Development of High-Power III-Nitride Light-Emitting Diodes for Solid-State Lighting

Yi Yang
West Virginia University

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Development of High-Power III-Nitride Light-Emitting Diodes for Solid-State Lighting

by

Yi Yang

Dissertation submitted to College of Engineering and Mineral Resources at West Virginia University in partial fulfillment of the requirements for the degree of

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In

Electrical Engineering

Xian-An Cao, Ph.D., Chair
Jeremy Dawson, Ph.D.
Parviz Famouri, Ph.D.
Lawrence A. Hornak, Ph.D.
Nianqiang Wu, Ph.D.

Lane Department of Computer Science and Electrical Engineering
Morgantown, West Virginia 2011

Keyword: InGaN LEDs, Photonic Crystal, Quantum Efficiency droop

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ABSTRACT
Development of High-Power III-Nitride Light-Emitting Diodes for Solid-State Lighting
Yi Yang

White light sources based on III-Nitride light-emitting diodes (LEDs) hold great promise for developing energy-efficient solid-state lighting (SSL) technologies. However, the optical output power of InGaN-based green and blue LEDs at high driving currents is limited by quantum efficiency (QE) droop and low light outcoupling efficiencies. The former is a phenomenon that LEDs suffer a decline in quantum efficiency as the driving current increases, and prominently occurs in LEDs with high In contents. Poor light outcoupling is a challenge facing LEDs of all colors. Due to a large contrast of refraction index between nitrides and air, the majority of photons generated in the active region are trapped inside LED chips and reabsorbed. To develop powerful LED lighting sources capable of high-current operation, new strategies must be developed to overcome the droop obstacle and improve the efficiency of light extraction.

The objective of the current work is to improve the external quantum efficiencies of InGaN-based green and blue LEDs from these two aspects. The first part of this dissertation presents studies of the underlying mechanisms of efficiency droop in InGaN-based LEDs and our effort to develop LEDs with reduced droop through structure optimization. We investigated the optical characteristics of InGaN-based multiple-quantum-well (MQW) LEDs on sapphire with peak emission ranging from green to ultraviolet over a wide injection range. The current dependence of both the QE and peak shift appears to be a strong function of the In content in the active region. The QE of the green LED peaks at a current density as low as 1.4A/cm$^2$, and decreases dramatically as current is increased, whereas the In-free deep-UV LEDs have a nearly constant QE at currents up 1 kA/cm$^2$. To understand the role of threading dislocations in the droop behaviors, green LEDs were grown and fabricated on free-standing GaN. The density of microstructural defects in the LED structure was substantially reduced, leading to a significant reduction in defect-assisted tunneling currents a ~65% peak internal QE. However, it suffered from even more dramatic efficiency droop which occurs at a current density as low as 0.3 A/cm$^2$. 
These results offer a strong support for the argument that carrier overflow from localized states and loss at interfacial misfit defects is the nonthermal mechanism of the efficiency droop. Reduction of misfit defects in green LEDs by using an strain-compensated InGaN/InGaN MQW structure led to reduced efficiency droop at high currents, suggesting that strain engineering provides a feasible solution to the droop problem.

The second part of the dissertation explores the applicability of photonic crystals (PhCs) as diffraction gratings for light outcoupling from InGaN-based LEDs. Time-domain modeling of GaN PhCs with triangular lattices was carried out to determine the photonic band structure and the desirable geometry of 2D PhC slabs for light-coupling. 2D PhC slabs of a triangular lattice with the lattice constant of 333 nm and airhole diameter of 200 nm were fabricated on top of blue LEDs using e-beam lithography and inductively-coupled plasma etching. A 50% enhancement of electroluminescence was achieved compared to similar LEDs without integrated PhCs. In order to minimize the adverse effects of sidewall plasma damage which lead to increased junction leakage and nonradiative recombination rates. We developed a new post-etching treatment technique which combined thermal annealing and sulfide passivation. Blue PhC LEDs subjected to annealing at 700 °C followed by (NH₄)₂S passivation exhibited a complete restoration of the electrical characteristics.
ACKNOWLEDGMENTS

Looking back at the long journey toward this point in my academic career, I am indebted to many people for their help. My first and deepest appreciation must go to my advisor Professor Xian-An Cao. He offered me such a great chance to work on nitride materials and light emitting diodes, which has become one of the most exciting fields among all of the scientific and engineering topics. His deep thoughts and inspirational suggestions have guided me through the scientific discovering process of my PhD study, and will surely become my invaluable possessions which will continue to influence my future research. In addition, I would like to thank my committee members – Prof. Jeremy Dawson, Prof. Parviz Famouri, Prof. Lawrence A. Hornak, and Prof. Nianqiang Wu – for their valuable suggestions and comments on my research.

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CHAPTER 1
Introduction

1.1 Overview and Motivation

The first Visible spectrum (red) light emitting diode (LED) debuted in 1962 [1]. The invention was followed by the demonstration of yellow LED in 1972 [2]. Due to the limited light emission efficiency, red and yellow LEDs were initially used in wrist watches and instrument panel indicators. Until early 1990s, LEDs operating in this portion of spectrum did not achieve the light efficiencies superior to those of incandescent lamps [3]. Although the first blue LED was made in 1971 [4], it has proved difficult to extend the wavelength to the range below 550 nm. In the following decade, blue LEDs were of little practical use because of the low efficiencies. Due to the lack of blue spectrum, the applications of LEDs were limited mostly to electronic indicators.

The main challenges to short wavelength LEDs were attributed to the growth problems of wide band gap semiconductors: 1) lack of suitable substrates, and 2) difficulties in making p-doped materials. With the problems unresolved, wide band gap semiconductors such as Group III-Nitrides can only be grown on foreign substrates, resulting in low quality crystals due to the mismatch in lattice constants and thermal expansion coefficients. Furthermore, the lack of p-doped semiconductors made it impossible to fabricate electronically driven bipolar devices. The key breakthrough came in late 1980s. Specular and crack-free GaN films were eventually achieved with a low-temperature AlN or GaN buffer layer grown by metalorganic chemical vapor deposition (MOCVD) [5,6]. P-type GaN was obtained by Mg doping of MOCVD films with a low energy electron beam irradiation (LEEIBI) treatment [7], and soon it was found that thermal annealing at 700 °C under N₂ ambient led to similar results [8]. The success in producing high quality GaN films made it possible to grow InGaN-based multiple-quantum-wells (MQWs), the key component to emit light with the wavelength below 550 nm. With the three primary colors available,
white light sources can be made either with proper mixtures or with the combination of blue LEDs and yellow phosphors. This opens up many important applications, such as large panel displays, outdoor signs or even general lighting.

At present, incandescent bulbs and fluorescent lamps are used as white light sources which have poor reliability and durability and a low luminous efficiency. A solid-state white light source would provide not only a longer lifetime, but also reduce the power consumption. Worldwide, lighting constitutes 20% of electricity consumption while its efficiency is typically lower than 25%. In contrast, efficiency of space heating has exceeded 90%. To this end, the development of highly efficient and reliable LEDs for solid-state lighting (SSL) has been very active in both industry and academia in the past decade. It is projected by the US Department of Energy that by 2015, if successful, SSL can reduce the overall electricity consumption for lighting by 25%.

The technology of SSL has advanced dramatically since the commercialization of blue LEDs in mid 1990s as presented in Fig. 1.1. The rapid development of technology has caused the LED light output to double about every 36 months since the 1960s, in a similar way to Moore’s law. Now, with the advantages of low turn-on voltages, small sizes and long lifetimes, SSL is of even more importance as energy conservation has become a global challenge. While great success has been achieved in the development of InGaN-based blue and green LEDs, there remain some major obstacles to achieving high-efficiency and high power InGaN-based blue/green LEDs required for widespread SSL applications. The output power of state-of-the-art green and blue LEDs at high currents is mainly limited by efficiency droop [10-12] and poor light outcoupling [13-15]. The former is observed as a reduction in quantum efficiency with increasing injection current and prominently occurs in LEDs with high In contents, whereas the latter is a challenge facing LEDs of all colors. Due to a large contrast of refraction index between nitrides and air, the majority of photons generated in the active region are trapped inside LED chips and lost due to reabsorption. To develop high power SSL sources, the droop obstacle must be overcome and new strategies for increasing light extraction from InGaN-based LEDs
must be explored. The aim of this study is to improve the high-current performance of InGaN-based green and blue LEDs from these two aspects, i.e. droop reduction and light outcoupling enhancement.

1.2 Thesis Organization

The dissertation is organized as follows: In Chapter 2, a general review of the III-Nitirde LED technologies is given. Further in the chapter, major factors limiting high-power operation of InGaN LED are discussed in detail. In Chapter 3, we investigate the nonthermal mechanism of efficiency droop in InGaN-based MQW LEDs at high currents through systematical optical and electrical characterization of LEDs with different In contents and material quality. Chapter 4 presents the growth, fabrication and characterization of green InGaN/GaN MQW LEDs on high-quality free-standing GaN substrates. Initial effort is made to reduce efficiency droop in green LEDs via strain engineering during the epitaxial growth. In Chapter 5, we study the effects of thermal annealing and sulfide passivation on the electrical characteristics of perforated blue LEDs, which resemble PhC-integrated emitters. It is demonstrated that a complete restoration of the LED electrical characteristics can be achieved by a combination of these two techniques. In chapter 6, in an effort to integrate photonic
crystals (PhC) with LEDs for light outcoupling enhancement, modeling is performed to optimize the design of the PhC structures and nanofabrication of 2D GaN and ITO PhC slabs are developed. PhC built on top of blue LEDs as diffraction gratings lead to a significant improvement in the light extraction efficiency. The final chapter presents a summary of the current work and discussion of future work.

