_2$. Second, the ionization energy of p-type dopants in both materials is large. The ionization energy describes the percentage of dopants that will contribute to free carriers at a given temperature. The ionization energy of Mg in GaN is around 210 meV, meaning only 1% of Mg atoms are ionized at room temperature. In order to dope the material to a certain level, 100X that dopant concentration needs to be introduced into the material. As a comparison, the ionization energies of boron and phosphorus as dopants in silicon are around 30 meV which means most dopants are ionized at room temperature.

Third, these materials are compounds, zinc oxide being an II-VI compound and gallium nitride being an III-V compound. Therefore, impurities must be incorporated into the correct lattice site of the material. In silicon, the dopants boron and phosphorus can reside at any lattice


point. In GaN, the Mg atom (a Group II element) must occupy a Ga site to act as a typical acceptor. Fourth, these materials want to self-compensate. They are both n-type by nature and typically want to stay in that configuration. Finally, compensation by foreign impurities can create a challenge. Oxygen impurities in GaN will act as a donor. Therefore, growth systems must be carefully cleared of oxygen contamination (39).

The reason why the ionization energies for holes in ZnO and GaN are so large can be explained by the hydrogenic model (13). The hydrogenic model describes the dopant atom as a hydrogen atom with its donor electron or hole as the single electron in a hydrogen atom. The electron or hole binding energy can be described by the electron binding energy in hydrogen atom with two modifications. The equation is adapted to take into account the relative permittivity and effective electron or hole mass of the host material. Furthermore the Bohr radius is calculated in the same manner. In the following equations, $E$ is ionization energy, $q$ is elementary charge, $m_o$ is mass of a free electron, $\varepsilon_o$ is free-space permittivity, $h$ is Planck’s constant, $m^*$ is effective mass, and $\varepsilon_r$ is relative permittivity.

\[
E = \frac{q^4 m_o}{2(4\pi \varepsilon_o h)^2} \left( \frac{m^*}{m_o} \frac{1}{\varepsilon_r} \right) = 13.6eV \left( \frac{m^*}{m_o} \frac{1}{\varepsilon_r} \right)
\]  
\[\text{Eq. 8}\]

\[
r_{Bohr} = \frac{4\pi \varepsilon_o \eta^2}{q^2 m_o} \left( \frac{m_o}{m^*} \frac{\varepsilon_r}{\varepsilon_{o,\varepsilon_r}} \right) = 0.05nm \left( \frac{m_o}{m^*} \frac{\varepsilon_r}{\varepsilon_{o,\varepsilon_r}} \right)
\]  
\[\text{Eq. 9}\]

The equations illustrate that the smaller the binding energy is, the greater the Bohr radius, and vice versa. If a host material demonstrates a small electron binding energy, and therefore a large Bohr radius, then the dopant electron will more easily become a free carrier. If the host material demonstrates a large electron binding energy, and therefore a small Bohr radius, then the dopant electron is tightly bound to its atom and does not easily become a free carrier. The same analogy applies for holes. The following table summarizes the electron and hole binding energies and Bohr radii for ZnO, GaN, and the commonly known Si. Looking at the hole binding energies, it can easily be seen that ZnO and GaN have much higher hole binding energies than silicon.
Table 4: Binding energies and Bohr radii for ZnO, GaN, and Si

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>GaN</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_f$</td>
<td>9.16</td>
<td>8.9</td>
<td>11.7</td>
</tr>
<tr>
<td>$m_e^*/m_0$</td>
<td>0.24</td>
<td>0.2</td>
<td>0.26</td>
</tr>
<tr>
<td>$m_h^*/m_0$</td>
<td>0.59</td>
<td>1</td>
<td>0.39</td>
</tr>
<tr>
<td>Electron Binding Energy (eV)</td>
<td>0.039</td>
<td>0.034</td>
<td>0.026</td>
</tr>
<tr>
<td>Hole Binding Energy (eV)</td>
<td>0.096</td>
<td>0.172</td>
<td>0.039</td>
</tr>
<tr>
<td>Electron Bohr Radius (nm)</td>
<td>1.908</td>
<td>2.225</td>
<td>2.250</td>
</tr>
<tr>
<td>Hole Bohr Radius (nm)</td>
<td>0.776</td>
<td>0.445</td>
<td>1.500</td>
</tr>
</tbody>
</table>

The following table shows possible donors and acceptors for GaN and their binding energies as a substitutional atom at either the Ga or N site. Mg is shown to have the most potential as an acceptor in GaN.

Table 5: Possible donors and acceptors for GaN. Tabulated from NSM. (41)
The following figures shows conceptually the hole binding energies of various acceptors. As can be seen, all hole binding energies are larger than the predicted 172 meV as predicted by the hydrogenic model. The additional binding energy can be due to the ability for the atom to actually fit in the lattice site due to physical size. The figure supports again that Mg is the most plausible acceptor for GaN. The ~250 meV hole binding energy is much larger than the native defect binding energy shown as ~30 meV. This native defect is most commonly reported as the nitrogen vacancy and the low binding energy gives reason for its prevalence in the material.

![Binding Energies](image)

**Figure 18:** Binding energies for substitutional acceptors in GaN. Also shown is the shallow nitrogen vacancy donor level, responsible for the intrinsic n-type nature of GaN. Taken from Strite et. al. (33)

### 3.2.4 Electrical and Thermal Breakdown

GaN and ZnO are both fairly robust in terms of electrical and thermal breakdown. Especially GaN has a high melting point and electric breakdown field as shown in the table below. These properties are desirable for photonic/electronic devices.
Table 6: Thermal and Electrical Breakdown Properties of ZnO, GaN, and Si as tabulated from (41) (33) (42)

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>GaN</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>3.36</td>
<td>3.35</td>
<td>1.12</td>
</tr>
<tr>
<td>Thermal Conductivity (W/cmK)</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1975</td>
<td>2500</td>
<td>1412</td>
</tr>
<tr>
<td>Breakdown Field (MV/cm)</td>
<td>&gt;1</td>
<td>5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

3.3 Photonic Properties

3.3.1 Emission Properties

GaN and ZnO are both direct bandgap materials; therefore an electron-hole recombination event can result in the emission of a photon with energy equal to the bandgap of the material. The wavelength of emission can be described by Eq. 6 as shown Chapter 1 and the results are shown in the following table.

Table 7: Wavelength of Emission for ZnO, GaN, and Si

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>GaN</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>3.36</td>
<td>3.35</td>
<td>1.12</td>
</tr>
<tr>
<td>Wavelength of Emission (nm)</td>
<td>369</td>
<td>370</td>
<td>1107</td>
</tr>
</tbody>
</table>

The emission properties of p-type GaN are red shifted to around 440 nm. The reason lies in the large binding energy of the Mg acceptor dopant. Since the binding energy is large, many acceptors are not ionized therefore leaving many holes available for recombination at the acceptor ionization energy level. Electrons from the conduction band are free to recombine with these holes and the result is emission of photons with energies less than the bandgap energy of GaN (43).
3.3.2 Carrier Lifetime and Diffusion Length

Carrier lifetime is a parameter that will hugely affect the efficiency of a light emitting diode. If the carrier lifetime is large, there is more of a chance for charges to separate and reach metal contacts rather than recombining. In a light emitting diode, it is desirable to have a small carrier lifetime in order for more photon emission.

Electron-hole generation can occur as an exciton or as a free electron-hole pair. The exciton binding energy of GaN is around 21-25 meV (44) and the exciton binding energy of ZnO is around 60 meV (42). Generally exciton transitions occur at lower temperatures since band-to-band transition will dominate when thermal energy is around 26 meV at room temperature. But ZnO has a high binding energy so excitons are favored at room temperature. In GaN, however, free e-h pair generation will dominate. In an exciton generation, the electron and hole are still bound by a Coulombic force and as a result, the exciton has less energy than the unbound electron and hole.

The lifetime of the free e-h pairs in GaN is around 500 ps (45). The lifetime for a ZnO exciton is around 200 ps (46). Coupled with the electron and hole mobility of the materials, one can find the diffusion length (L) of the carriers. Electron mobility of GaN is around 440 cm$^2$/Vs at room temperature (41) and hole mobility is around 10 cm$^2$/Vs, as experimentally found by Hall measurement setup. Electron mobility of ZnO nanorods is around 20 cm$^2$/Vs at room temperature (47) and hole mobility can be estimated to be 10 cm$^2$/Vs or less (48). The diffusivity (D) is first calculated using the Einstein relationship in the following equation where $k$ is Boltzmann’s constant, $T$ is temperature, $q$ is elementary charge, and $\mu$ is mobility. Diffusion length (L) is then calculated a function of diffusivity and carrier lifetime ($\tau$).

$$D = \frac{kT}{q \mu} \quad \text{Eq. 10}$$
The diffusion length describes how far the carrier will travel on average, before recombining. The table below summarizes the calculated values. As shown in the table, ZnO and GaN have relatively very fast carrier lifetimes as compared to a material such as silicon. This characteristic gives them the advantage in a light emitting diode application.

### Table 8: Diffusion Lengths for ZnO, GaN, and Si

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>GaN</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Mobility, $\mu_n$ (cm$^2$/Vs)</td>
<td>20</td>
<td>440</td>
<td>801</td>
</tr>
<tr>
<td>Hole Mobility, $\mu_p$ (cm$^2$/Vs)</td>
<td>10</td>
<td>10</td>
<td>437</td>
</tr>
<tr>
<td>Electron Lifetime (sec)</td>
<td>$2 \times 10^{-10}$</td>
<td>$5 \times 10^{-10}$</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hole Lifetime (sec)</td>
<td>$2 \times 10^{-10}$</td>
<td>$5 \times 10^{-10}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Electron Diffusivity (cm$^2$/s)</td>
<td>0.518</td>
<td>11.4</td>
<td>20.746</td>
</tr>
<tr>
<td>Hole Diffusivity (cm$^2$/s)</td>
<td>0.259</td>
<td>0.259</td>
<td>11.318</td>
</tr>
<tr>
<td>Electron Diffusion Length (um)</td>
<td>0.09</td>
<td>0.78</td>
<td>144.03</td>
</tr>
<tr>
<td>Hole Diffusion Length (um)</td>
<td>0.06</td>
<td>0.12</td>
<td>336.43</td>
</tr>
</tbody>
</table>

### 3.4 The Special Case of InGaN

InGaN is a very interesting material in photonics because the compositional range of In$_x$Ga$_{1-x}$N from $x=0$ to 1 extends from near-IR to near-UV wavelength, covering the entire visible spectrum (35). This material property is very advantageous applications such as photovoltaics, light emitting diodes, and lasers (49). And just like ZnO and GaN, the entire InGaN compositional family has wurtzite crystal structure and a direct bandgap.
3.4.1 Phase Segregation

Research in this area has been limited though because of the immiscibility gap that exists in the InGaN family of materials, resulting from the large mismatch in lattice constant between GaN and InN, and commonly leading to phase segregation in the material (51) (52). Therefore, the limit of InN incorporation in InGaN has typically been around 30% (49). Methods of fabricating thin films are typically MOCVD, HVPE, or MBE (53) (54) (55) (56).

Recently, an advancement has been made to enable growth across the entire range of InGaN by a specific three-zone low-temperature halide chemical vapor deposition technique (12).