1.3 References

CHAPTER 2
Literature Review of III-Nitride LEDs

For the last three decades, remarkable progress has been made in development of the III-nitrides AlN, GaN, InN, and their family of material alloys for optoelectronics and electronics applications [1-2]. Wurtite GaN, AlN, and InN have direct room-temperature bandgaps of 3.4 eV, 6.2 eV, and 0.7 eV, respectively [3]. Light emitting diodes (LEDs) and laser diodes (LDs) based on GaN and its alloys can, in principle, cover the range from deep ultraviolet (UV) through visible to the far infrared (IR) region (see Fig. 2.1), which is not possible with the III-V materials system based on Arsenic (As)-based and phosphide (P)-based alloys.

![Energy bandgap versus lattice constant for wurtzite III-nitride and zincblende III-phosphide semiconductor alloy systems employing Al, In, and Ga](image)

*Fig. 2.1 Energy bandgap versus lattice constant for wurtzite III-nitride and zincblende III-phosphide semiconductor alloy systems employing Al, In, and Ga [3].*

Large scale displays, modern traffic lights or public lighting nowadays use GaN-based LEDs. Significant effort has been invested in development of efficient and reliable LEDs which emit comfortable white light, as there is a huge market potential for replacing bulbs and fluorescent tubes currently used. Apart from the long lifetime, the other advantages are substantial energy savings as well as a reduction of CO₂ emissions through greater efficiency.
2.1 Fundamental material properties of III-nitrides

2.1.1 Crystallography of III-nitrides

Like most other semiconductor materials, III-nitrides have tetrahedrally coordinated atomic arrangements that result in either cubic (zincblende) or hexagonal (wurtzite) lattice structures. For AlN, GaN and InN the zincblende structure is metastable while the wurtzite variant is stable and easier to grow. Therefore, most research has been focused on the wurtzite form which, as a consequence, has given better results up to date for optoelectronic applications.

The hexagonal wurtzite unit cell of GaN is illustrated in Fig. 2.2, where the sublattices of gallium and nitrogen atoms are shown in gray and dark, respectively. In hexagonal wurtzite lattice atoms are tetrahedrally bonded to the nearest neighbors. The unit cell is characterized by the lattice parameters \( c \), \( a \), and \( u \), and consists of alternating biatomic closed-packed (0001) planes of Ga and N pairs stacked in an ABAB sequence. The lattice constant \( c \) defines the spacing of two identical hexagonal lattice planes, and the lattice parameter \( a \) describes the distance of atoms in the hexagonal lattice plane. The dimensionless parameter \( u \) characterizes the bond length along the \( c \)-axis, and provides information of the distortion of the unit cell. The other group III-N semiconductors, InN, AlN and their ternary and quaternary compounds have the same crystalline structure, in which group-III atoms occupy the sublattice shown with Ga atoms in Fig. 2.2. Lattice constants \( a \), \( c \), and \( u \) for GaN, InN, AlN are listed in Table 2.1 [1]. The group III nitrides lack an inversion plane perpendicular to the \( c \)-axis, thus the surfaces of the crystals have either a group III element (Al, Ga or In) polarity or an N polarity. This means that the direction of the atomic bonds are different along the [0001] and [0001\( ^\)\)] directions. The polarity of the films has a major effect on both surface properties and on the piezoelectric field of the group-III nitrides. GaN grown on (0001) sapphire by molecular beam epitaxy (MBE) is commonly N-polar, and Metalorganic Chemical Vapor Deposition (MOCVD) grown Ga-polar [4-5]. The polarization properties and the influence of the polarity on the internal fields will be described in more detail in section 2.3.
2.1.2 Electronic Band Structure of III-nitrides

In direct band gap semiconductors the conduction band minimum is located at the same electron wave vector \( k \) value as the valence band maximum. Direct band gap semiconductors are especially important for optoelectronic applications since radiative transitions from conduction band minimum to valence band maximum have a much higher probability than in indirect band gap semiconductors.

Figure 2.3 represents the calculated electronic band structure of hexagonal wurtzite GaN near the fundamental gap at \( k=0 \) in the \( k \)-space. The valence band

\[ \begin{array}{|c|c|c|c|}
\hline
\text{Lattice constant} & \text{GaN} & \text{InN} & \text{AlN} \\
\hline
a \ (Å) & 3.189 & 3.534 & 3.111 \\
\hline
c \ (Å) & 5.185 & 5.718 & 4.978 \\
\hline
u & 0.377 & 0.382 & 0.379 \\
\hline
\end{array} \]

Table 2.1 Lattice constants \( a, c \) and \( u \) for GaN, InN and AlN.

**Fig. 2.2 Hexagonal wurtzite crystal structure of GaN.**

**2.1.2 Electronic Band Structure of III-nitrides**

In direct band gap semiconductors the conduction band minimum is located at the same electron wave vector \( k \) value as the valence band maximum. Direct band gap semiconductors are especially important for optoelectronic applications since radiative transitions from conduction band minimum to valence band maximum have a much higher probability than in indirect band gap semiconductors.

Figure 2.3 represents the calculated electronic band structure of hexagonal wurtzite GaN near the fundamental gap at \( k=0 \) in the \( k \)-space. The valence band
maximum and the conduction band minimum have the same \( k \)-value, and the valence band is split into three different bands (A, B and C) by crystal field and spin orbit coupling. The bands and their corresponding exciton energies \( (E_b) \) are labeled in Fig. 2.3. At room temperature the experimental band gap of GaN is 3.44 eV [6].

\[ \begin{align*}
\text{CBM} & \quad E_c = 18 \text{ meV} \\
E_A^b = E_B^b = 20 \text{ meV} & \quad E_g = 3.504 \text{ eV} \\
\text{VBM} & \quad \Delta E_{AB} = 6 \text{ meV} \\
\Delta E_{BC} = 37 \text{ meV}
\end{align*} \]

*Fig. 2.3 Calculated electronic band structure of hexagonal wurtzite GaN near the point \(-k=0\) [25]. The directions parallel and perpendicular to the c-axis are denoted by \( k|| \) and \( k\perp \), respectively.*

The major advantage of the III-N material system is that by alloying GaN with InN and AlN the band gap of the ternary or quaternary alloy can be tuned continuously from 6.2 eV (pure AlN) to 0.7 eV (pure InN) as shown in Fig. 2.1. Until recently the commonly quoted value for the optical band gap of InN was 1.89 eV, but new measurements have shown evidence of a much smaller band gap between 0.65 and 0.9 eV [7]. The energy range from 6.2 eV to 0.7 eV covers the spectral range from deep UV to infrared. However, as the In or Al content of InGaN and AlGaN films is increased the growth of high quality material becomes more difficult due to the different optimum growth conditions of In and Al containing III-N alloys [8].

In ternary and quaternary compounds the change of the band gap energy with composition can be described by linear interpolation with the inclusion of a bowing parameter \( b \). The bowing parameter represents the magnitude of the second order
correction to the linear dependence. For quaternary In\textsubscript{x}Al\textsubscript{y}Ga\textsubscript{1-x-y}N alloy the energy band gap can be written as [9]

\[ E_g(x, y) = xE_{g,\text{InN}} + yE_{g,\text{AlN}} + (1-x-y)E_{g,\text{GaN}} - b_{\text{Al}}(1-y) - b_{\text{In}}(1-x). \] (2.1)

Where \( b_{\text{Al}} \) and \( b_{\text{In}} \) are the bowing parameters related to Al and In composition, respectively. In-containing alloys are more complex to model, because the bowing parameter \( b_{\text{In}} \) is believed to depend strongly on the In and Al content [9].

### 2.1.3 Epitaxial Growth of GaN and its alloys

Since GaN crystals are currently not available in sufficient size and reasonable cost, thus up to now, heteroepitaxial growth has been a practical necessity and the choice of substrate is critical. Possible substrate materials should have low thermal expansion and lattice mismatch with the grown crystals. Also, they should be unaffected by the growth chemistries (such as NH\textsubscript{3} or H\textsubscript{2}) at high growth temperatures (in excess of 1000°C in some cases). Under these constraints, the most popular substrate materials used currently for hexagonal wurtzite GaN are silicon carbide (SiC) and sapphire (Al\textsubscript{2}O\textsubscript{3}). High quality GaN can be grown on SiC polytypes 4H and 6H. The lattice mismatch of SiC with GaN is only 3.5 %, and SiC substrates have good electrical conductivity. The main drawback of SiC as a substrate is the large difference in thermal expansion coefficient in comparison to that of GaN, which leads to tensile stress in GaN films. Also the cost of 4H and 6H polytype substrates is high. By far the most popular substrate for optoelectronic applications is \( c \)-plane (0001) sapphire. Sapphire substrates have good thermal stability and low cost. The drawbacks of sapphire, the large lattice mismatch with GaN (16 %) and the difference of thermal expansion coefficients of GaN and Al\textsubscript{2}O\textsubscript{3}, can be managed. In table 2.2 the most important material constants of GaN and the substrates 6H-SiC, AlN and sapphire, are given.

The lattice mismatch (16%) between GaN and sapphire, the main substrate for commercial LEDs, resulted in a high density of structural defects. Typical values of threading dislocation density (TDs) in GaN films grown on sapphire are \( \rho \sim 10^8 \text{--} 10^{10} \text{ cm}^{-2} \) which may be further reduced to values \( \rho \sim 5 \times 10^6 \text{--} 10^7 \text{ cm}^{-2} \) using an epitaxial
lateral overgrowth (ELOG) technique or on bulk GaN substrates [10]. For InGaN/GaN MQWs structure, the surface of the GaN barrier located on top of the MQWs is characterized by the presence of pits with inclusions at the center of the pits. As shown in Fig. 2.4, the pits, also known as V-defects, has a shape of an open hexagonal, inverted pyramid that is defined by the six \{10\bar{1}1\} planes [11]. Thus, in cross-section view this defect appears as an open ‘‘V’’. V-defects are believed to have originated from either TD or generated from the stacking mismatch boundaries induced by stacking faults in the InGaN layer due to strain relaxation [11].

![Fig. 2.4 SEM image (top-view) of the typical V-defects terminated by a hexagonal apex in InGaN/GaN QWs.](image)

Densities of about 10⁶ cm⁻² are fatal in conventional III-V semiconductor devices since dislocations act as non-radiative recombination centers in GaN-based devices as well [10]. However, being known for the high efficiencies in blue and green emissions, InGaN QWs’ immunity to the structural defects drew much research attention in the last decade. Till now, it is believed that the luminescence in blue or green LEDs came from the radiative recombination within the In-rich regions, acting as quantum dot (QD)-like structures due to the phase segregation (indium inhomogeneity) in InGaN layers. Phase segregation in InGaN alloys can be
attributed to the low miscibility of InN in GaN [12]. It has been predicted theoretically, and demonstrated experimentally that the QD-like structures confined the carriers not only vertically (along the growth direction) but also laterally so that the diffusion towards the surrounding defects was suppressed [13-14]. In Fig. 2.5, a high-resolution transmission electron microscope (HR-TEM) image reveals QD-like structure in an InGaN QW structure [15].

<table>
<thead>
<tr>
<th>Materials</th>
<th>GaN</th>
<th>AlN</th>
<th>6H-SiC</th>
<th>Sapphire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>a</td>
<td>3.189</td>
<td>3.111</td>
<td>3.081</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>5.185</td>
<td>4.979</td>
<td>15.092</td>
</tr>
<tr>
<td>Thermal expansion coefficient (10^-6K^-1)</td>
<td>a</td>
<td>5.6</td>
<td>4.2</td>
<td>4.2</td>
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<tr>
<td></td>
<td>c</td>
<td>3.2</td>
<td>5.3</td>
<td>4.7</td>
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<tr>
<td>Thermal Conductivity (W cm^-1 K^-1)</td>
<td></td>
<td>2.1</td>
<td>2.9</td>
<td>4.2</td>
</tr>
</tbody>
</table>

*Table 2.2 Lattice constants, thermal expansion coefficients, and thermal conductivity of GaN and the substrates sapphire, AlN, and 6H-SiC.*

*Fig. 2.5 HR-TEM image showing indium inhomogeneity in an InGaN/GaN QWs. On the left is the lattice image, and on the right is the concentration of indium as determined from quantitative analysis of the image on the left [15].*
2.2 Overview of InGaN LED Technologies

$\text{In}_x\text{Ga}_{1-x}\text{N}$ has emerged in the past few years as the most important material for short-wavelength optoelectronics. The successful application of this material in the active layers of LEDs demonstrated convincingly the enormous potential of the group III-nitrides since the development of the first GaN-based p-n junction blue LED in 1991 by Nakamura et al. [16]. The GaN:Si/GaN:Mg LED developed by Nakamura et al. had an output power of 42 $\mu$W and an external quantum efficiency of 0.18% at a forward current of 20 mA. In 1993, Nakamura et al. were involved in the development of the first p-GaN/InGaN/n-GaN double heterostructure blue LED [17]. The active area consisted of a 20 nm $\text{In}_{0.20}\text{Ga}_{0.80}$ layer between the n-type and p-type GaN. These LEDs had an output power of 125 mW and an external quantum efficiency of 0.22% at a forward current of 20 mA. In 1994, Nakamura et al. fabricated the first AlGaN/InGaN/AlGaN double heterostructure [18]. The active area consisted of a 50 nm $\text{In}_{0.06}\text{Ga}_{0.94}$ layer and the LED had an output power of 1500 $\mu$W and an external quantum efficiency of 2.7%. Nakamura further reported the first highly efficient AlGaN/InGaN/AlGaN double heterostructure around 1994 [19]. The LED had 3 mW output power and EQE of 5.4% at a forward current of 20 mA. Increasing the indium mole fraction from 0.06 to 0.19, a blue-green LED was also realized.

The first single quantum well (SQW) InGaN-based LED structure was introduced in late 1994 by Nakamura [20]. It was found that when the $\text{In}_x\text{Ga}_{1-x}\text{N}$ active layer becomes thin, the strain is not relieved by the formation of misfit dislocations thereby improving the crystal quality of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ active layer. The active region of the device consisted of a 2 nm $\text{In}_x\text{Ga}_{1-x}\text{N}$ layer and the indium mole fraction varied between 0.02 and 0.07, which changes the peak wavelength of the InGaN-based SQW LEDs from blue to yellow. The blue SQW InGaN-based LEDs had 4mW output power and an EQE of 7.3% at a forward current of 20 mA. The output power of the yellow and green SQW InGaN-based LEDs was relatively small compared to the blue
LED probably due the large lattice mismatch and hence the poor crystal quality of the In$_x$Ga$_{1-x}$N well layer. A schematic layer structure based on a typical In$_x$Ga$_{1-x}$N quantum well and a photograph of a typical blue InGaN-based LED are shown in Fig. 2.6 and Fig. 2.7, respectively. The actual LED structure, grown on a low-temperature buffer, consists of an n-doped GaN layer, an InGaN/GaN multiple quantum wells (MQWs) active region, an AlGaN electron blocking layer, and a p-doped GaN contact layer. The n-doped GaN layer is typically 2-4 μm thick and doped with silicon. Typical carrier concentration in the n-layer is in the order of 1~5 × 10$^{18}$ cm$^{-3}$. The InGaN QW width is practically limited to a maximum of 5 nm due to the spatial separation of electron and hole wave functions caused by the piezoelectric polarization. The emission wavelength is determined by the concentration of In in the QWs as well as the thickness of the QWs due to the quantum confinement stark effect (QCSE) [21]. In blue LEDs the In content is around 20%, while in green LEDs In content is around 30%. Growth of the MQW stack is problematic because the InGaN QWs need to be grown at temperatures below 900°C, whereas the GaN barriers grown at such temperatures exhibit rough surface morphology which can deteriorate the optical quality of the MQW stack.

The major challenge for InGaN LEDs is the efficiency gap in the green–yellow region of the spectrum. As shown in Fig. 2.8, InGaN LEDs exhibit high EQEs in the violet and blue regions, but longer wavelength devices, achieved by increasing indium content in active region, show a notable drop in efficiency. This efficiency loss could
be attributed to a number of material issues, but the dominant cause is still unclear.

AlGaInP-based LEDs, in contrast, have shown impressive performance in the red region, but lose efficiency at shorter wavelengths. An indirect-bandgap crossover in the green–yellow region provides an explanation for efficiency loss in these AlGaInP alloys, and their improved performance in the green–yellow region is therefore far less likely. Improving LED performance within the “green–yellow gap” is a major focus of SSL research efforts, and a number of approaches are being explored. To attain the long-term SSL performance targets, these efforts will need to achieve high internal quantum efficiencies (IQEs) of $\geq 90\%$ at particular green and yellow wavelengths.

InGaN alloys are generally believed to be the most promising semiconductors for bridging the green–yellow gap. Unlike AlGaInP alloys, they possess a direct energy bandgap across the visible spectrum and present no intrinsic roadblock to high efficiency optical emission. While efficiency clearly drops off in the green region, state-of-the-art InGaN LEDs near 530 nm have now demonstrated 100 lm/W output and 80 lm/W performance at 35 A/cm$^2$, and IQE values have been estimated to be greater than 30% at 50 A/cm$^2$ [24]. These achievements have provided strong
motivation for pushing the limits of high-performance InGaN to longer visible wavelengths. The efficiency loss in the green–yellow region is inextricably linked with the evolution of InGaN material properties with increasing indium content of the alloy. Substantial research over the past decade has revealed InGaN alloys to have a complex array of properties that evolve with indium composition and negatively impact material quality and optical efficiency. The nature of the radiative recombination that occurs in these devices is still under controversy. The emission mechanisms in InGaN-based QW devices are not well understood and the literature reports observations and arguments for two different radiative recombination mechanisms. One is based on piezoelectric fields in the In$_x$Ga$_{1-x}$N layers [22] and the second is based on spatial indium inhomogeneity across the In$_x$Ga$_{1-x}$N layers [23]. The investigation of both the piezoelectric fields and spatial inhomogeneity as potential emission mechanism in InGaN-based MQW devices will be described in detail in Chapter 3.

### 2.3 Major Factors Limiting High-power Operation of InGaN LEDs

#### 2.3.1 Quantum Efficiency Droop in InGaN LEDs

A principal advantage of SSL over traditional lighting technologies is its high energy efficiency. Their efficiency has seen a continual and significant improvement over the last few years. However, InGaN LEDs have been reported to suffer from the substantial reduction of efficiency at the elevated injection current required in practical high brightness applications often dubbed as the “efficiency droop” or “efficiency roll-off”. As the current density is increased beyond the point (10A cm$^{-2}$–50A cm$^{-2}$) at which the maximum injection efficiency is attained a monotonic drop in quantum efficiency is noted especially in blue and green InGaN/GaN QW LEDs, even under short-pulse, low duty cycle and constant temperature injection as well as continuous wave (CW) conditions. This efficiency droop phenomenon is observed across a broad wavelength spectrum of InGaN/GaN LEDs [26-27] and also with deep ultraviolet (UV) AlGaN/AlN LEDs [28-29] (see Fig. 2.9). In order for
LEDs to be used in general lighting applications and pave the way for energy reduced consumption, it is imperative for them to produce high luminous fluxes, which necessitate high current levels, with high efficiencies. However, to date, there is still a lack of consensus about the main mechanism responsible for the high-current efficiency drop in blue and green LEDs. Many models have been proposed to explain the efficiency droop. Among them are inefficient carrier injection due to electron leakage [30-31], carrier delocalization from In-rich regions [32-33], piezoelectric polarization causing electron-hole separation [34], and Auger nonradiative recombination which dominates at high carrier densities [35].