3.4.2 InGaN Nanowire Full Composition Tunability

The method of deposition is a low-temperature chemical vapor deposition. A three-zone furnace setup was used as illustrated in the following figure. Gallium trichloride (GaCl₃) powder was used as the precursor for gallium and was located in Zone 1 of the furnace in one of three central tubes. Indium trichloride (InCl₃) powder was used as the precursor for indium and was located in Zone 2 of the furnace in a second central tube. Finally, a third central tube was used to carry ammonia gas as a precursor for nitrogen. Nitrogen gas was used as a carrier gas for the GaCl₃, InCl₃, as well as the outer tube. The substrate was located 1 cm downstream of the central tube ends.
Figure 21: Three zone furnace setup for synthesizing InGaN nanowires across the compositional spectrum.

During synthesis, the GaCl$_3$ precursor is heated to 55°C and the InCl$_3$ precursor to 400°C, resulting in Ga and In vapor. The vapor is carried by nitrogen downstream and the plumes forming at the central tube exits result in a mixing of the vapors, from pure Ga at the outer edge of the GaCl$_3$ tube to pure In at the outer edge of the InCl$_3$ tube, and covering the entire compositional range in between. The vapor precipitates onto the substrate and nanowires are formed.

Figure 22: Characterization of InGaN nanowire array, taken from points along the whole compositional spectrum including a) photoluminescence, b) absorption, and c) bandgap energy as a function of composition taken from Kuykendall (12)

During synthesis, the substrate is held at a temperature of 550°C. This low temperature synthesis seems to aid in the solid phase immiscibility gap of InGaN. Furthermore, the nanowire structure could be beneficial as well in order to relax the strain caused by the large lattice mismatch.
This ability to create the whole compositional range of InGaN material in nanowire form could mean huge steps forward for light emitting diodes. This concept is further explored in Chapter 5.
Chapter 4. Zinc Oxide Nanowire LED

This chapter explores the first light emitting diode architecture of this dissertation that exploits nanoscale properties, namely waveguiding of nanowire cavities. The diode platform was based on a p-type GaN thin film and intrinsically n-type ZnO vertical nanowire array. A heterojunction rather than a homojunction array was chosen due to material availability and capability. P-type GaN thin film deposition was achieved as was the ability to grow a vertical array of ZnO nanowires. These two materials are actually well-suited due to their low lattice mismatch of 1.9% (37).

Hybrid nanowire array/thin film based LEDs have been reported previously as mentioned in Chapter 2. Other examples include ZnO nanowire arrays that have been fabricated on p-type GaN thin films (57) (58) and p-type Si substrate (59). Additional reports of single nanowire light emitting diodes include n-GaN single nanowire based diodes on p-GaN thin films (60) and p-Si substrates (61). This architecture in particular demonstrates a solution based growth of a ZnO nanowire array on a p-type GaN thin film. It is one of the first nanowire LEDs to study waveguiding behavior of the electroluminescence by the vertical nanowire array device architecture.

In the following sections, design considerations will first be discussed. P-GaN fabrication will then be described as well as ZnO nanowire array growth. This will be followed by device fabrication and characterization. Then waveguiding results will be analyzed.

4.1 Heterojunction Diode Design

GaN and ZnO form a Type II heterojunction alignment as shown in the figure below. The band offset is minimal however and for all intents and purposes, the GaN and ZnO junction could almost be considered a homojunction, especially because their bandgaps are similar. Typically, Ni capped with Au is used as an Ohmic contact to p-type GaN (62) and Ti capped with Au is used as an Ohmic contact to n-type ZnO (63). The dopant concentrations are estimated to be around $N_A = 5 \times 10^{17}$/cm$^3$ for the p-type GaN thin film and $N_D = 1 \times 10^{16}$/cm$^3$ for the intrinsically n-type ZnO nanowires (42).
Figure 23: Band Alignment of p-GaN/n-ZnO LED device before creating junction.

When the materials are connected, the band diagram equilibrates as follows. The valence band offset is experimentally observed to be about 1eV (64).

Figure 24: Band Alignment of p-GaN/n-ZnO before and after thermal equilibrium is reached.

In designing the device architecture, light emitting diode efficiency needs to be re-explored and design considerations need to be made in efforts to improve the efficiency. The functional requirements are listed as the three major efficiency parameters as described in Chapter 1 as well as the capacity for device fabrication. The capacity for device fabrication denotes the ability to repeatably and reliably make a working device from the nanowire entities.
**Table 9: Design Considerations of a p-GaN thin film/n-ZnO nanowire array light emitting diode**

<table>
<thead>
<tr>
<th>Functional Requirements</th>
<th>Design Considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiative Efficiency</td>
<td>Epitaxial growth; Few defects and surface traps</td>
</tr>
<tr>
<td>Internal Quantum Efficiency</td>
<td>Short carrier lifetimes; Long enough diode to promote recombination; Ohmic contacts</td>
</tr>
<tr>
<td>Extraction Efficiency</td>
<td>Index considerations of materials for internal reflection guided light; Waveguiding</td>
</tr>
<tr>
<td>Device Fabrication</td>
<td>Aligned Array; Homogenous growth in density and dimension</td>
</tr>
</tbody>
</table>

Radiative efficiency describes the fraction of excited carriers that recombine radiatively versus non-radiatively. In other words, it describes how many carriers recombine and emit a photon versus how many carriers recombine and result in heat generation. Non-radiative traps to consider are surface states on the nanowires, interface traps at the p and n junction, and defect traps in the materials themselves. The ZnO nanowires will be grown epitaxially from the p-type GaN thin film. Due to their low lattice mismatch, this will inherently reduce the number of interface traps. Defect traps in the p-GaN are difficult to improve due to challenges in making the p-type material in and of itself. Defects in the ZnO nanowire itself should be very low since it is epitaxially grown from the substrate and nanowires in general have been shown to be single crystalline and highly defect free although surface states could have a detrimental effect (65).

Internal quantum efficiency describes the fraction of current that contributes to excited carriers. The materials chosen have relatively short carrier lifetimes as described in Chapter 3. This property lends itself well to light emitting diode functionality. The device geometry (placement of contacts) should allow for enough travel distance to promote recombination rather than have the carriers reach the contacts. In consideration, the nanowire lengths must be long enough to promote recombination. Finally, Ohmic contacts should be made so there is no voltage drop at the contacts (or in other words, wasted electrical energy).

Extraction efficiency describes the fraction of photons that actually leave the device after being generated. Efforts are made to create an aligned vertical array of nanowires to promote natural waveguiding of the light out along the long axis of the nanowire. Also, the morphology of the nanowire already lends itself to more chances for the light to escape the device as described in optical advantages under Chapter 1. More light in general should escape the device as compared to a thin film device architecture.
Finally, the nanowires need to be grown in a way that device fabrication can be performed reliably and repeatably. An aligned array with nanowires of homogenous growth in density and dimension is necessary to be able to repeat fabrication procedures and create a device that functions correctly.

### 4.2 P-type GaN Thin Films

The p-type GaN thin films were grown by a colleague, Woong Kim, at the Lawrence Berkeley National Laboratory. The method of growth for the p-type GaN thin film was metal organic chemical vapor deposition (MOCVD). The growth was carried out in a shower head reactor which should aid in homogenous growth conditions. The substrate was c-plane sapphire for reasons previously discussed in Chapter 3. As magnesium is the accepted dopant for p-type GaN (also discussed in Chapter 3), the precursor used was Cp₂Mg or cyclopentadienyl magnesium.

![Reactor used for growth of p-GaN thin film](image)

**Figure 25:** Reactor used for growth of p-GaN thin film

The growth parameters are tabulated below. Presence of hydrogen during growth can help to reduce the concentration of nitrogen vacancies, as well as increase the solubility of the acceptor. However, hydrogen also forms acceptor-H neutral complexes which essentially provide hole compensation and therefore, needed to be annealed out during a post thermal annealing step. As discovered by Nakamura (23), the annealing step must be carried out in N₂ ambient rather than NH₃ ambient.
Table 10: Growth parameters for p-type GaN thin film

<table>
<thead>
<tr>
<th></th>
<th>Nucleation</th>
<th>Buffer</th>
<th>p-GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>530</td>
<td>1040</td>
<td>1015</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>665</td>
<td>250</td>
<td>125</td>
</tr>
<tr>
<td>TMG (sccm)</td>
<td>10</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>NH₃ (sccm)</td>
<td>1500</td>
<td>4500</td>
<td>5000</td>
</tr>
<tr>
<td>Cp₂Mg (sccm)</td>
<td></td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

The mechanism for growth is illustrated in the figure below. The precursors were trimethylgallium ((CH₃)₃Ga), ammonia (NH₃), and bicyclopentadienylmagnesium (Cp₂Mg). The Mg replaces the Ga sites in the lattice in order to act an ionized acceptor.

![Growth mechanism schematic for p-type GaN](image-url)

The thin film grown had a thickness of 1 µm. A Hall measurement on the thin film revealed that the dopant concentration was approximately \( p = 4.5 \times 10^{17} /\text{cm}^3 \) and the hole mobility was \( \mu_p = 12 \text{ cm}^2/\text{V·s} \). These values are consistent with typically reported p-type GaN thin films (62).

4.3 ZnO Nanowire Synthesis

ZnO nanowire synthesis was carried out using two methods, a solution phase approach and a gas phase approach. Both approaches were adapted from previously reported work (65) (66).
4.3.1 Solution Phase

The solution phase growth method is a simple, low temperature approach to growing a vertically aligned nanowire array. The method was the hydrolysis of zinc salt in water. The precursors were as follows.

0.025M Zinc Nitrate Hexahydrate \([\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}]\)  
0.025M Hexamethylenetetramine (HMTA) \([\text{C}_6\text{H}_{12}\text{N}_4]\)  
0.001M Polyethyleneimine (PEI)

The batch solution was usually prepared in quantities of 500 mL, consisting of 3.719 g Zinc Nitrate Hexahydrate, 1.753 g HMTA, and 2 g PEI and enough filtered deionized water to fill the 500 mL mark. The solution was heated to 100°C with a stir bar under a stir rate of 250 RPM. The solution color would turn from milky white to pale yellow. The solution was then filtered through 200nm Whatman filter paper to remove all initial particulates that formed. The remaining solution could be stored for around 2 weeks for nanowire synthesis.

The batch solution was separated into 100 mL beakers for each nanowire growth episode. The substrates were rinsed with acetone, isopropyl alcohol, and deionized water to remove any organic contaminants and dipped in 10:1 hydrofluoric acid solution for 1 minute to remove any oxides. They were then taped by double sided carbon tape to holders in order for the substrates to suspend at around a 45° angle in the solution. They were placed in that configuration so that any particulates that formed in the solution during growth would not fall onto the substrate and interfere with nanowire growth but also any bubbles in the solution would not rise and get stuck on the surface of the substrates.

The growth solution was heated to 95°C and once the solution temperature reached ~85°C, the substrate holder was inserted into the solution. The total growth time was 2 hours for the precursors in the solution to completely deplete and the result was ~2µm tall ZnO nanowires. Care was taken during each growth episode to make sure any bubbles that formed did not get stuck anywhere on the substrate surfaces, otherwise voids would form on the substrate. In order to get long enough nanowires to improve LED operation (as explained in the previous section), the growth procedure was repeated two more times resulting in nanowire lengths of around 5-6 µm.
The growth mechanism is as follows. There is a thermal decomposition of the zinc salt in water to form zinc-hydroxyl complexes. Solid ZnO nuclei are formed by the dehydration of these complexes at a certain pH and temperature. The ZnO crystal continues to grow by condensation of the surface hydroxyl groups with the zinc-hydroxyl complexes. The HMTA is an additive that decomposes during the reaction and increases the pH (by forming NH₃) to above 9 to promote 1-dimensional nanowire growth. The PEI is also an additive that inhibits radial growth but allows axial growth by adsorbing to certain crystal faces.