![Normalized External Quantum Efficiency of UV, near UV, blue, and green LEDs as a function of operating current in continuous wave.](image)

**Fig. 2.9** Normalized External quantum efficiency of UV, near UV, blue, and green LEDs as a function of operating current in continuous wave.

### 2.3.2 Droop Mechanisms

#### 2.3.2.1 Auger Recombination

Auger non-radiative recombination transfer the excess electron energy released to another carrier rather than a photon. In case of Auger recombination, these other carriers are electrons or holes that are excited into higher energy levels within the same band (see Fig. 2.10). The probability of Auger process decreases significantly
with increasing energy band gap and it is generally considered negligible in wide-gap materials.

![Diagram of energy bands]

Fig. 2.10 Schematic illustration of intraband Auger recombination (k – electron wavevector).

Auger recombination on the efficiency droop is typically analyzed by the formula

\[ \eta_{IQE} = \frac{Bn^2}{(An+Bs^2+Cn^3)} \]  (2.2)

where \( A \) (s\(^{-1}\)), \( B \) (cm\(^3\) s\(^{-1}\)), and \( C \) (cm\(^6\) s\(^{-1}\)) are the Shockley-Read-Hall nonradiative recombination, the radiative recombination, and the Auger nonradiative recombination coefficients, respectively. Figure 2.11 plots the results for different sets of parameters. Only Auger parameters of \( 10^{-31} \) cm\(^6\) s\(^{-1}\) or higher values induce severe efficiency droop [36].

Several theoretical groups calculated the III-nitride Auger coefficient directly. Hader et al. [37] used a microscopic many-body model and a relatively simple \( kp \) bandstructure model to study radiative and Auger recombination in InGaN QWs. They extracted a very small coefficient of \( C=3.5\times10^{-34} \) cm\(^6\) s\(^{-1}\) for the direct band-to-band Auger process. An extension of this model to phonon-assisted Auger recombination did not indicate any relevant influence of Auger recombination on the efficiency droop [38]. Furthermore, if an inherent process such as Auger
recombination were solely responsible for the efficiency droop, already available laser action with required high injection level, would not have been feasible.

2.3.2.2 Polarization Effects and Electron Leakage

One factor that has long been thought to limit the efficiency of InGaN materials is the strong polarization effects that arise from their wurtzite crystal structure. In particular, piezoelectric and spontaneous polarization along the polar [0 0 0 1] (c-axis) crystal direction leads to large (>1 MV/cm) electrostatic fields in the quantum well (QW) active regions of InGaN LEDs. As shown in Fig. 2.12, these substantial electric fields pull the electrons and holes towards opposite sides in quantum wells, resulting in the reduced overlap between wave functions. The reduced overlap adversely affects GaN-based optical devices in 2 ways: i) decreasing the radiative recombination efficiencies; ii) shifting the emission to longer wavelengths (read-shift) as a result of Quantum Stark Confinement Effect (QCSE) [39].

Fig. 2.11 IQE plots with different Auger parameters [36].
Coexisting with the Auger recombination theory is a second hypothesis that more directly attributes droop to electron leakage induced by the energy barrier reduction by built-in polarization [40]. With the typical Ga-polar growth of nitride LEDs, the polarization charges at the MQW–EBL interface are positive, which leads to electron accumulation at this interface and strong negative band bending. Figure 2.13 shows the substantial modification of InGaN LED bandstructure due to interfacial polarization charges and related internal fields (occurring for polar crystal orientations as discussed in the previous section). Triangular band profiles of QWs and barriers as well as a reduced effective bandgap of electron block layers on the p-side of the device are all manifestations of these strong polarization effects, which may lead to ineffective hole injection into the active region and electron leakage out of the active region; The cause and effect relationship of these phenomena at high injection currents—whether poor hole injection drives increased electron leakage or whether electron leakage further limits hole injection—is not entirely clear, but both effects may contribute to reduced radiative recombination in the active region at high current densities [40].

Fig.2.12 Schematic illustration of the energy bands of an InGaN/GaN QW a) without polarization effects and b) in the presence of spontaneous $P_{sp}$ and piezoelectric $P_{pe}$ polarization.
2.3.2.3 Carrier Overflow

The flow of electrons beyond the QWs is a common problem in InGaN LEDs and it is a reason for the typical application of an AlGaN electron blocker layer (EBL) on the p-side of the MQW active region. However, the EBL isn't often able to completely stop electron leakage in InGaN LEDs, as shown in Fig. 2.14. Several publications suspected electron leakage over the EBL to be related to the LED efficiency droop [41-42].

However, earlier numerical LED device simulations did not show an efficiency droop despite the inclusion of electron leakage current [43]. The main reason for the missing efficiency droop was the high band offset ratio of $\Delta Ec/\Delta Ev = 70:30$ assumed for nitride semiconductors, therefore, the theoretically calculated EBL energy barrier was too high to allow for sufficient electron leakage. Numerical LED simulations were able to link electron leakage to efficiency droop only after reducing the AlGaN...
In GaN, the heavy hole has an effective mass of about 1.4 times that of an electron in a vacuum \((m_0)\), but the electron effective mass is \(\sim 0.2m_0\). As seen in Fig. 2.15, low hole mobility and large hole confinement energies might lead to nonuniform hole distribution across the QWs in InGaN LEDs, and primarily population of the QW closest to the p-side of the junction [46]. Such a build-up of carriers in an ultrathin (~2.5 nm) QW translates to fairly high carrier densities of \(>10^{18} \text{ cm}^{-3}\) at currents as low as 50 mA in standard high-power LEDs. Furthermore, The absence of the efficiency droop in photo excitation experiments where carriers are only photogenerated in the QWs with generation rates orders of magnitude larger than those encountered in high electrical injection levels indicates that the efficiency droop is also likely related to the unbalanced carrier injection (due to the disparity of hole and electron concentrations on the p-side and n-side, respectively), poor hole transport, and carrier or current overflow associated with the lighter and more abundant electrons [46]. By employing p-type-doped barriers or a lightly n-type-doped GaN injection layer just underneath the InGaN multiple quantum wells (MQWs) on the n side, in order to bring electron and hole injection to balanced levels, better efficiency retention has been observed at higher current levels [46], above 1100 A/cm². These results suggest that poor transport through the barriers in the QW region due to large hole effective mass and low hole concentration (limited by P type doping) leads to serious electron overflow in the active region and represents perhaps one of the main mechanisms responsible for the observed efficiency degradation.
InGaN LEDs employ MOW structures, where the active region is bounded on both sides by higher band-gap materials, are expected to yield more efficient light extraction. The external quantum efficiency of LED device is determined not only by the internal quantum efficiency (probability of conversion of electrons and holes into photons) but also by the probability that a photon emitted from the active layer will escape from the high-index compound semiconductor material into the lower index surrounding material. The internal quantum efficiency is a measure of the fraction of photons generated by each injected electron inside the active layer of the LED. Therefore, the total (external) quantum efficiency $\eta_{EQE}$ is usually split up into the internal quantum efficiency $\eta_{IQE}$ and the optical extraction efficiency $\eta_{EXE}$

$$\eta_{EQE} = \eta_{IQE} \times \eta_{EXE} \quad (2.3)$$

Where $\eta_{EXE}$ is given by

$$\eta_{EXE} = \eta_A \times \eta_F \times \eta_c \quad (2.4)$$

**Fig.2.15 Model calculation of energy band and hole concentration distribution for MQWs with 12nm (a) and 3nm (b) barriers [46].**
and where $\eta_A$ is the absorption efficiency, $\eta_F$ is the Fresnel loss efficiency, and $\eta_c$ is the critical-loss efficiency.

The contribution to the loss associated with the reflection at the semiconductor/air interface is called the Fresnel loss. When light passes from a medium of refractive index $n_2$, which is the active layer, to a medium with the refractive index $n_1$, being air in this case, a portion of the radiation is reflected at the interface. Assuming smooth interface, this loss is given in the case of normal incidence by

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2 \quad (2.5)$$

The Fresnel-loss efficiency can thus be defined as $\eta_F = (1 - R)$ representing the fraction of photons escaping the semiconductor surface. We should keep in mind that the surface can be roughened and/or epoxy dome can be placed to increase this efficiency.

As seen in Fig. 2.16, photons incident on the air/semiconductor interface from the semiconductor side at an angle larger than the critical angle $\theta_c$ suffer total internal reflection (TIR). By Snell’s Law, $n_1 \sin \theta_1 = n_2 \sin \theta_2$, this critical angle, assuming smooth interface, the critical angle is given by:

$$\theta_c = \sin^{-1}\left(\frac{n_1}{n_2}\right) \quad (2.6)$$

The area of the escape cone, therefore, can be expressed as:

$$A_{\text{escape}} = 2\pi r^2 \left(1 - \cos \theta_c\right) \quad (2.7)$$

Under spontaneous emission and statistic average approaches, in the case of $n_2 \gg n_1$ the ratio of light escaping from the top surface of the LED can be calculated by

$$\frac{P_{\text{escape}}}{P_{\text{source}}} = \frac{(1 - \cos \theta_c)}{2} \left(1 - R\right) \approx \frac{\theta_c^2}{4} = \frac{(n_1/n_2)^2}{4} \quad (2.8)$$
Just as with conventional III–V LEDs, light trapping inside LED chips is a primary limitation for producing efficient GaN-based LEDs. As shown in Fig. 2.17, the refractive index of GaN is ~2.4-2.5 at blue wavelengths, much larger than that of sapphire ($n = 1.6$) and air ($n = 1.0$), the solid angle spanned by each extraction cone corresponds to 4% of the total solid angle, limiting the light extraction to 24% at best. A large portion of the generated light is trapped and rattles around until it is absorbed by the semiconductor, substrate or contact metals. Based on ray-tracing simulation, we have found that the extraction efficiency of a planar blue LED on sapphire is about 12% without encapsulation, and about 27% with epoxy encapsulation.

![Fig. 2.16 Definition of the escape cone by the critical angle $\theta_c$.][47]

![Fig. 2.17 Schematic illustration of a GaN-Based LED model. The light ray in the LED is classified into three modes: surface mode, waveguide mode and substrate mode.][48]
2.4 References


[38] S. Koch, private communication
CHAPTER 3
Investigation of the non-thermal Mechanism of Efficiency Droop in InGaN LEDs

3.1 Introduction

White light sources based on III-Nitride light-emitting diodes (LEDs) hold significant promise for general illumination [1-3]. To compete with fluorescent and other conventional lighting sources, it is essential to develop high-efficiency LED packages operating at high current densities [3]. However, the state-of-the-art InGaN-based LEDs are not suitable for high-current operation as they suffer a significant drop in quantum efficiency at high injection level [4-10]. As described in detail in Section 2.4.1., Efficiency droop is often observed for commercially available blue and green LEDs, with quantum efficiency peaking at < 20 A/cm². This behavior is even seen in LEDs driven with short and low-duty cycle pulses, when thermal effects due to self-heating are suppressed [8,9].

Understanding the underlying nonthermal mechanism of the efficiency droop in quantum efficiency at high currents is of high interest from the viewpoint of material physics as well as technological implications for solid-state lighting. Different mechanisms have been suggested to account for the efficiency droop behavior of InGaN LEDs, including inefficient carrier injection due to electron leakage [4,5], carrier delocalization from In-rich regions [6-8], piezoelectric polarization causing electron-hole separation [9], and Auger nonradiative recombination which dominates at high carrier densities [10]. However, to date, there is still a lack of consensus about the main mechanism responsible for the high-current efficiency drop in blue and green LEDs.

In this work, we compare the current-dependent electroluminescence (EL) of InGaN-based green, blue, near-UV and UV LEDs, which differ from each other mainly in the In mole fraction in the active region. Self-heating is minimized by pulsing the LEDs with small duty cycles, allowing us to investigate the nonthermal
effects on the optical characteristics of the LEDs at elevated injection currents.

3.2 Experimental details

All the LEDs were grown on (0001) sapphire substrates with a low-temperature GaN buffer layer using metalorganic chemical vapor deposition. A schematic of the general structure is shown in Fig. 3.1. The structures of the green, blue and near-UV LEDs consisted of a 2.5 μm Si-doped n-GaN layer (n~5x10^{18} cm^{-3}), a multiple-quantum-well (MQW) active region comprising 10 pairs of undoped InGaN well (~3 nm) and Si-doped GaN barrier layers (~10 nm), a 0.05 μm p-type AlGaN electron-blocking layer and a 0.2 μm p-GaN contact layer (Mg concentration ~1x10^{19} cm^{-3}). The respective nominal indium mole fractions in the MQWs were 0.30, 0.17 and 0.09 for the green, blue and near-UV LEDs. The UV LED had 5 pairs of AlInGaN QWs with a small amount of In (1-2%), sandwiched between n- and p-type AlGaN carrier-confining layers. LEDs with a size of 300×300 μm^2 were fabricated using a standard fabrication technology. First, part of the p-type layers was etched to form mesas by inductively coupled plasma etching. Ti/Al/Ti/Au and thin Ni/Au were then deposited on the exposed n-type and p-type layers, respectively, followed by an annealing in air at 550 °C to form ohmic contacts. Finally, a 0.2 μm-thick layer of sputtered SiO_2 was deposited to protect the mesa sidewalls.

![Fig.3.1 Schematic of the structure for the green, blue and near-UV LEDs.](image-url)
The electrical characteristics of the LEDs were measured at room temperature using an Agilent 4156C semiconductor parameter analyzer. The EL intensity and spectra of the LEDs were recorded using an Ocean Optics fiber-optic spectrometer under both continuous wave (CW) and pulsed operation with the injection current ranging from $10^{-4}$-0.7 A. For the pulsed characterization, the frequency was fixed at 1 kHz, whereas the duty cycle was varied from 0.1% to 2%. The short pulses, in the range of 1-20 μs, significantly reduced the average injection power, and therefore largely eliminated any thermal effects caused by self-heating on the LED characteristics. As shown in Fig. 3.1, the room-temperature peak energies of the LEDs at 20 mA were 2.39 eV (green), 2.63 eV (blue), 3.03 eV (near-UV) and 3.36 eV (UV). Listed in Table 3.1., the CW radiative powers of unencapsulated chips measured at 20 mA in an integrating sphere were 2.1 mW, 3.0 mW, 1.5 mW, and 0.35 mW for the green, blue, near-UV and UV LEDs, respectively, corresponding to external quantum efficiencies (EQE) in the range of 0.5%-6%.

![Fig. 3.1 Measured peak energy of UV, near-UV, blue, and green LEDs at room temperature.](image-url)
3.3 Results and Discussion

Figure 3.3 shows the I-V characteristics of the LEDs. The forward voltages at 20 mA of the visible LEDs are comparable, in the range of 3.4-3.6 V, whereas it is much higher (~4.8 V) for the UV LED. It is clear that a significant portion of the voltage applied to the UV LED drops across the AlGaN cladding layers, which are less conductive than the GaN layers in the visible LEDs. On semilogarithmic scale, the forward currents of all the LEDs in the intermediate injection regime can be described by $I = I_0 \exp(eV/E)$, and the extracted ideality factors are >2, indicating dominant defect-assisted tunneling currents as observed in typical nitride LEDs on foreign substrates [11].

![Forward I-V characteristics of the InGaN-based LEDs at room temperature.](image-url)

Table 3.1 Indium contents, radiative powers, forward voltage at 20mA of UV, near-UV, blue, and green LEDs.

<table>
<thead>
<tr>
<th>LEDs</th>
<th>Green</th>
<th>Blue</th>
<th>Near-UV</th>
<th>UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>In %</td>
<td>0.30</td>
<td>0.17</td>
<td>0.09</td>
<td>0.01~0.02</td>
</tr>
<tr>
<td>Radiative Powers (mW)</td>
<td>2.1</td>
<td>3.0</td>
<td>1.5</td>
<td>0.35</td>
</tr>
<tr>
<td>Vf (V) @20 mA</td>
<td>3.4</td>
<td>3.6</td>
<td>3.3</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Figure 3.4 illustrates the EL spectra of the near-UV LED at increasing CW and pulsed currents. In CW mode, the peak is initially located \( \sim 3.0 \) eV and shows little shift with increasing current until the current reaches 100 mA, after which it exhibits a noticeable red shift due to self-heating effects. In pulse mode, the LED was driven up to 700 mA, corresponding to a current density of \( \sim 1 \) kA/cm\(^2\). The peak energy is nearly constant over the entire current range. The absence of temperature-induced red shift suggests that self-heating is substantially suppressed. The full width at half maximum (FWHM) of the spectra increases slightly with increasing current, from 0.10-0.12 eV.

![EL spectra for the near-UV LED with increasing CW current (left) and pulsed current with a duty cycle of 1% (right). The spectra are shifted in the vertical direction for clarity.](image)

Similar data for the green LED is shown in Figure 3.5. Under CW operation, a large blue shift \( \sim 80 \) meV of the emission peak is seen as the current varies from 0.1 mA to 200 mA. As the injection current is further increased, the peak shifts toward the lower energy due to self-heating. The large current-induced blue shift of EL is one characteristic feature of InGaN-based green and blue LEDs with relatively high In mole fractions in the active regions [12]. It occurs because of band filling of localized states resulting from the compositional or thickness fluctuation of InGaN QWs. Screening of the piezoelectric field in the QWs by the injected carriers would also
lead to a blue shift of the emission peak. However, the absence of noticeable blue shift in the near-UV LED (see Fig.2), suggests that (i) the influence of piezoelectric field is minimal, due presumably to effective screening by Si doping in the barrier layers [13,14]. (ii) much weaker localization effects in the near-UV LED due to improved composition homogeneity and thickness uniformity of the low-In InGaN active layers.

Under pulsed operation, the green spectra exhibit a monotonic blue shift over the entire current range, up to a maximum amount of ~106 meV, indicating negligible self-heating in pulse mode. Another interesting feature in Fig. 3 is that the FWHM also appears to be a strong function of the injection current. A spectrum broadening by a factor of 2 is the further evidence of band filling.

Figure 3.6 depicts the peak energies of the near-UV and green LEDs as a function of CW current and pulsed current for different duty cycles. The peak shift of the near-UV LED over the entire current range is minimal (~10 meV) under pulsed injection for all duty cycles, whereas CW injection above 200 mA leads to significant amount of red shift. Similar peak energy evolution has been observed for the UV LED. In contrast, the EL peaks of the blue and green LEDs show a large amount of blue shift with increasing injection current, as shown in Fig. 4 (bottom). Particularly as
current is increased from 0.1 to 100 mA, a pronounced 76 meV blue shift is seen for the green LED. While the peak shift for 2% duty cycle saturates at >400 mA, due likely to thermal effects, the blue shift trend continues up to 700 mA for duty cycles of 0.1%-1%, indicating that self-heating is largely eliminated in the LED when pulsed with duty cycles below 1%. We have found that the total amount of peak shift decreases as the In content in the active region decreases. The blue shift of the peak energy at 700 mA with respect to the value at 1 mA are 106 meV, 75 meV and 14 meV for the green, blue and near-UV LEDs, respectively.