As mentioned previously, this growth procedure is adapted from previous work (65). The previous work used non-epitaxial growth substrates so in order to initiate growth, seeding such as ZnO nanoparticles or Zinc Acetate annealed to form ZnO particles were used. In this report’s growth scenario, no catalysts were used because the growth substrate was GaN, a material very well lattice matched to ZnO.
The outcome was an entirely vertical array of ZnO nanowire with nominal diameters of around 100-600 nm. Evidence of epitaxial growth shows in the hexagonal cross section of the nanowires, indicating they are growing in the [0001] growth direction and have a wurtzite hexagonal crystal structure, exactly mimicking the crystal structure of the p-GaN thin film. It is speculated that the diameters of the nanowires are dictated by the defect characteristic of the thin film (i.e. grain boundaries). The density of wires is around $4.5 \times 10^5$/mm$^2$. Finally, an observation is made that the surface of the substrate is completely clean and only nanowire formation is evident.

### 4.3.2 Gas Phase

The second ZnO nanowire array growth approach is the chemical vapor transport (CVT) method. This method is in the gas phase and utilizes the well-known vapor-liquid-solid growth mechanism (67). As mentioned above, the growth mechanism is adapted from a growth mechanism previously reported (66).

The experimental setup is shown in the figure below. A one-inch quartz tube was placed in a furnace with a smaller half-inch alumina tube inside. Inside the alumina tube was an alumina boat filled with 1:1 ZnO powder to graphite powder. The powder was previously ground with mortar and pestle to form a very fine, very well mixed powder. An argon flow was set up through the tube and the substrate was placed on the alumina boat, downstream from the powder. The furnace was set to rise to 900°C and hold for 30 minutes. At that temperature there is a carbothermal reduction of the ZnO powder to form Zn vapor and carbon monoxide.

![Figure 29: Schematic of setup for gas-phase growth of ZnO nanowire array, furnace used in gas-phase growth, and schematic of vapor generation and substrate placement.](image)
The growth mechanism as stated before is the vapor-liquid-solid method as shown in the figure below. The substrate was previously sputtered with ~10 nm of gold as a growth catalyst. As the temperature rises, the Au film melts and forms tiny droplets. The Zn vapor travels to the substrate and reacts with the Au to form a Zn-Au liquid alloy. The droplets saturate and Zn begins to precipitate out at the substrate surface (the lowest interface energy). The Zn then reacts with the CO or any other oxygen still left in the system and ZnO is formed. The nanowire continues to grow as more Zn precipitates from the droplet.

![Vapor-Liquid-Solid growth mechanism of ZnO nanowires](image)

**Figure 30:** Vapor-Liquid-Solid growth mechanism of ZnO nanowires

The resulting nanowire array is vertically aligned and shown in the figure below. Dimensions are around 100-250 nm in diameter and 3 µm in length. Cross section is hexagonal, indicating growth direction is again in the [0001] direction. The density of wires is around 3x10⁶/mm². Concerns from the SEM images are that the growth is very patchy (non-uniform) and the interface between the p-GaN and nanowires is unclear. It appears that there may be a thin film growth at the base of the nanowires.

**Figure 31:** SEM images of ZnO nanowire array grown by gas-phase approach
4.4 Device Fabrication

The light emitting device fabrication was as follows. After the p-type GaN thin film was grown, the ZnO nanowire array was fabricated. For the solution approach, nanowires were grown all over the chip. After growth, a cotton swab soaked in HCl was used to wipe the nanowires from half of the chip in order to contact the p-GaN. On the gas phase approach, the chip was simply masked during catalyst deposition so that gold was only deposited on half of the chip.

Poly (methyl methacrylate) or PMMA was spun onto the device chip to fill in the nanowire array and prevent shorting when creating a contact to the n-type array. Specifically, the solution was 950 PMMA 5% in Anisole. The PMMA on the p-GaN side of the chip was then wiped off with a cotton swab soaked in acetone. A 2 minute oxygen plasma etch was used to etch back the PMMA from the tips of the nanowires and remove any residual PMMA left on the p-type GaN thin film.

Finally, Ni/Au contacts were ebeam evaporated onto the p-type GaN side and Ti/Au contacts were ebeam evaporated onto the n-type ZnO nanowire array therefore completing the device. The resulting device schematic is shown below.

![Device schematic](image-url)

**Figure 32:** Schematic of completed ZnO nanowire array/p-GaN thin film LED device

The spin coating of the nanowires took a little bit of care. If PMMA was merely dropped onto the substrate and spun at the usual rate of around ~2500 RPM, all of the PMMA will spin right off the surface without filling in the array. Therefore, two droplets of PMMA were placed on the substrate and allowed to sit for 5 minutes, while the viscous fluid slowly started to sink into the array. Then the substrate was ramped up very slowly from 0 RPM to 5000 RPM over the course of two minutes. This protocol resulted in the best fill of the nanowire array, most conformal coating over the whole chip, and minimal clumping of the nanowire tips. The figures below show the resulting filled nanowire array for the solution grown wires.
After the PMMA spin, the samples were baked in a furnace set to ramp up from room temperature to 150°C over 30 minutes, then immediately cooled down slowly with the furnace lid still closed. The purpose of the bake was to bake out any solvents and harden the PMMA. The reason the bake was cooled down very slowly was to prevent clumping of the nanowires. The figures below show the nanowire array after the two minute oxygen plasma etch to remove the PMMA from the tips of the nanowires. The rough nature of the tips of the nanowires in the SEM suggests the etch back was successful and an Ohmic contact can then be formed to the nanowires. It is imperative to see that there are no voids in the PMMA which would cause shorting of the device during metal contact deposition.

**Figure 33:** Top down and 45° degree tilted SEM images of the solution grown ZnO nanowire array

**Figure 34:** SEM images of solution grown ZnO nanowires after oxygen plasma etch

### 4.5 Characterization and Analysis

This section will summarize the two-point electrical, photoluminescence, and electroluminescence measurements of the devices.
4.5.1 Comparison of Synthetic Methods

Room temperature photoluminescence measurements were carried out to reveal the properties of the materials grown. The photoluminescence source was the continuous wave 325 nm line of a Helium Cadmium (HeCd) laser that came in at a 22° glancing angle to hit the substrate. The photoluminescence spectra was then collected by a Nikon microscope coupled by a multimode fiber to a spectrometer with a liquid nitrogen cooled silicon charge coupled device (CCD). The figures below show the experimental setup as well as the mechanism for photoluminescence emission in E-k space.

![Photoluminescence experimental setup and mechanism](image)

**Figure 35:** a) Photoluminescence experimental setup and b) Mechanism for emission

The figure below is a schematic of what areas of the device were interrogated. Since the interrogation spot size was on the order of 100 µm, the pGaN thin film and ZnO nanowire area could be excited separately.

![Device interrogation schematic](image)

**Figure 36:** Schematic showing different areas of the device being interrogated
The following graphs shows the photoluminescence of the p-type GaN thin film and ZnO nanowire array for solution grown wires (on the left) and gas phase grown wires (on the right). On both graphs, the p-GaN thin film luminescence centers around 440 nm. This red shift in the emission from the band edge is commonly accepted as conduction band to acceptor level transitions as described in Chapter 3.

Figure 37: Photoluminescence spectra of solution grown and gas-phase grown ZnO nanowire array

The photoluminescence spectra of the solution grown wires show a small band edge peak around 380 nm and a large “yellow” defect peak. This defect peak is commonly seen in ZnO materials and attributed to defects such as interstitial oxygen ions (65). The gas-phase grown ZnO wires show a large band edge peak and minimal defect peak. This difference suggests that there are many more deep level traps in the solution grown nanowires resulting in energy transitions less than band to band and therefore resulting in larger wavelength emission as illustrated below.

Figure 38: a) Schematic of band to band and band to deep trap transitions in n-ZnO and b) schematic of band to acceptor transitions in p-GaN
The difference in quality of the two nanowire arrays is most likely due to the different growth temperatures. The solution grown wires are grown at 95°C and the gas phase grown wires are grown at 900°C. It is commonly known that high growth temperatures can anneal out material defects (68). Even so, the advantage of the solution grown wires are that the growth procedure is much more simple and low cost and the morphology of the nanowires appears to be more clean suggesting a good p-GaN to ZnO interface.

### 4.5.2 Solution Phase ZnO Nanowire Devices

The solution ZnO light emitting diodes showed rectifying current-voltage behavior. A typical I/V curve is shown below. Turn on voltage was around 3.5 V and visible forward bias electroluminescence occurred around 10V. Emission was observed to come from the p-type GaN thin film at the p-n junction which suggests this is truly injection electroluminescence.

![Figure 39: a) I/V curve of typical solution phase ZnO nanowire array LED, b) Schematic of LED device and where EL is localized, and c) Camera image of device EL](image)

In order to check the fidelity of the device, multiple contacts were made on the same chip to test current-voltage characteristics across different parts of the LED. A junction across the p-type GaN was made and the resulting I/V curve was nearly Ohmic as expected.
When a contact is made across the nanowire array, an n-p-n junction is formed, or in other words, two back to back reverse rectifying junctions. In one current direction, one of the p-n junctions is in forward bias and the other p-n junction is in reverse bias. In the opposite current direction, the first p-n junction is then reverse biased and the other p-n junction is forward biased. This leads to expected I/V curves with reverse rectifying characteristics.
Room temperature electroluminescence was collected and typical results are shown in the following graph. The substrate was probed and electrically excited with a Keithley voltage source. Emission was detected with the same setup as described in the photoluminescence measurements. Blue light was detectable by the naked eye by around 10 V.

There are two visible peaks in the spectra, one dominating at around 410 nm and another broader peak in the yellow region. The 410 nm peak is attributed to band to acceptor transitions in the p-type GaN. This is further supported by the fact that visible to the human eye, the emission is originating from the p-GaN thin film at the p-n junction. It is blue-shifted from the usual 440 nm peak probably by contributions of interband transitions in either the GaN or ZnO. The broad yellow peak can be associated with the deep level traps either in the film or the nanowires.

It is interesting to note that as voltage is stepped up, the change in dominant peak intensity increases. This is in contrast to the defect related peak which seems to rise linearly with a linear increase in voltage. Therefore, as bias voltage increases, the 410 peak begins to dominate over the defect peak. This observation can be supported theoretically since as the voltage is increased, the band bending at the p-n junction is decreased, and there is an exponential increase in number of carriers that have enough energy to traverse the barrier.
4.5.3 Gas Phase ZnO Nanowire Devices

The gas phase grown ZnO nanowire array devices did not behave as typical diodes. Devices only exhibited electroluminescence under reverse bias. The onset of electroluminescence was around -5 V.

Figure 43: a) Schematic of LED device and where EL is localized, b) and c) Camera images of device EL at 25V reverse bias

A test of the current voltage characteristics of the device revealed that it did not show typical diode behavior. The device was probed across the P-P junction. This junction should reveal an Ohmic contact although the shape of the curve suggests two back to back Schottky contacts. Current-voltage across the p-n junction should be rectifying and the graph suggests it is, however, the turn-on voltage is much higher at around 5V and reverse breakdown onset is very
early. The n-p-n junction should show back to back reverse rectifying curves. The curve is clearly linear, suggesting a short.

![I/V curves for P-P junction (a), P-N junction (b), and N-P-N junction (c)](image)

**Figure 44:** I/V curve for a) P-P junction, b) P-N junction, and c) N-P-N junction

From these results, there are clearly several problems with the device. The p-p Schottky curve suggests that the contacts made to the p-type GaN device are not Ohmic. The n-p-n Ohmic curve suggests that there may be a thin film growth at the base of the nanowire array that is shorting that junction. An inspection of the SEM images shown in the previous section suggests this may be the case.

Room temperature electroluminescence spectra for the reverse bias case are shown below. Again, there was no measurable electroluminescence in the case of forward bias. The light emission is visibly originating from the p-GaN thin film layer directly under the p-GaN contact. Due to the location of origin of the emission, it is believed that tunneling electroluminescence is occurring rather than injection electroluminescence. As discussed in Chapter 1, tunneling electroluminescence occurs when a diode is reverse biased to the point that electrons can tunnel in from the metal contact and recombine with the holes in the p-GaN material. This phenomenon has been previously reported in a single GaN nanowire LED device (61). The shape of the spectra has similarities to the spectra shown for the solution grown ZnO nanowire array LED. There is again a peak around 410 nm attributed to the band to acceptor transitions in the GaN as well as a broad defect peak which can be attributed to the defect transitions in the GaN.
4.6 Device Waveguiding

The potential for enhanced extraction efficiency by the vertically oriented nanowire array was assessed. The solution grown ZnO LED devices were used as a test platform since those devices exhibited normal functioning injection electroluminescence. Waveguiding has already been demonstrated in ZnO nanowires under photo excitation (69) (70). The index of refraction of PMMA is 1.492 and 2.008 for ZnO (48). Therefore, the calculated ideal single mode cavity diameter for a ZnO nanowire embedded in PMMA is around 200nm for the emitted wavelength of the p-GaN (15).

Below is a schematic for the experimental setup for waveguiding analysis. An optical fiber was placed 1 cm away from the emission source at varying degrees of theta from normal and emission spectra were collected.
Figure 46: a) Schematic showing waveguided light through a nanowire and b) Schematic of experimental setup to detect emission at various degrees from normal.

The following graph shows the emission spectra collected at various degrees from normal. The most intensity is collected at 0 degrees from normal, or directly above the device, and intensity falls off as the angle is increased. This waveguiding nature has been explored before (2) (3). Both groups demonstrate enhanced light extraction from a conventional GaN multiple quantum well LED by growing a vertically aligned ZnO nanowire array above the LED. Their device geometry, however, is different from the one reported in this dissertation in that this nanowire array is a functioning part of the diode rather than an added feature. This distinction means higher extraction efficiency due to unneeded coupling loss between the LED and nanowire array.

![Graph showing emission spectra](image)

Figure 47: Emission spectra from ZnO LED device at collected at various angles from normal.

The accepted emission pattern from a planar thin film LED should be a Lambertian pattern as shown in the figure below (71).

![Graph showing Lambertian pattern](image)
The assumptions are made that an equivalent LED, but with a planar structure rather than a nanowire array, would give off a typical Lambertian spatial distribution of light and give off the same total number of photons. Comparing the normalized integrated intensity with degrees from normal for the test device and a theoretical control device shows that the emission profile has been modified by the nanowire array. Furthermore, there is calculated to be a 13% increase in light output in the vertical direction.

**Figure 49**: Integrated intensity of emission from light emitting diodes plotted against degrees from perpendicular and compared to a typical Lambertian emission pattern.

### 4.7 Conclusions

A nanowire LED device has been designed, fabricated, and characterized. Waveguiding of light along the vertically oriented nanowire array is suggested to improve extraction efficiency
in the vertical direction as compared to a typical planar LED design by about 13%. The platform of the diode consisted of an intrinsically n-type ZnO nanowire array grown epitaxially from a p-type GaN thin film. Two methods were used for the ZnO nanowire array, a hydrothermal method and chemical vapor transport method.

In the solution grown ZnO nanowire array LED, the device had rectifying current-voltage behavior with turn-on voltage around 3.5 V and detectable light emission at around 10 V. Emission dominated in the p-GaN thin film at the p-n junction with a large peak centered around 410 nm and was attributed to the band to acceptor transition in the p-GaN material. A smaller broader peak occurred around 550 nm and was attributed to deep trap transitions both in the GaN and ZnO materials.

The emission is believed to dominating from the GaN for a number of reasons. The large amount of surface area in the nanowire structure suggests that there are many dangling bonds which act as deep level traps. Therefore, non-radiative recombination is most likely dominating in the nanowire side, rather than band to band transitions. Mobility of the minority carriers (electrons) in GaN may be smaller than the mobility of the minority carriers (holes) in ZnO, possibly due to very high impurity concentrations in GaN, thus increasing scattering. Therefore, electron-hole pairs have more chance to recombine in GaN. On a similar note, the distance the electron must travel from the junction to the contact is much larger in GaN than the distance for the hole in ZnO. Therefore, the probability of recombination is again greater in GaN. Also, it is documented that hole injection across the junction from GaN is difficult (72) meaning more electrons are crossing the junction to GaN rather than holes crossing the junction to ZnO.

The turn on voltage of 3.5 V is reasonable as compared to calculated theoretical built in voltage of 3.16 V as shown in the band diagram in the beginning of the chapter. The late onset of detectable emission is most likely due to the abundance of deep level traps in both the ZnO and GaN. Once those traps begin to saturate, then band to acceptor transitions and band to band transitions resulting in photonic emission are detectable.

The gas phase grown ZnO nanowire array LED did not result in a correctly functional light emitting diode. The current voltage behavior mimicked a back to back reverse rectifying characteristic. This behavior is attributed to the bad metal contact to the p-type material that proved not to be Ohmic. Reverse bias electroluminescence was observed in the p-type GaN directly under the metal contact and this was explained by tunneling electroluminescence of electrons from the metal contact to the p-type material. Another issue was the apparent thin film growth at the base of the nanowire array as evident by the short in the n-p-n current voltage characteristics and SEM images. This messy interface between the p-type and n-type material could be part of the reason that there was no detectable forward bias emission. A bad interface suggests many interface traps can exist to quench all carriers. The high temperature growth of the ZnO nanowire array at 900°C could also have modified the p-type GaN electronic and material structure.
Chapter 5. Tunable Nano-LED

This chapter explores the second light emitting diode architecture of this dissertation that exploits nanoscale properties, namely capability of synthesizing high indium nitride concentration InGaN compounds in nanowire form. As previously discussed in Chapter 3, the InGaN compositional family is very attractive as materials for light emitting diodes because the family covers the entire range of the visible spectrum (35). However, it is a challenge to create InGaN with indium nitride concentrations of more than 30% due to phase segregation issues (49).

The platform for this second architecture consists of an InGaN nanowire array grown on top of a conventional InGaN/GaN multiple quantum well (MQW) light emitting diode structure. The mechanism for emission is electrical pumping of the MQW LED to produce blue emission from the InGaN quantum wells. The blue emission in turn photo-excites the InGaN nanowire array and the nanowires photoluminesce at a wavelength according to their bandgap (or composition).

There really is no previous work similar to this platform due to the fact that the InGaN full compositional synthesis capability has only been developed in this laboratory. Other methods of tunable LED include those mentioned in Chapter 2, such as quantum dot decorated LEDs and multiple peak emission from InGaN quantum wells with varying sizes of embedded InN nanoparticles (27) (28).

In the following sections, the GaN/InGaN MQW thin film LED will first be discussed, including structure, device fabrication, and characterization. Then fabrication and characterization of the InGaN nanowire array LED will be discussed and analyzed.

5.1 InGaN Multiple-Quantum-Well Thin Film LED

The GaN/InGaN multiple quantum well LED is based on a commercially available substrate made by Epistar Company based in Taiwan. A bare LED device was first fabricated to obtain control characteristics, such as current-voltage and electroluminescence.

5.1.1 Device Fabrication

The substrate was a two-inch wafer produced by Epistar Company. The specific properties of the structure or growth method were not divulged due to proprietary issues however the type is described as ES-WQBH3NA by the company. An SEM analysis of the wafer cross section revealed that the thickness of all the thin films combined was around 5.205 µm grown on top of a sapphire substrate. A closer view revealed around 11 quantum wells that totaled around 150 nm. Each InGaN well was approximately 4 nm with 10 nm GaN cladding layers. The top
p-type GaN layer is measured to be 255 nm. The n-type layer is approximated to be about 4.8 µm thick.

**Figure 50:** SEM of Epistar Company GaN/InGaN MQW structure

The fabrication process to make the thin film light emitting diode is fairly simple. The two inch wafer was wafer sawed into 1 cm x 0.5 cm rectangular chips for individual devices. Approximately 1/3 of the chip was masked by aluminum foil and SiO₂ was deposited over the unmasked areas as an etch mask. A SiO₂ thickness of at least 300 nm was used even though the etch chemistry has a fairly high selective ratio of 5.6 (73). The thin films were either deposited by RF sputtering or e-beam evaporation. Sputtering seemed to be a much controllable deposition method.

**Figure 51:** a) Schematic of fabrication steps to expose n-GaN thin film for metal contact and b) SEM image of transition area between p-GaN film and exposed n-GaN film

The etching step is necessary to reveal the n-type GaN layer in order to make an n-GaN metal contact. A reactive ion etch (RIE) was used to etch away the GaN and InGaN layers. An etch depth of at least 400 nm was needed to reach the n-type layer. The RIE was done at the Nano Fabrication Facility at University of California, Santa Barbara. The etch recipe was as follows: chamber pressure = 0.2 Pa, bias power = 150W, ICP power = 500W, Cl₂ flow rate =
22.5 sccm, $\text{N}_2 = 7.5$ sccm, and time = 70 seconds. After the etch, a dip in 10:1 HF solution was used to remove the SiO$_2$ mask. The etching results are shown in the figure above and below. The above SEM shows the transition area between the p-type GaN and n-type GaN. There is a clear contrast between the two areas. A measurement in the Dektak Profilometer revealed that the etch depth was around 400 nm.

The SEM images below show detail of the p-type GaN surface and n-type GaN surface after etching. The etch pits on the n-GaN are typical of a GaN etch and are indicative of dislocations in the film (74) (75).

![Figure 52: SEM images of p-type GaN surface and n-type GaN surface after RIE etch](image)

The final step for fabrication was to deposit contacts on the thin films. A shadow mask was used with 1.5 mm holes in a hexagonal pattern and 2.5 mm pitch. Gold of 60 nm thickness was sputtered onto the device.

### 5.1.2 Thin Film LED Characterization

The thin film LED structure was electrically probed and subjected to a forward bias voltage. In a forward biased quantum well diode structure, the carriers will fall into the energy wells at the junction and be stuck there. Recombination will occur across the bandgap of the well material; therefore the wavelength of emission is dictated by the bandgap of the InGaN quantum well material, or in other words, its compositional makeup. A schematic of the band diagram with a single well quantum well structure is shown below. The band diagram is shown at zero applied voltage as well as forward applied voltage.
Figure 53: Band diagram of PN Junction with single quantum well, shown at zero applied voltage and forward applied voltage

The resulting electroluminescence was perceptible from the thin film layers directly beneath the p-type contact. Emission spectra at various input voltages are shown in the graph below. The emission is centered around 467 nm, corresponding to a bandgap of 2.655 eV and suggesting an In\textsubscript{x}Ga\textsubscript{1-x}N quantum well composition of around x = 0.24 (12).

Figure 54: a) Schematic of GaN/InGaN MQW Thin Film LED showing location of electroluminescence emission and b) Emission spectra at various input voltages

5.2 InGaN Nanowire LED Design
In the following sections, the LED structure is modified to incorporate InGaN nanowire arrays of various compositional ranges and as a result, various wavelengths of emission. The goal is to demonstrate a tunable LED device by tuning the bandgap of the InGaN nanowires through compositional changes.