Figure 3.7 shows the normalized EQE –current (η-I) characteristics of the near-UV and green LEDs under CW and pulsed operation. For the near-UV LED, the EQE in CW mode peaks at ~30 mA, and then decreases rapidly with increasing current. It drops to 50% at ~230 mA. The EQE in pulse mode also peaks at ~30 mA, but then decreases at a moderate rate. The discrepancy can be attributed to severe self-heating at high CW currents. Again, the fact that the η-I curves for different duty cycles are almost identical is indicative of the elimination of self-heating under pulsed
injection. Therefore, the observed EQE droop of the pulsed LED is caused solely by a nonthermal mechanism. The bottom part of Fig. 5 illustrates the current-dependent EQE of the green LED. The efficiency exhibits a similar droop behavior. However, the EQE reaches the maximum at a much lower current and drops with a much steeper slope compared to the case for the near-UV LED. The characteristic current which marks the peak EQE is as low as ~1 mA (1.4 A/cm²), underscoring the fact that a nonthermal mechanism is responsible for the efficiency droop.

The light output-current ($L-I$) characteristics of all four LEDs pulsed with a duty cycle of 0.1% are shown in Fig. 3.8. As discussed above, the thermal effects are essentially negligible under this injection condition. The blue LED is the most efficient. Its $L-I$ curve is linear at low currents, but becomes sublinear at high currents, indicating a reduced EQE. Similar behaviors are seen for the green and near-UV LEDs, in contrast to the linear $L-I$ characteristics of the UV LED over the entire injection range. While the green LED outperforms the near-UV LED below 50 mA, it is less bright at higher currents due to more severe efficiency droop.
Figure 3.9 compares the vastly different $\eta$-$I$ characteristics of all four LEDs pulsed with a duty cycle of 0.1%. Except the UV-LED, all other LEDs suffer a droop in EQE as current exceeds a characteristic current. There are two important features in the data, evidencing the different extents of nonthermal effects in the LEDs: (i) the characteristic current increases with decreasing emission wavelength or the In content in the active region. It ranges from 1 mA for the green LED to 5 mA for the blue LED to 30 mA for the near-UV LED. (ii) The efficiency decrease after the droop is increasingly dramatic with increasing In content in the InGaN QWs. Particularly for the green and blue LEDs, the normalized EQE drops to 50% at 200 mA and 600 mA respectively. These LEDs are not suitable for high-power operation since most input power is converted into heat rather than light at elevated currents. In contrast, for the UV LED, the EQE reaches the maximum at ~300 mA, and remains nearly constant as current are further increased. As mentioned earlier, different mechanisms have been proposed to explain the efficiency droop behavior of blue and green LEDs. Since the LEDs studied in this work have similar material quality and device structures, the difference in the current injection process should be small, and is unlikely the cause for the remarkably different $\eta$-$I$ characteristics. Auger recombination rate is proportional to $C n^3$ (C is Auger recombination coefficient and n is carrier density).
It is therefore expected that the influence of the Auger process will increase with increasing injection current and become dominant at high currents. Given the reported values of C on the order of $\sim 10^{-30} \text{cm}^6 \text{s}^{-1}$ [10], the efficiency drop in the LEDs, which starts at a current density as low as 1.4 A/cm$^2$, may not be attributed to Auger nonradiative recombination. If the droop behaviors indeed arise from Auger processes, our results would suggest that C of nitride alloys is a strong function of In content, contradicting the finding in ref 10. Finally, we can also rule out piezoelectric polarization, which separates electron-hole pairs and thus lowers radiative recombination rates, as the main cause for the efficiency droop. As pointed out earlier, polarization-induced charges at the QW/barrier interfaces may be effectively screened by free electrons from Si doping in the GaN barrier layers, as evidenced by the minimal peak shift in the near-UV LED. The polarization-induced electric field is further screened by the injected carriers in the QWs. Therefore, its influence, if exists, would tend to diminish as the injection level is increased. At 700 mA, the sheet carrier density is estimated to be $\sim 6 \times 10^{12} \text{cm}^{-2}$, sufficient to counteract all the influence of piezoelectric polarization on the $\eta$-$I$ characteristics [14].

Our results can be interpreted as evidence of current overflow from localized states being the underlying nonthermal mechanism of the efficiency droop. In blue and green LEDs, radiative recombination of carriers at localized states plays an important role in light emission. As current injection is increased, electrons will be

![Figure 3.9 Normalized EQE of the green, blue, near-UV and UV LEDs.](image)
released to the conduction band due to filling up of the localized state band. The electrons can thus be captured by defects and recombine nonradiatively with injected holes, leading to a reduction in EQE. This conclusion is supported by the fact that the decrease in EQE of the green LED seen in Fig. 3.7 is accompanied by a monotonic peak blue shift and spectrum broadening up to 700 mA, both indicative of band-filling of localized states. Since all the LEDs were grown on sapphire substrates, the densities of threading dislocations are on the same order ~10^{9} \text{ cm}^{-2}. However, as the In content increases, the material quality of InGaN degrades considerably. The existence of other types of microstructural defects which can be readily reached by the overflowed carriers may explain the extreme low characteristic current density and sharp decrease in EQE of the green LED. On the other hand, the radiative recombination in the UV LED is dominated by band-to-band transition due to the lack of localization effects [15], consistent with the absence of current-induced peak blue shift. Therefore, its performance is affected by defects even at low currents. As expected, it has lower EQE at low injection level, but suffers minimal efficiency decrease at high currents.

### 3.4. Summary

In summary, InGaN-based LEDs with peak emission ranging from green to UV are characterized under CW and pulsed operation. High-current droop in the quantum efficiency is observed for all the visible LEDs pulsed with a duty cycle below 1%. The efficiency of the blue and green LEDs peaks at a current density as low as 1.4 A/cm^{2}, and drops dramatically as the injection current is increased. A monotonic blue shift of the peak energy with increasing current is seen up to ~1 kA/cm^{2}. In contrast, the UV-LED has a peak energy nearly independent of the injection current and a constant quantum efficiency at high injection conditions. These results support the argument that current overflow from localized states is the major nonthermal mechanism underlying the observed efficiency droop of the InGaN LEDs. Defect reduction, in the InGaN active layers in particular, is therefore crucial for developing efficient SSL sources operating under high current conditions.
3.5 References


CHAPTER 4
Study of efficiency droop in green LEDs on bulk GaN substrates

4.1. Growth of green LEDs on Bulk GaN Substrates

The desire to further improve device performance drove people to grow III-nitride films on native GaN substrates. Most of the commercially available nitride-based devices are grown on sapphire or SiC substrates. The mismatches in lattice constants and thermal expansion coefficients between the substrates and the epitaxial films manifest itself as a high density of threading dislocations and residual biaxial stress in the device structures [1-2]. Compared with those built on sapphire, devices fabricated homoepitaxially on GaN substrates have exhibited superior performances [3-4]. Due to the scalability and the high growth rates (up to several hundred microns per hour), hydride vapor phase epitaxy (HVPE) is currently one of the most promising techniques to produce bulk GaN substrates. The development of bulk GaN is still in the early stage, and several critical problems remain to be resolved. Difficulty in obtaining large-size substrates is one of the main challenges. Currently, 2-inch free standing GaN substrates are only available for mass production by growing bulk GaN on GaAs substrates by HVPE and remove the GaAs substrates by aqua regia [5].

The growth procedure for nitride devices can be significantly simplified as the homoepitaxy process does not require additional steps, such as surface nitridation and low temperature buffer growth. The defects, impurities, and stress in the epilayers would be greatly reduced, leading to improved performance, yields, and scalability to larger substrates. Devices may further take advantages of the high thermal and electrical conductivity of GaN substrates. In this work, InGaN/GaN MQWs green LEDs are grown on sapphire and bulk GaN substrates. The structural, electrical and optical properties of the LEDs are compared so as to further shed light on the role of dislocations and the physical origin of QE droop behaviors.
The 300 µm thick free-standing GaN substrates were produced using HVPE. Atomic force microscopy (AFM) measurements showed that the density of threading dislocations, which were decorated by etch pits, was \( \sim 10^7 \text{ cm}^{-2} \). The Green LED structures investigated in this study were grown on c-plane sapphire and the Ga-face of the GaN substrates using metalorganic chemical vapor deposition (MOCVD) by Invenlux, Inc. Prior to the LED growth, a 100 nm GaN was first deposited on sapphire as a buffer layer. The LED structure consisted of a 2 µm n-GaN layer (Si\textasciitilde5x10^{18}\text{ cm}^{-3}), a 10-period InGaN/GaN MQW active region with 3 nm QWs and 12 nm doped quantum barriers, a 0.05 µm p-type AlGaN cladding layer and a 0.3 µm p-GaN contact layer (Mg \textasciitilde2x10^{19} \text{ cm}^{-3}). The nominal indium mole fraction in the active regions was \( \sim 0.27 \). AFM images of the LED epilayers over a 5 µm x 5 µm area is illustrated in Fig. 4.1. V-defects with a size of 50-200 nm and a density of \( \sim 1-3 \times 10^7 \)
cm$^2$ are seen in the LED on sapphire. Most of the V-defects originate from the intersection of dislocations with InGaN QW layers, where large strain promotes their formation [6-7]. In contrast, the LED on GaN is free of surface pits, and a terrace-step structure is clearly seen, suggesting that smooth 2D step-flow growth was achieved despite a high-In content in the MQWs. Cross-sectional Transmission Electron Microscopy (TEM) measurements in Fig 4.2 showed that the density of threading dislocations reaching the active region in the LED on sapphire was $\sim1 \times 10^9$ cm$^{-2}$, whereas it is much lower in the homoepitaxial LED and is expected to be similar to that in the GaN substrate [4]. The root-mean-square roughnesses of the LEDs on sapphire and GaN are 1.4 nm and 0.5 nm, respectively.