### 5.2.1 Device Fabrication

The device fabrication begins with the same steps as the control device mentioned above with some additional steps as shown in the figure below. After removal of the silica mask, the chip was placed in a furnace for InGaN nanowire array growth. The nanowire growth was done by a colleague, Chris Hahn. This chip was masked by a piece of double polished sapphire to shield the n-type GaN area. This step is necessary for contact to the n-type layer. The final step of the fabrication was to deposit gold as contact material using the same stencil mask as mentioned above. Gold is not ordinarily known as a metal which forms an Ohmic contact to either p-type GaN or n-type GaN. However the films appear to be highly doped which means any depletion region caused by the metal-semiconductor contact is relatively small and negligible. Gold was used because it is highly conductive and non-reactive.

**Figure 55:** Fabrication procedure for InGaN nanowire array/InGaN MQW LED device
5.2.2 Single Composition Nanowire Growth Procedure

The InGaN nanowire growth procedure was adapted from the procedure previously reported by Kuykendall (12). In his procedure, a three zone furnace was used to create an array of nanowires that had a compositional range from pure GaN to pure InN across a single chip as described in Chapter 3. The growth procedure was modified to aim for a homogenous single composition growth on the LED structure. The InCl\textsubscript{3} and GaCl\textsubscript{3} precursors were mixed together in a single inner tube. The ratio of InCl\textsubscript{3} to GaCl\textsubscript{3} precursor determined the ultimate compositional makeup of the InGaN nanowire array. The reason for desiring a single composition of InGaN is that recombination will want to occur across the smallest bandgap in the device. Therefore having a compositional spread will likely only result in emission from the smallest bandgap composition, namely the pure InN. Instead by tuning the single compositional array, it is possible to tune the ultimate emission of the LED.

5.2.3 Morphology of Wires

The SEM images shown below show the InGaN nanowire array grown on the InGaN MQW LED chip. The array is well aligned vertically. The average nanowire diameter is around 30 nm. The total height of the growth is around 533 nm. From the images showing the substrate, it appears that there is a buffer layer thin film growing at the base of the nanowires. The buffer layer thickness is approximately 133 nm and the actual nanowires are around 400 nm tall. This gives the nanowires a 13.3 aspect ratio.
Figure 56: SEM images of an InGaN nanowire array grown on top of an InGaN MQW thin film structure. Cross sectional view shows small buffer layer beneath nanowire array.

The SEM images of the nanowire array look fairly similar even for different compositions of InGaN. The morphology actually looks better than the ones in the previously reported synthesis. They are very well aligned, homogeneous in dimension and have fairly constant diameter from top to bottom. The improvement in morphology is most likely attributed to the growth substrate. The array is grown on a very thick GaN thin film, where lattice matching is much better than the growth substrates used in the previous paper (Si(111), sapphire, and quartz).

The SEMs below show the nanowire morphology at the transition area between the InGaN nanowire array and the masked area. The morphology is different in this area probably due to the effects of the masking chip sitting on top of the growth substrates. The chip would have caused a disturbed fluid flow right at the vicinity of the mask location.
SEM images were also taken of the covered n-type GaN thin film area. The double polished sapphire chip worked well as a mask in preventing growth of the InGaN nanowires. The crater-like appearance of the thin film did not have anything to do with the InGaN nanowire growth. The craters were already present as a result of the reactive ion etch. The small particles that appear in the SEM are, however, residue from the InGaN nanowire growth. They are probably little particles of InGaN but ultimately did not prove a hindrance to device performance.

**Figure 57:** SEM images of nanowire morphology in transition area between InGaN nanowire growth and masked area

**Figure 58:** SEM images of n-GaN layer masked by double polished sapphire chip during InGaN nanowire growth

### 5.3 InGaN Nanowire LED Characterization and Analysis

The InGaN nanowire LED was found to behave as an n-p-n junction. InGaN, like ZnO and GaN, is intrinsically n-type. Electroluminescence occurred only in one current direction,
when the LED p-n junction was forward biased. In the following sections, the InGaN nanowire LED will be characterized by current-voltage, transmittance, photoluminescence, and electroluminescence measurements.

5.3.1 Electrical

The stencil mask evaporation of gold contacts on the device allowed for probing across different areas of the device. The schematic below shows possible contact points on the completed device. The convention will be followed that probing the contact on the top of the nanowire array is the “p”-contact and probing on top of the n-GaN thin film is the n-contact.

![Figure 59: Schematic of InGaN nanowire array LED with metal contacts](image)

The current voltage characteristics are shown in the following graphs. As keeping to convention, positive voltage denotes when the device is biased such that the LED p-n junction is forward biased and negative voltage denotes when the device is biased such that the LED p-n junction is reverse biased. The blue curve on the left graph shows the typical rectifying current-voltage shape for a control device as described in the first section of this chapter. This device has no InGaN nanowire array grown on top. It is a typical diode rectifying curve. The red and orange curves represent typical curves in a InGaN nanowire array LED device. The current-voltage shape is that of a back to back reverse rectifying device. In other words, it represents two back to back p-n junctions.

The graph on the right shows current-voltage characteristics from a single InGaN nanowire array LED device showing curves corresponding to contact across the nanowire array (“p”-“p”), across the junction (“p”-n), and across the n-GaN thin film (n-n). Predictably, the current-voltage across the n-GaN thin film is Ohmic. Across the “p”-n junction, there is a back to back rectifying characteristic but with higher currents in the forward bias direction. And across the “p”-“p” junction, there is also a back to back rectifying characteristic.
Figure 60: Current-voltage measurements across the “p”-“n” junction of a control device and two InGaN nanowire LED devices, and b) Current-voltage measurements for one InGaN nanowire LED device across the “p”-“p”, “p”-“n”, and n-n junctions

The current-voltage characteristics agree with the band structure of the device. Shown below is a schematic of the n-InGaN/p-Ga/n-GaN band structure, with the InGaN quantum wells not shown for simplicity. There is one p-n junction between the p-GaN and the n-InGaN and another p-n junction between the p-GaN and the n-GaN. The junctions are in reverse configurations. The distinction to note is that the InGaN bandgap is smaller than the GaN bandgap which creates small conduction and valence band offsets.

At zero bias, there are barriers to motion for all carriers. When the n-p-n junction is forward biased, or in other words the p-GaN/n-GaN junction is forward biased, the band diagram is in the configuration shown in b). The majority carriers from the p-GaN and n-GaN begin to diffuse, get trapped in the quantum wells in the junction and recombine there. When the n-p-n junction is reverse biased, or in other words the p-GaN/n-GaN junction is reverse biased, the band diagram is in the configuration shown in c). The holes from the p-GaN are free to diffuse over to the n-InGaN and the electrons from the n-InGaN are more free to diffuse over to the p-GaN however there is a barrier to diffusion due to the conduction band offset resulting from the difference in bandgap of the two materials.
Figure 61: Band diagram of n-InGaN/p-GaN/n-GaN junction showing a) zero bias, b) forward bias, and c) reverse bias

The carrier motion is reflected in the current-voltage shapes. The InGaN nanowire LED device curve is back to back rectifying however the increase in current per voltage step is greater in forward bias than in the reverse bias case. The reason lies in the fact there is an additional barrier to motion on the n-InGaN/p-GaN junction due to the conduction band offset. In the “p”-“p” curve on the right graph, the reverse rectifying curves are symmetric. In this electrically pumped configuration, there are back to back n-InGaN/p-GaN junctions. Both junctions have the conduction band offset therefore the curve is symmetric.

5.3.2 Photoluminescence and Transmittance

Optical measurements were first carried out to characterize the InGaN nanowire arrays. UV-VIS transmittance measurements were carried on a Shimadzu UV-VIS-NIR Scanning Spectrophotometer (UV-3101PC). The double polished sapphire masks used on top of the LED chips during growth also had the same nanowire array growth as the LED chip. Those sapphire pieces were used in the transmittance measurements. The photoluminescence measurements were carried out on the actual LED device chips, under excitement from the 325 line of a Helium Cadmium laser. The photoluminescence spectra was then collected by a Nikon microscope coupled by a multimode fiber to a spectrometer with a liquid nitrogen cooled silicon charge coupled device (CCD).

Figure 62: UV-VIS transmittance and photoluminescence of InGaN nanowire arrays for three different samples

From the transmittance measurements, absorbance can be calculated. A graph of the absorbance squared over the wavelength range can give an estimate of the bandgap of the material by taking the x-intercept of the linear region of the absorbance curve and finding the corresponding bandgap energy to the wavelength. From the photoluminescence measurements,
the center wavelength of the emission peak can be used to find corresponding bandgap energy. The In$_x$Ga$_{1-x}$N composition can then be estimated using the graph from Kuykendall (12).

**Table 11:** Calculated bandgap and In$_x$Ga$_{1-x}$N composition from transmittance and photoluminescence measurements

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Transmittance Experiment</th>
<th>Photoluminescence Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavelength</td>
<td>Bandgap</td>
</tr>
<tr>
<td>TF20</td>
<td>532 nm</td>
<td>2.33 eV</td>
</tr>
<tr>
<td>TF31</td>
<td>512 nm</td>
<td>2.42 eV</td>
</tr>
<tr>
<td>TF30</td>
<td>492 nm</td>
<td>2.52 eV</td>
</tr>
</tbody>
</table>

The bandgap and composition calculations for the transmittance and photoluminescence experiments are not in exact agreement however the trend is the same. The photoluminescence values are taken as the more accurate estimate of bandgap energy. Also, those values are more likely to be true since the transmittance measurements were done on the double polished sapphire chips with only the InGaN nanowire array grown on top. The photoluminescence experiment was done on the array on the actual LED chips. It is possible that the compositional growth on the double polished sapphire did not exactly match that on the LED chip.

### 5.3.3 Electroluminescence

Electroluminescence measurements were then performed on the device. The setup combined a probe station and microscope/spectrometer setup. Two probes with bent probe tips were used to probe the LED device under a 5X objective. The device was centered such that the area of emission was located in the middle of the field of view. The electroluminescence spectra was then collected by a Nikon microscope coupled by a multimode fiber to a spectrometer with a liquid nitrogen cooled silicon charge coupled device (CCD).

![Figure 63: Camera images showing electroluminescence measurement setup](image)
Electroluminescence from the devices was very bright. Onset of emission was around 3.5-4.5V for different devices. The images below show camera images of the electroluminescence from the sample named TF20 at around 6V forward bias voltage. The nanowire array on this sample was shown in the previous section to have a bandgap around 2.1 eV and material composition of In$_{0.46}$Ga$_{1-0.46}$N. The first two columns show the glowing 1 cm x 0.5 cm device. The first column is with ambient room light on and the second column is from ambient room light off.

The blue light is the 467 nm electroluminescence from the InGaN quantum wells of the LED structure. The emission originates from under the contact but also scatters all through the substrate to create the all over glow. The red-orange luminescence appearing as a circular glow around the top contact is the photoluminescence from the InGaN nanowire array, excited by the blue electroluminescence underneath the array. The first row shows raw images directly taken from the camera. The bottom row shows images from the camera with a 532 nm long pass edge filter. The purpose of this filter was to block the 467 nm signal coming from the QW structure to see the photo-excited luminescence of the InGaN nanowire array.

The last column on the right shows camera images with and without the 532 edge filter through the eyepiece of the Nikon microscope. For scale, the circular contact is 1.5 mm in diameter. It is interesting to note on the top image of the contact, the 467 nm blue emission is visible coming out of the side of the chip. In the bottom image of the contact, the blue emission is completely filtered out.

**Figure 64:** Camera images of sample TF20 with nanowire array of material composition In$_{0.46}$Ga$_{1-0.46}$N; Images show unfiltered emission and emission with 532 long pass edge filter
The graphs below show the corresponding luminescence spectra for sample TF20. The graph on the left shows raw spectra from the device. In the spectra, two distinct peaks are clearly evident, the peak at 467 nm corresponding to the electroluminescence from the InGaN quantum wells and a broader peak at 590 nm which corresponds to the photoluminescence from the InGaN nanowire array. The graph on the right shows spectra with a 532 long pass edge filter inserted to remove the dominating 467 nm QW peak.

**Figure 65:** Electroluminescence spectra of sample TF20 with material composition In$_{0.46}$Ga$_{1-0.46}$N; Spectra show unfiltered emission and emission with 532 long pass edge filter.

The images below show camera images of the electroluminescence from the sample named TF31 at around 6V forward bias voltage. The nanowire array on this sample was shown in the previous section to have a bandgap around 2.14 eV and material composition of In$_{0.42}$Ga$_{1-0.42}$N.

In this device, the ultimate color output is an aqua blue-green as opposed to the reddish-orange in the previous device. When the edge filter is placed in front of the camera, the resulting color is much more yellow as opposed to red-orange in the previous device. Also, an interesting observation is that in the previous device, the right column images are very similar in color, whereas in this device, the color turns from aqua-marine to yellow. The reason is because the ultimate color in this device still has a major tail below the 532 nm mark whereas the above device did not.
Figure 66: Camera images of sample TF31 with nanowire array of material composition In$_{0.42}$Ga$_{1-0.42}$N; Images show unfiltered emission and emission with 532 long pass edge filter.

The graphs below show the corresponding luminescence spectra for sample TF31. At low voltage inputs, two distinct peaks can still be resolved. However as the voltage input increases, the FWHM of the peaks increases and the peaks begin to merge together. At high voltage inputs, it’s apparent that the blue 467 nm peak red shifts and the 580 nm nanowire peak blue shifts and the result is a somewhat broad 510 nm peak with a large red tail.

Figure 67: Electroluminescence spectra of sample TF31 with material composition In$_{0.42}$Ga$_{1-0.42}$N; Spectra show unfiltered emission and emission with 532 long pass edge filter.
The images below show camera images of the electroluminescence from the sample named TF30 at around 6V forward bias voltage. The nanowire array on this sample was shown in the previous section to have a bandgap around 2.28 eV and material composition of In$_{0.38}$Ga$_{1-0.38}$N. This device emits a very blue color. The blue is not quite as deep blue as the emission from the InGaN quantum well, but is a bit more turquoise blue. The camera image does not necessarily show the distinction well however the color difference is definitely distinct to the human eye.

Figure 68: Camera images of sample TF30 with nanowire array of material composition In$_{0.38}$Ga$_{1-0.38}$N; Images show unfiltered emission and emission with 532 long pass edge filter

The graphs below show the corresponding luminescence spectra for sample TF30. At this nanowire composition, two peaks can no longer be resolved. However, the peak shape is clearly different from the control electroluminescence shown in the previous section with just the 467 nm peak. There is a definite red tail that corresponds to the contributing emission from the nanowire array.
5.3.4 Analysis

In the InGaN nanowire array LED device structure, the InGaN nanowire array is excited from below by the electroluminescence of the LED InGaN QW structure. The emission of the LED InGaN QW structure is centered around 467 nm. A fraction of the 467 nm emission is absorbed by the InGaN nanowire array and the other fraction is transmitted through the array. Of the light that is absorbed by the InGaN nanowire array, a fraction of the excited carriers recombine and result in photoluminescence and the resultant wavelength of emission is determined by the composition of the InGaN nanowire material. The final emission of the device is a combination of the transmitted 467 nm signal from the InGaN QW and the photoluminescence of the InGaN nanowire array.

Figure 69: Electroluminescence spectra of sample TF30 with material composition In$_{0.38}$Ga$_{1-0.38}$N; Spectra show unfiltered emission and emission with 532 long pass edge filter

Figure 70: Schematic of color conversion for InGaN nanowire array LED device
In order to further analyze the device quantitatively, curve fitting was done on the electroluminescence spectra. An example of the peak fits is shown below for device TF20 at 7.75 V input voltage. The fits were Gaussian curves. The fit is not entirely accurate; however it provides an estimate for the amount of blue photons transmitted and the amount of photons reemitted at a longer wavelength. In the spectra, the middle area between the two peaks is much higher than both peak-fit curves combined. This suggests that the reemitted peak is not Gaussian in nature, but rather has a much greater blue tail. Two reasons are possible as explanation. This contribution can be attributed to high energy input photons that do not completely relax to the band edges before recombining and emitting light. Also, the nanowire array is not homogenous over the entire sample and a significant spread in material composition could be present. This inhomogeneity could be GaN heavy, leading to the asymmetric peak.

![Graph showing curve fitting](image)

**Figure 71:** Example curve fitting shown for spectra of device TF20 at 7.75 V input voltage

The curve fitting for the devices TF31 and TF30 were not as clear as the two peaks could not be resolved. However a best guess was performed using the knowledge of the center of peak for the control device and the center of peak from the photoluminescence studies on the InGaN nanowire array.

The graphs below show how the maximum peak value changes and how the area under the peak changes as a function of input voltage for both the blue 467 nm QW peak and 590 nm nanowire peak on Device TF20. All the resulting curves can be described as exponential. This observation seems reasonable for any general diode since an increase in voltage causes a decrease in the barrier in the diode junction. A step decrease in the junction barriers results in an exponential growth in the number of carriers that have enough energy to diffuse across the junction.
Figure 72: Graphs comparing the Peak 1 and Peak 2 maximum values and areas at different input voltage levels for device TF20

In the case of maximum peak value, the 467 nm peak increases at a faster rate than the 590 nm peak. In contrast, the integrated area under the peak increases at a more similar rate however there is still a slower increase for the 590 nm peak. This difference can perhaps be explained by suggesting that as input voltage increases, more higher-than-band-edge-energy recombinations occur in the nanowire array. Perhaps this is because there is such an increase in influx of the 467 nm blue light that the states near the band edge become saturated. Before those saturated states have a chance to recombine, higher energy electron-hole pairs recombine without relaxing down to the band edge. The general downward trend of both ratios, as shown in the right hand graphs, suggests that in general, the recombination rate cannot keep up with the exponential increase in 467 nm as input voltage increases.

So far the output peaks have been compared in relation to each other. A different avenue of analysis would be to compare the two output peaks to a theoretical 467 nm input peak from just the QW emission. In other words, of the light that is emitted by the quantum wells, some light is transmitted straight through the nanowire array and some is absorbed by the array and reemitted according to the material composition of the array.
In order to perform this analysis, it was necessary to estimate the transmittance of the 467 nm emission through the InGaN nanowire array. Double polished sapphire chips were used as growth masks during growth on the LED chips. These chips were used for the following transmittance measurements. The UV-VIS spectrophotometer experiment was useful to find transmittance over a range of wavelengths for low power inputs, but a more interesting measurement is transmittance of the nanowire array specifically from the emission of a bare LED QW chip at different input voltages, and therefore different input light powers. An experiment was set up to find transmission properties for exactly this measurement as shown in the figure below.

**Figure 73:** Experimental setup for transmission of LED QW emission through InGaN nanowire array

The control LED chip was electrically pumped and an emission spectrum was collected for 0.01 second acquisition time through a 20X objective lens. Keeping exactly everything the same, the InGaN sample chip was placed between the bare QW LED and the objective. The field of view was visually checked to make sure all incoming light to the microscope was blocked by the InGaN chip. A second emission spectrum was collected in this configuration. The graphs below show the before and after spectra for sample TF30 at 7.8 V input voltage. The typical symmetric 467 nm narrow peak can be seen from the control device. After blocking with the InGaN nanowire array, some 467 nm emission transmits through and some emission gets absorbed and reemitted at a longer wavelength.
Figure 74: Emission spectra of control device and control device blocked with InGaN nanowire array grown on double polishes sapphire chip.

Spectra were collected for all three devices, TF20, TF31, and TF30 at voltage inputs of 6.1V, 7.0V, and 7.8V. A baseline was first established before transmittance values were calculated. A bare double polished sapphire chip was inserted in the emission path of the control chip and emission spectrum was collected. The loss in emission accounts for those photons that are reflected off the two surfaces of the double polished sapphire chip as well as any photons that are scattered due to the substrate. By comparing the maximum peak value of the control device with and without the double polished sapphire chip presence, a transmittance of 85% is calculated through the double polished sapphire chip.

Finally, transmittance values were calculated at 467 nm taking into account the emission lost due to just the double polished sapphire chip. The results are shown below for the three different devices at three different voltage inputs.

Figure 75: Transmittance of Devices TF20, TF31, and TF30 for 467 nm emission from LED chips as a function of voltage
Transmittance seems to have a slight downward trend as a function of increased voltage input. Also, transmittance has an upward trend as a function of decreasing In$_x$Ga$_{1-x}$N composition. This observation can be explained since a smaller bandgap of InGaN will be able absorb more of the spectrum. Transmittance values are tabulated below. The values for transmittance at 467 nm using the UV-VIS Spectrophotometer as well as the control LED experiment are shown below. The UV-VIS values are definitely at the minimum limits of the instrument and therefore the LED experiment is much more believable.

**Table 12:** Transmittance measurements for devices TF20, TF31, and TF30 using two experimental methods

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>UV-VIS Experiment Transmittance at 467nm (%)</th>
<th>LED Experiment Transmittance at 467 nm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TF20</td>
<td>0.04578</td>
<td>0.493</td>
</tr>
<tr>
<td>TF31</td>
<td>0.0351</td>
<td>0.599</td>
</tr>
<tr>
<td>TF30</td>
<td>1.23749</td>
<td>2.071</td>
</tr>
</tbody>
</table>

Using these transmittance values, the input 467 nm integrated intensity can be calculated by assuming the intensity of the output 467 nm peak is the transmitted 467 nm emission and that the transmittance of the wavelengths surrounding 467 nm is approximately the same. The calculated input intensity minus the transmitted intensity should result in the amount of emission absorbed by the InGaN nanowire array. By dividing the integrated intensity of the long wavelength peak by the estimated amount of emission absorbed by the InGaN nanowire array, a conversion efficiency can be found. This conversion efficiency describes a photon to photon conversion and not an energy to energy conversion.

**Figure 76:** Photon conversion efficiency for devices TF20, TF31, and TF30
As shown in the graphs above, the conversion efficiency of all three devices stabilize around the same value of 0.3-0.4%. The initial values in the first two devices seem higher which means absorption maybe be slightly higher at low input voltages for these higher InN concentration arrays or could also be a result of noise in the system. However, the values of 0.3-0.4% transmittance seem reasonable and believable, especially because the different devices are performing similarly to each other.

5.4 Conclusions

An InGaN nanowire array QW LED has been demonstrated. The device was an n-p-n junction with reverse rectifying current-voltage characteristics. Light emission occurred only when the QW p-n junction was forward biased. The mechanism of luminescence was the electroluminescence of the InGaN QW LED which in turn photoexcited the InGaN nanowire array. The array would in turn reemit photons according to the bandgap of the nanowire, or in other words the material composition of the nanowire. The ultimate color of emission was a combination of the transmitted 467 nm blue light produced by the emission of the quantum wells and the longer wavelength emission of the nanowire array excited by the 467 nm absorbed light.