4.2. Fabrication of green LEDs on bulk GaN

In order to compete with fluorescent and other conventional lighting sources, it is essential that the cost of LEDs is further reduced and their efficiency is improved. One way to meet the cost and performance targets is to drive LEDs at much higher current densities without compromising emission efficiency and operating lifetime [8]. III–nitride LEDs grown and fabricated on sapphire are not suitable for high-power operation for several reasons. First, LEDs grown on sapphire contain a high density of threading dislocations, which may accelerate device degradation particularly at high currents. Second, due to the insulating substrate, LEDs on sapphire are normally fabricated in a lateral device configuration. Mismatch between the n-type and p-type current spreading layers may cause severe current crowding and localized self-heating [9]. Finally, sapphire has a rather poor thermal conductivity, limiting heat dissipation and, therefore, the maximum operational temperature and power. Homoepitaxial LEDs would overcome all these drawbacks. High material quality, along with the good thermal and electrical conductivity of the substrate, makes homoepitaxial LEDs more suitable for high current and high-temperature operations.

To examine the impact of device geometry on high-current performance, 300 μm × 300 μm top-emitting green LEDs with both lateral and vertical structures were fabricated on HVPE GaN using standard photolithography and dry etch techniques. A
thin NiO$_x$/Au was used as the semitransparent p-type Ohmic contact, whereas Ti/Al/Ti/Au was used as the n-type metallization. The top contact pattern and schematic cross-section of the LEDs are shown in Fig. 4.2. Some p-type finger projections were added to the bondpad to alleviate current crowding by reducing the current spreading distance. The vertical LED has an emitting area ~20% larger than the lateral LED because the mesa structure is not needed. The lateral device has a conventional asymmetric structure similar to the LED fabricated on sapphire. The vertical LED on GaN has a symmetric structure and contact geometry similar to conventional AlInGaP LEDs grown on conductive GaAs. Current spreads uniformly under the p-type bondpad metal. By adding the cross-shaped fingers, lateral current paths in the transparent contact are considerably reduced, leading to a nearly uniform current distribution and light emission.

Fig.4.2 The schematic cross-section (left) and microphotographs (right) of vertical green LEDs on GaN and lateral LEDs on Sapphire.
4.3. Comparison of droop behaviors of green LEDs on Sapphire and GaN

The optical characteristics of the LEDs were measured using a silicon photodiode-array fiber-optic spectrometer under both continuous wave (CW) and pulsed operation with the injection current ranging from $10^{-6}$-0.6 A. Self-heating in the LEDs was substantially reduced during the pulsed characterization, where a frequency of 1 kHz and a duty cycle of 1% were used.

Figure 4.3 compares the current-voltage (I-V) characteristics of the LEDs. The junction leakage currents in the LED on GaN at reverse bias and low forward bias are dramatically reduced by more than two orders of magnitude compared to those in the LED on sapphire. This correlates well with the reduced dislocation density in the LED grown on GaN. An ideality factor of 2.12 can be extracted from the intermediate section of the forward I-V curve of the LED on GaN, suggesting that the injection currents in this regime are mainly recombination currents. This is in contrast to the dominant defect-assisted tunneling currents in the LED on sapphire [4].

![Typical I-V characteristics of green LEDs grown on sapphire and GaN substrates.](image)

Figure 4.4 shows the electroluminescence (EL) spectra of the LEDs at increasing pulsed currents from 0.1-300 mA. The presence of Fabry-Perot interference fringes is
a characteristic feature for LEDs grown on sapphire. As expected, they are absent in the LED on GaN. The peak wavelengths of the two LEDs at 20 mA are almost identical ~520 nm. The spectra exhibit a monotonic blue shift with increasing injection current. Up to 600 mA (850 A/cm$^2$), the maximum current applied to the LEDs, the blue shift is ~107 meV. The current-induced blue shift, accompanied by a significant spectrum broadening, occurs mainly due to band filling of localized states originating from compositional fluctuation of InGaN alloys. The similar amounts of peak shift and alloy broadening suggest approximately the same degree of InGaN compositional fluctuation despite very different growth modes on two different substrates.

Figure 4.5 (a) presents the L-I characteristics of the LEDs measured in pulse mode. Green light emission can be easily detected from the LED on GaN at currents below 1 μA due to low junction leakage. Below 0.1 mA, it significantly outperforms the LED on sapphire. However, the dependence of light intensity on current is superlinear, suggesting a significant influence of junction leakage and nonradiative recombination of injected carriers at low bias. Above 0.1 mA, the L-I curve is nearly linear on a
log-log scale as the injection efficiency approaches unity and radiative recombination becomes dominant. The light intensity of the LED on sapphire increases rapidly and reaches the linear regime at ~2 mA. At 10 mA, the LED on sapphire is actually 30\% brighter than the LED on GaN. Ray-tracing simulation showed that the former has a higher chip-to-air extraction efficiency (by 28\%) due to the smaller refractive index and higher transparency of sapphire compared to HVPE GaN. The internal quantum efficiencies (IQE) of the two LEDs at 10 mA are therefore comparable. This finding is consistent with our previous study of blue LEDs grown on bulk GaN [4], and further corroborates the conclusion that dislocations play a minor role in light emission of green LEDs due to strong carrier localization effects.

![Fig.4.5](image_url) Fig.4.5 (a) L-I characteristics of green LEDs on a log-log scale. (b) Normalized IQE of green LEDs as a function of pulsed injection current (duty cycle = 1\%).

Figure 4.5 (b) compares the normalized EQE of the LEDs as a function of pulsed current. The EQE of both LEDs rises rapidly with increasing current and rolls off as current exceeds a characteristic current. The peak EQE of the LED on GaN is ~33\% higher. Using calculated light extraction efficiencies, the IQE is found to be ~ 65\%, which is 71\% higher than that of the LED on sapphire. It is striking that the EQE of the LED on GaN peaks at 0.2 mA (~0.3A/cm²), which is one order of magnitude lower than that in the LED on sapphire as well as typical commercial green LEDs.
The EQE decreases rapidly and continuously with increasing current, by 50% at 10 mA. This is in sharp contrast to the characteristics of UV LEDs, which attain a saturated efficiency at elevated currents [10-12]. Despite better material quality, the LED on GaN exhibits even more rapid efficiency droop. This confirms that nonradiative recombination at dislocations is not the physical origin of this unusual behavior. Since the droop occurs at such a low current (~0.3 A/cm$^2$) and a low bias (~2.4 V), it is plausible that neither Auger nanradiative recombination [13] nor electron over-injection enhanced by polarization fields [14] plays a significant role.

The above results agree well with our previous studies which led to a conclusion that current overflow from localized states and lost at misfit defects in the MQWs is the underlying mechanism of the efficiency droop in InGaN LEDs. The extremely small characteristic current, which marks the onset of EQE droop in the green LED on GaN, is believed to be the combined result of efficient carrier injection at low bias and significant delocalization at high currents. In the low injection regime, there are three current components [15]: leakage current $I_L$, radiative recombination current $I_R$, and nonradiative recombination current $I_{NR}$. The shunt leakage paths in the LEDs include dislocations and deep-level traps outside the active region. $I_R + I_{NR} = I_{inj}$ represents the total current injected into the active region. If the shunt resistance is $R_L$, $I_{inj}$ can also be written as:

$$I_{inj} = I - I_L = I - \frac{V}{R_L}$$ \hspace{1cm} (4.3.1)

The EL efficiency is given by:

$$\eta = \frac{I_R}{I} = \frac{I_{inj}}{I} \frac{I_R}{I_R + I_{NR}} = \eta_{inj} \frac{1}{1 + \beta}$$ \hspace{1cm} (4.3.2)

where $\eta_{inj}$ is the injection efficiency, and $\beta = \frac{I_{NR}}{I_R}$. As current increases, filling up the leakage paths and nonradiative recombination centers, $\eta_{inj}$ increases and $\beta$ decreases, leading to a rapid increase in $\eta$. However, as $I_{inj}$ further increases, the localized state band in the MQWs will be filled up, some electrons will be released to the conduction band, where they may move around and be captured by deep-level traps such as misfit defects, which are more readily reached than dislocations. As a
consequence, $\beta$ increases rapidly. At this point, $\eta_{ inj}$ approaches to unity. Thus $\eta$ rolls off after reaching the maximum. The LED on GaN has much lower densities of tunneling defects and leakage channels (larger $R_L$). Therefore, it has a higher $\eta_{ inj}$ at the same bias than the LED on sapphire, resulting in an earlier and faster rise in EQE. However, the microstructural properties of the InGaIn/GaN MQWs in the two LEDs are expected to be similar except the difference in dislocation density, thus the carrier overflow from localized states would take place at a similar injected current. From Eq. (4.3.1), with a larger $R_L$, the LED on GaN is expected to have a smaller characteristic current. We have found that the characteristic current increases and EQE droop becomes less steep at elevated temperatures for both LEDs. This is due to thermal band filling at high temperatures diluting the effect of band filling of localized states via carrier injection [12].

4.4. Reducing efficiency droop by strain engineering

Due to the lattice mismatch between GaN and InN (up to 11%), large strain in conventional InGaIn/GaN MQW structures leads to the generation of a high density of misfit dislocations at the InGaIn/GaN interface. The strain also enhances phase separation and the polarization electric field in high-In content InGaIn QW layers. The misfit dislocations cause defect-assisted carrier leakage and nonradiative recombination of excitons [16]. For the InGaIn material system, the most regularly observed surface defects are V-pits, which have a shape of an open hexagonal, inverted pyramid that is defined by the six \{1011\} planes [17]. V-pits are believed to have originated from either TD [18] or generated from the stacking mismatch boundaries induced by stacking faults in the InGaIn layer due to strain relaxation [19].