The color of emission was tunable by tuning the material composition of the InGaN nanowire array, and therefore tuning the bandgap. As discussed in the beginning of the chapter, high indium nitride concentration InGaN compounds are nearly impossible to produce stably in thin film form due to phase segregation issues. However it was reported recently that high indium nitride concentrations of InGaN can be stably synthesized in nanowire form. Using this synthesis, varying compositions of InGaN nanowire arrays were grown on the LED chips to produce luminescence by LED light excitation. In the previous sections, three specific devices were studied which ranged in In$_x$Ga$_{1-x}$N compositions from x=38 to x=46. The resulting color of emission was tuned from aqua blue, to blue-green, and finally red-orange.

Shown below are color camera photos of devices with varying InN compositions with the 532 nm long pass edge filter in place. The resulting color spectrum of the devices range from cold yellow, warm yellow, orange, red-orange, and red. The luminescence is not believed to be a result of any type of defect emission. The reason is because the physical color of the nanowire array corresponds well to the photoluminescence wavelength of emission. In the figure below, the corresponding devices are shown below the glowing devices. The previous work had already correlated the physical color and photoluminescence results with EELS compositional analysis (12).
The device fabricated is not the ideal structure in terms of efficiency however it is the first device fabricated incorporating the high InN concentration InGaN nanowire arrays. Efficiency is not optimized because energy is lost during color conversion of the 467 nm emission to the longer wavelength nanowire emission. A p-n junction device incorporating a p-GaN thin film and n-InGaN nanowire array could possibly result in less energy loss. This device was attempted however no light emission could be detected. The reason is most likely due to the poor quality of the fabricated p-GaN thin films used in the experiment. Future work in this area will be to attempt these devices again.

An interesting note though is that the n-p-n junction did not show any light emission when the device was biased such that the p-GaN/n-InGaN junction was forward biased. In this configuration, there should be recombination occurring over the p-GaN/n-InGaN junction and possibly photonic emission corresponding to the bandgap of p-GaN or n-InGaN. It was surprising to not see emission because the p-GaN thin film on the LED device is much better quality than a standalone p-GaN thin film. The reason is that the p-GaN thin film on the LED is grown over a very thick n-type layer. The defects in the films mostly arise from the lattice mismatch to the sapphire substrate so the thick n-type layer should already have the opportunity to ease out those defects. This suggests that the interface formed between the p-GaN and n-InGaN may be rich in defects. These defects would result in only non-radiative recombinations. Future work on these devices should address those issues.
Chapter 6. Metal Enhanced InGaN Nano-LED

This chapter explores the third and final light emitting diode architecture of this dissertation that exploits nanoscale properties, namely enhancement of electroluminescence by metal coating of nanopillar LEDs.

The platform for the metal coated nanopillar LED is based on the same InGaN/GaN QW thin film structure as used in the previous chapter. The nanopillar is formed top-down and coated with a spacer layer, then a metal cladding layer. The metal cladding layer is proposed to provide two mechanisms for electroluminescent enhancement. First it serves as a metallic cavity that confines the light within the pillar. Second, the local electric field caused by surface plasmons at the metal/dielectric interface can be in close enough proximity to enhance radiative recombination in the emission medium.

![Figure 78: Schematic of metal-coated nanopillar LED device](image)

Previous work has shown fabrication of InGaN QW nanopillars by nanosphere lithography (76). Other research groups have achieved electroluminescence from nanosphere lithography top-down fabricated InGaN nanopillars (77) as well as interference lithography fabricated (78) and self-assembled Ni nanomask fabricated (79). However no work has studied the possible enhancement of electroluminescence by metal coating the devices. One group has shown lasing in an InGaAs nanopillar after it was metal coated (17).

In the following sections, the GaN/InGaN MQW nanopillar fabrication and resulting LED will first be discussed. Then fabrication and characterization of the metal-coated nanopillar LED will be discussed and analyzed.
6.1 InGaN Multiple-Quantum-Well Nanopillar LED

The GaN/InGaN multiple quantum well LED purchased from Epistar Company in Taiwan was again the platform for this nanopillar device. The concept of the nanopillar LED was first explored before integrating metal coatings.

6.1.1 Nanopillar Formation and Device Fabrication

The two inch wafer was first wafer sawed into 1 cm x 0.5 cm rectangular chips for individual devices. To form the nanopillars, silica beads were used as etch masks in a common lithography form known as nanosphere lithography. The silica beads used in this study were either 320 nm beads made by Bangs Laboratory or 1500 nm beads made by Duke Scientific. The dilution of the silica solution was modified to match the dilution of pillars desired on the actual chip. Typically, between 5-100 µL of concentrated silica solution was diluted with a 15 mL mixture of 2:1 isopropanol to water. The chip was then dipped one time into the solution. The trick to getting single nanospheres, rather than aggregates, was to quickly blow dry the chip after the dip. A typical spread of silica beads is shown in the SEM image below.

![Figure 79: SEM showing dilute distribution of single nanopillars](image)

The beads were used as masks during a reactive ion etch (RIE) of the chip. The RIE was done at the Nano Fabrication Facility at University of California, Santa Barbara. The etch recipe was as follows: chamber pressure = 0.2 Pa, bias power = 150W, ICP power = 500W, Cl₂ flow rate = 22.5 scem, N₂ = 7.5 scem, and time = 105 seconds. The etching results are shown in the figure below. It is imperative to etch deep enough to expose the n-type GaN layer. The resulting pillar diameter is approximately dictated by the silica bead diameter with some tapering due to etching of the bead over the etch time. The resulting nanopillars are circular in cross section and
around 500 nm in height. Etch rate is around 4 nm/sec. This number however cannot be taken as general for all GaN substrates. Purchase of different batches of wafers proved that etch time varied by about ± 1 nm/sec, a large variation. The disparity seems to be attributed to the defect condition of the thin films. A larger defect density leads to faster etch rates. Evidence was seen in a substrate that had a higher etch rate and resulted in lots of etch pits in the surrounding thin film, an indicator of high defect density. This observation is also seen in literature (80).

![Figure 80: SEM images of resulting nanopillars after RIE](image)

After the etch, the silica bead can be removed by a 1 minute dip in 10:1 HF solution. The resulting top surface can be seen in the SEM image below.

![Figure 81: SEM of nanopillars after HF etch to remove silica bead mask](image)

To complete the device, the substrate is spin coated with PMMA. PMMA was wiped off half of the substrate for n-contact. An oxygen plasma etch was used to reveal the tops of the nanopillars for p-contact. Finally, gold was sputtered on the device using a shadow mask to create metal contacts to both the p-GaN and n-GaN.
6.1.2 Nanopillar LED Characterization

The resulting device is shown in the schematic below. Several contacts were made enabling interrogation of P-N, P-N-P, and N-N connections. Onset of electroluminescence occurred around 2.5 V forward bias.

![Schematic of metal contacts to nanopillar LEDs](image)

**Figure 82:** Schematic of metal contacts to nanopillar LEDs

The following graphs show the current-voltage characteristics of the nanopillar LED. The n-n contacts are Ohmic as expected. The p-n junction is rectifying with no leakage current even at a reverse bias of 10 V. The n-p-n junction is back to back reverse rectifying, also as expected.

![Current-voltage characteristics of nanopillar LED](image)

**Figure 83:** Current-voltage characteristics of nanopillar LED
Electroluminescence is centered around 450 nm corresponding to a bandgap of 2.756 eV and suggesting an $\text{In}_x\text{Ga}_{1-x}\text{N}$ composition of around $x = 0.21$ (12). The early onset of electroluminescence suggests that the metal contacts are very good with no voltage drop loss.

**Figure 84:** Electroluminescence spectra of nanopillar LED

Below are images of the electroluminescence from the device. The left image is a direct shot of the 0.5 cm x 1 cm device chip. The image on the right is taken through the microscope eyepiece and through a 5X objective lens. The circular shape is the 1.5 mm diameter gold contact. For this given dilution level of nanopillars, there are around 100-500 nanopillars per contact pad. Each dot seen in the image represents one nanopillar. The overall glowing blue is merely scattered light within the substrate.

**Figure 85:** Camera images of electroluminescence taken as a direct shot of device and through the microscope eyepiece
6.2 Metal Coated Device Design

Aluminum was chosen as the metal cladding layer because its plasmon frequency is matched to the blue emission of GaN material. Silver would also be a well matched material as its plasmon frequency is matched to a longer blue emission wavelength comparable to emission of InGaN. A spacer layer is necessary between the emissive material and metal coating because carriers generated in the material would get quenched by the metal. A spacer material of alumina is chosen for this device.

6.2.1 Device Fabrication

The device fabrication for the metal coated pillar is much more challenging than the bare nanopillar LED. The fabrication procedure is shown in the figure below. After creation of the nanopillar by RIE etch, the silica bead was left on. This was to ensure that in a later step, a clean metal contact could be made to the nanopillar top. A thin spacer layer of alumina was deposited over the whole chip by atomic layer deposition (ALD). The layer was around 8 nm thick. This thickness was used to ensure tunneling of carriers would not occur but also was thin enough so that the electric fields produced by surface plasmons would still have an effect on the emissive material.

Tape was used to remove the bead from the tops of the pillar. The tape was placed on the chip and a razor blade was slid across the chip to promote adhesion to beads. This was done several times. The tape was then lifted off to remove the beads. PMMA was spun onto the substrate and etched back by oxygen plasma dry etch to reveal the tops of the pillars. Nickel was then deposited by e-beam evaporation to form an Ohmic contact to the p-type GaN. The unwanted metal was lifted off with the PMMA in an acetone sonication. The result was nickel metal residing only over the tops of the nanopillars.

One third of the chip was masked, and a thin film of aluminum was e-beam evaporated onto the chip, approximately 60 nm. The film conformally coated the nanopillars over the alumina spacer layer. This layer acts as the metal cladding layer as mentioned in the beginning of the chapter. The chip was subjected to a PMMA spin again and an O₂ plasma etch was used to reveal the tops of the pillars. The PMMA was wiped off the third of the substrate that did not have aluminum deposition. A scribe was used to scratch the alumina on that portion of the chip in order to make a contact to the n-GaN. Finally, gold was sputtered onto the device using a shadow mask to created contacts to the tops of the nanopillars as well as the n-GaN.
The fabrication step with the most difficulty was the tape removal of the beads. In the first attempts, the alumina was deposited after an HF removal of the silica beads. Then a solution BHF etch as well as an argon mill dry etch were attempted to remove the alumina layer. The BHF etch, however, was uncontrollable and too much alumina was removed. The argon mill dry etch was also hard to control since this physical etch removed any type of material including the nitride layers.
The tape removal method seemed to have the cleanest result with a guaranteed clean contact to the top of the nanopillar. However, yield was low. It was very difficult to get many of the beads to be removed. The SEM images above show an alumina coated nanopillar with the silica nanosphere still attached. The SEM image on the right shows a nanopillar after tape removal of the silica bead. The tape removal should be a very plausible method upon closer inspection of the image on the left. The alumina coating of the nanopillars with nanospheres attached show a natural weak point at the nanosphere/nanopillar junction. If the tape adheres well to the sphere, the sphere should break off easily at the interface. The image on the right shows the clean removal of a nanosphere. It is apparent on the surface of the nanopillar that a clean inner surface without any alumina coating is left for metal contact.

The sheer number of fabrication steps for this device also results in lower yield for working devices.

6.3 Metal Coated Device Characterization

6.3.1 Electrical

The current voltage characteristic of a metal coated nanopillar device is shown in the figure below as compared to a control device with no metal coating. The control device clearly shows a rectifying behavior. In contrast, the metal coated device exhibits large current levels in reverse bias conditions.

The addition of the metal layer modifies the current-voltage behavior. A possible cause of the large leakage current in the reverse bias condition can probably be attributed to carriers...
that spread across the metal coating layer and tunnel through to the n-type GaN film through the thin alumina layer.

### 6.3.2 Electroluminescence

Electroluminescence was successfully demonstrated for the metal coated nanopillars. Attempts were made to produce very low density samples so individual nanopillars could be assessed. This idea was important in order to reveal whether there was true enhancement of electroluminescence by the metal coating.

The camera images below show a metal coated sample that encompassed only five nanopillars. The image on the left shows electroluminescence in complete darkness and the image on the right shows electroluminescence with the microscope light barely on to reveal the probe and size of the metal contact. The additional dots on the left image are just due to reflections of the real nanopillar emission.

![Camera images through eyepiece and 5X objective of electroluminescence from metal coated nanopillars](image.png)

**Figure 89:** Camera images through eyepiece and 5X objective of electroluminescence from metal coated nanopillars

The spectra below on the left shows electroluminescence of a control device which is exactly the same as the test device but without the aluminum metal coating. In other words, the control device also has an alumina spacer layer and was fabricated in the same way as the metal coated nanopillar. The contact pad probed for the control device had a total of 26 nanopillars. The spectra on the right shows photoluminescence of the metal coated device when excited by the 325 nm line of a HeCd continuous wave laser. The n-side of the device shows the 380 nm band edge of the GaN as well as the broad 580 nm defect peak of the GaN. When the beam is localized in an area with nanopillars, a sharp 450 nm peak appears. The p-side of the device showed very weak photoluminescence due to blocking of source and emitted light by the aluminum thin film.
Both of the spectra below show electroluminescence of metal coated nanopillars. The two different spectra are of two different contact pads on the same device. One contact pad revealed three nanopillars. The other contact pad revealed 23 nanopillars.

**Figure 90:** a) Electroluminescence spectra of control device without metal coating and b) Photoluminescence of metal coated device

6.3.3 Analysis

In order to do an analysis of electroluminescent enhancement, an apples-to-apples comparison of electroluminescent intensity needed to be established. The total electroluminescence would need to be divided by the number of nanopillars to get individual nanopillar contributions. The aluminum layer on the test device accounted for much more blockage of the generated light as compared to the control device. Besides the aluminum layer, everything about the two devices was exactly the same. Therefore, transmittance measurements
were done on equivalent e-beam evaporated aluminum films on a glass slide. It was assumed that the actual amount of light generated by the metal coated nanopillars could be estimated by accounting for the transmittance of the aluminum thin film.

UV-VIS transmittance measurements of aluminum thin films are shown in the graph below. At a wavelength of 450 nm, the transmittance of a 40 nm thin film was 0.990% and the transmittance of a 60 nm thin film was 0.125%.

![Graph showing UV-VIS transmittance of aluminum thin films](image)

**Figure 92:** UV-VIS Transmittance of aluminum thin films

The relevant calculations are shown below. The number of counts per pillar was 808, 433, and 348 for the control device and two test devices, respectively. When the number of counts is adjusted for the emission lost through the aluminum thin film, the number of counts per pillar changed to 808, 346,667, and 278,261. These numbers correspond to an enhancement factor of 429 and 345 for the two test devices. This would be an extraordinary enhancement.

**Table 13:** Possible enhancement factor for metal-coated nanopillars

<table>
<thead>
<tr>
<th>Sample</th>
<th>EL Counts at 450 nm</th>
<th>Input Voltage (V)</th>
<th># of Pillars</th>
<th>Counts/Pillar</th>
<th>Transmittance of Al Film</th>
<th>Adjusted Counts/Pillar</th>
<th>Enhancement Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>21000</td>
<td>13</td>
<td>26</td>
<td>808</td>
<td>1</td>
<td>808</td>
<td>1</td>
</tr>
<tr>
<td>DAR51</td>
<td>1300</td>
<td>11</td>
<td>3</td>
<td>433</td>
<td>0.00125</td>
<td>346,667</td>
<td>429</td>
</tr>
<tr>
<td>DAR51B</td>
<td>8000</td>
<td>13</td>
<td>23</td>
<td>348</td>
<td>0.00125</td>
<td>278,261</td>
<td>345</td>
</tr>
</tbody>
</table>
6.4 Conclusions

The work done for this device architecture is still in its infancy and care should be taken before believing the enhancement factors. There are a number of factors that could play a role in ultimate modification of the numbers. First, enhancement values were taken for similar input voltages on the devices. However, the addition of the aluminum on the test devices could mean the circuit characteristics of the device are changed and a similar overall input voltage doesn’t necessarily mean a similar drop in voltage across the p-n junctions. Care should be taken to verify that the pillars were completed in the correct function. The assumption is made that the nanopillars are completely encased in the aluminum thin film. Some SEM images suggest there may be cracking at the nanopillar tops meaning some leakage of light may be occurring.

That being said, there is believed to be an enhancement in electroluminescence due to the metal coating. The actual enhancement value is unclear however with the data at hand, it is very likely that there is some enhancement. As stated earlier, the number of counts per pillar where 808, 433, and 348 for the control device and two test devices, respectively. The intensity dropped by only a factor of ½ going from the control device to the metal coated device. Visually, the metal coating is believed to have been blocking much more than 50% of the emission. Therefore, enhancement is believed to be occurring.
Chapter 7. Summary and Conclusions

The goal of this research was to explore some potential advantages that nanoscale effects can offer to light emitting diode functionality. Light emitting diodes are based on injection electroluminescence from semiconductor materials. They can be highly efficient and robust and have the potential to replace all lighting applications in the future. Some drawbacks, however, include low efficiency at certain wavelengths and a drop in efficiency at high injection currents. Another drawback is availability of color and color tunability. The aluminum gallium indium phosphide compositional family covers only the spectrum from red to yellow-green. A move to the indium gallium nitride family would be ideal, revealing the entire visible range with just one compound material.

The first chapter of this dissertation explored the physics behind light emitting diodes and revealed the potential advantages of nanoscale materials. Nanowires are grown bottom-up, and often epitaxially from a host material. This method of synthesis leads to single crystalline, low-defect materials and good interface quality between the host and nanowire material. These properties could improve the internal quantum efficiency of light emitting diodes. Nanowires also form natural optical cavities and can result in waveguiding of light along its long axis, potentially improving extraction efficiency. The second chapter surveyed the current status of light emitting diodes, both commercially and at the research level. Common materials were mentioned as well as current efficiencies. Novel research approaches to tunable light as well as nanoscale light emitting diodes were mentioned including single nanowire devices and nanowire array devices.

Chapter three provided background information for the materials used in this dissertation. Various material, electrical, and optical properties of the materials zinc oxide, gallium nitride and indium gallium nitride were detailed. These properties are necessary to understand in order to comprehend and fully analyze the resulting characteristics of the light emitting diodes that are made from these materials. These materials are attractive because they are all direct bandgap semiconductors. Zinc oxide and gallium nitride are large bandgap materials that emit light in the blue region and the compositional family of indium gallium nitride spans the entire visible spectrum.

Finally, chapter four explored the first platform for a nanowire light emitting diode, consisting of an intrinsically n-type zinc oxide nanowire array grown epitaxially from a p-type gallium nitride thin film. The nanowire array was grown by two methods: a hydrothermal approach and chemical vapor transport approach. The resulting array in both cases was completely vertically oriented. Only the solution grown nanowire array LED resulted in injection electroluminescence. Emission was localized in the p-GaN thin film directly beneath the junction and spectra centered around 440 nm, which is associated with the band to acceptor transitions in p-type GaN. The solution grown nanowire array LED was tested for spatial emission pattern and was found to have a 13% increase in light output in the vertical direction, or parallel to the nanowire length, as compared to a thin film device.
Figure 93: Summary of results from zinc oxide nanowire array light emitting diodes including a) schematic of device, b) SEM image of nanowire array, and c) light emission from device

Chapter five explored a second light emitting diode architecture which took advantage of the ability to synthesize $\text{In}_{x}\text{Ga}_{1-x}\text{N}$ materials in nanowire form with $x$ greater than 30%. This capability is a huge challenge in thin film synthesis due to phase segregation issues. The platform was an InGaN nanowire array grown on top of a thin film based InGaN quantum well LED. Electrically pumped emission from the QW LED photo-excited the InGaN nanowire array and the resulting luminescence was a combination of transmitted QW electroluminescence and color converted photoluminescence from the InGaN nanowire array. The ultimate color emission was tunable by tuning the material composition of the InGaN nanowire array and therefore tuning its bandgap. The colors achieved ranged from blue, to blue-green, and finally red-orange.

Figure 94: Summary of results from indium gallium nitride nanowire array light emitting diodes including a) device schematic, b) SEM image of nanowire array, and light emission from devices with nanowire composition of c) $\text{In}_{0.46}\text{Ga}_{0.54}\text{N}$, d) $\text{In}_{0.42}\text{Ga}_{0.58}\text{N}$, and e) $\text{In}_{0.38}\text{Ga}_{0.62}\text{N}$
The final light emitting diode architecture was explored in chapter six. Potential electroluminescence enhancement was explored by metal coating of nanopillar LEDs. The metal cladding layer could provide two mechanisms for electroluminescent enhancement. It serves as a metallic cavity that confines the light within the pillar and the local electric field caused by surface plasmons at the metal/dielectric interface can be in close enough proximity to enhance radiative recombination in the emission medium. The large surface area to volume ratio of the nanopillars meant that surface plasmons from the metal coating had a higher probability of interaction with the indium gallium nitride. Nanopillars were fabricated top-down from an InGaN quantum well thin film LED structure using nanosphere lithography. The nanopillars were coated with an alumina spacer layer and aluminum metal cladding layer. Enhancement factor of the electroluminescence, as compared to a nanopillar device without metal coating, was on the order of 400. However, the fidelity of these results needs to be further explored due to concerns of light leakage through cracks in the metal layer.

Figure 95: Summary of results from metal coated nanopillar light emitting diodes including a) schematic of device, b) SEM image of single nanopillar, and c) light emission from device

In all, nanoscale based light emitting diodes were explored to study potential advantages over conventional thin film LEDs. Three platforms were studied and improvements were observed including higher extraction efficiency due to waveguiding of light along the length of the nanowires, full-spectrum compositional tunability due to capability of growing high indium nitride concentration InGaN material in nanowire form, and enhanced electroluminescence due to increase in radiative recombination due to surface plasmons.

A plethora of research concepts in nanowire light emitting diodes have yet to be explored. This area is still relatively new and the combinations of materials, design platforms, and nanoscale effects yet to be discovered and analyzed seem without bounds. There are some interesting concepts that can springboard directly from the architectures explored here. ZnO/GaN LEDs are a good material system to study. Core-shell or axial nanowire LEDs from these materials could result in very interesting devices. In the case of the high indium nitride composition InGaN nanowire arrays, much effort should be placed in making direct p-GaN/n-InGaN devices. This would prove to be a very useful device without the loss in energy from color conversion. Finally, much work has yet to be done on metal coated nanopillar LEDs, including an analysis of spacer layer thickness, metal coating material, metal thickness,
nanopillar dimensions, etc. The mechanism behind enhanced electroluminescence should also be studied in detail.

I am a true believer in light emitting diode technology. The huge research efforts in existence now toward solid-state lighting will undoubtedly lead to the performance and cost requirements necessary to implement world-wide conversion to LED lighting. It will not be surprising to me if the future exists where my grandchildren will only be able to find incandescent lightbulbs and fluorescent lamps at the museum.
Bibliography