Several different methods have been reported to reduce the strain in InGaIn QWs. A decreased blueshift was observed in pre-strained growth of InGaIn/GaN MQW by inserting an extra InGaIn layer of lower In content between the n-GaN cladding layer and the high In InGaIn/GaN MQW active region [20]. Another way to control the strain in InGaIn/GaN MQWs is to use InGaIn templates for the epitaxial growth of LED structures with high In contents. Such InGaIn templates can be prepared by
growing a thick relaxed InGaN layer on top of a GaN/sapphire substrate, [21]. In addition, employing a p type InGaN layer instead of p-GaN as a hole injection layer in the LED structure was also found to be effective in strain reduction in the InGaN/GaN MQWs, resulting in the mitigation of the QCSE [22].

As described in previous sections, carrier overflow from localized states and lost at misfit defects in the MQWs is believed to be responsible for the efficiency droop in InGaN LEDs. Therefore, droop may be reduced by reducing the misfit density by the means of strain engineering. To validate this assumption, in the last section of this chapter, we will present the growth and characterization of green LEDs, which have an strain-compensated InGaIN/InGaN MQW active region.

The LED structure, as shown in Fig. 4.6, was grown on (0001) sapphire substrates with a low-temperature GaN buffer layer using metalorganic chemical vapor deposition. It consisted of a strain-compensating template on top of a Si-doped n-GaN layer (n~5x10^{18} cm^{-3}), a MQW active region comprising 10 pairs of In_{0.27}Ga_{0.73}N well (~3 nm) and undoped In_{0.1}Ga_{0.9}N barrier layers (~10 nm), a p-type AlGaN electron-blocking layer and a p-GaN contact layer (Mg concentration ~1x10^{19} cm^{-3}). A reference sample with conventional InGaN/GaN MQWs was also grown under similar conditions. LEDs with a size of 300x300 μm^2 were fabricated using a standard fabrication technology. First, part of the p-type layers was etched to form mesas by inductively coupled plasma etching. Ti/Al/Ti/Au and thin Ni/Au were then deposited on the exposed n-type and p-type layers, respectively, followed by an annealing in air at 550 °C to form ohmic contacts.

![Fig.4.6 Schematic of the structure for a strain-compensated green LED](image)
Figure 4.7 plots the EL spectra of the LEDs at increasing pulsed currents from 5-100 mA. The peak wavelengths of the two LEDs at 5 mA are almost identical ~517 nm. The spectra exhibit a monotonic blue shift and spectrum broadening with increasing injection current. As the current is increased from 5 to 100 mA, the peak wavelength for the conventional sample shifts by 16.0 nm; the peak wavelength for the strain-engineered sample shifts by 7.9 nm. The current-induced blue shift occurs due to band filling of localized states and screening of the polarization field. Since both the localization effects and piezoelectric effects increase with strain, the smaller peak shift in the InGaN/InGaN MQW LEDs reflects reduced strain in this LED, which is an expected result of strain compensation.

Normalized EQE calculated from integrated EL intensity as a function of the 

**Fig.4.7 EL spectra of strain-compensated (top) and conventional (bottom) green LEDs with increasing pulsed current (duty cycle =1%). The peak intensity is normalized to unity and the spectra are shifted in the vertical direction for clarity.**

Normalized EQE calculated from integrated EL intensity as a function of the
pulsed current is plotted in Fig. 4.8 for the LEDs under investigation. The EQE of both LEDs rises rapidly with increasing current and droops as current exceeds a characteristic current. For the InGaN/GaN MQW LED, the maximum EQE is reached at 5 mA (~7.5 A/cm²) and a strong droop is observed at higher currents. In contrast, for the InGaN/InGaN MQW LED, the onset of droop was pushed to 20 mA (~30 A/cm²) and the EQE displays greatly reduced droop. The latter is therefore better suited for high-current operation. The droop reduction can be explained by a lower density of misfit defects in the InGaN/InGaN MQW LED as a result of strain compensation. As carriers delocalize from localized states under high injection conditions, they are less likely captured by defects, but still undergo radiative recombination and contribute to light emission.

**Fig. 4.8 Normalized EQE of strain-compensated and conventional green LEDs with increasing pulsed current (duty cycle =1%).**

### 4.5. Summary

In summary, we have demonstrated that the material quality and electrical properties of InGaN/GaN MQW green LEDs can be greatly improved by growing the structures on freestanding GaN substrates. The green LED on GaN has a peak IQE at 65%, 71% higher than similar LEDs grown on sapphire. However, they exhibit an even more rapid efficiency droop as injection current increases. The efficiency peaks at an extremely low current density ~0.3 A/cm², far lower than that in typical green
LEDs on sapphire. This is attributed to the combined effect of efficient carrier injection into the active region and carrier delocalization inside the active region. These findings further suggest that TDs are leakage paths in InGaN green LEDs, but play a minor role in light emission and are not responsible for the efficiency droop behaviors. Mitigation of QE droop was achieved by employing strain-compensated InGaN/InGaN MQWs, suggesting that strain engineering may provide a valuable means for reducing efficiency droop in blue and green LEDs.

4.6 References


CHAPTER 5
Fabrication and passivation of microperforated LEDs

5.1. Introduction

In a typical light-emitting diode (LED), a large fraction of light emitted from the active region is reflected at the semiconductor/air interfaces and lost inside the LED chip due to the large contrast of refraction index between semiconductor and the surrounding media, according to Snell’s law [1]. The low light extraction efficiency is a primary limitation to producing high-power red, green and blue LEDs required for solid-state lighting [2]. For GaN-based blue LEDs grown on sapphire, light outside the escape cones is trapped within a thin epitaxial structure. The extraction efficiency is limited to \(1/4n^2 = 4\%\) per GaN/air interface, and the overall extraction efficiency of a planar LED is found to be \(\sim 12\%\) by ray-tracing calculation [3]. The integration of photonic crystals (PhCs) is one of the most promising approaches that are being explored to improve light extraction from LEDs [4-8]. With appropriate parameters, two-dimensional (2D) PhCs consisting of periodic arrays of nanoscale air holes may exhibit photonic band gaps in the visible wavelength range. The waveguided modes inside LED chips can be suppressed if the wavelength of interest falls into the photonic band gaps.

2D PhCs are typically fabricated using nanolithography and plasma etching. To date, almost all the studies of photonic bandgap effects in the context of light extraction have focused on 2D PhCs separated from the active regions of LEDs, i.e. the PhCs were fabricated around or atop the light emitting regions [4-7], where they diffract waveguided light, leading to promising yet limited enhancement of light emission in off-plane directions. It has been predicted that more pronounced improvement in light extraction can be achieved if PhCs are incorporated in the light-emitting regions [8]. In this case, the generated light can only be coupled to
radiation modes, whereas the undesirable waveguided light emission is inhibited. Unfortunately, LEDs having large-area sidewalls may severely suffer from increased junction leakage and nonradiative recombination due to the presence of plasma-induced defects [9-10]. Plasma damage in GaN and related materials takes different forms including lattice defects and nitrogen vacancies, and act as electronically active bandgap states [9-15]. In order to take full advantage of the photonic bandgap effects, it is essential to develop appropriate post-plasma etching treatment to remove plasma damage generated on the nanohole sidewalls. Various methods have been proposed to remove plasma damage in GaN, including thermal annealing [11-12], wet etching [13], dielectric passivation [11-14], and plasma healing [10]. None of these methods, however, produces a full recovery, and in the meantime is compatible with device processing.

In this chapter, we report on a study of the effects of thermal annealing and sulfide passivation on the electrical characteristics of microperforated blue LEDs, which resemble LEDs integrated with 2D PhCs, and demonstrate that a complete restoration of the LED electrical characteristics can be achieved by a combination of these two techniques.

5.2. Fabrication and characterization of microperforated blue LEDs

The blue LED epilayer was grown on a (0001) sapphire substrate with a low-temperature GaN buffer layer using metalorganic chemical vapor deposition. The structure consisted of a 2.2 μm n-GaN layer (Si~5x10^{18} cm^{-3}), a 8-period InGaN/GaN multiple-quantum-well (MQW) active region with ~2 nm wells and 12.5 nm quantum barriers, a 0.08 μm p-type AlGaN cladding layer and a 0.2 μm p-GaN contact layer (Mg ~9x10^{19} cm^{-3}). A Ni/Au/Ni (10/10/100 nm) film was first deposited on the p-GaN layer. 300 μm × 300 μm LED mesas were formed using photolithography and inductively coupled plasma (ICP) etching. An array of microholes with a diameter of 1 or 3 μm and spacing of 2-10 μm were then created in the Ni/Au/Ni metal by lithography and wet etching. The microhole patterns were transferred into the LED
structure by ICP etching using the thick top Ni metal as a hard mask. The etch depth was ~0.7 μm to ensure that the microholes were etched through the MQW active region down to the n-GaN layer. The remaining Ni was selectively etched, leaving the bottom Ni/Au (10/10 nm) as a semitransparent p-contact. The Ti/Al/Ti/Au n-type metallization was deposited by e-beam evaporation and annealing at 600 °C was performed for 2 min in air. The LED fabrication was completed after the deposition of Ni/Au (20/200 nm) bonding pads. Figure 5.1 represents the schematic of process flow for fabrication of microperforated LEDs. The SEM image of microholes, along with light emission from a microperforated blue LED is shown in Fig. 5.2. For comparisons, standard LEDs without microholes were also fabricated and used as control. The total sidewall areas of the microperforated LEDs are 4-30× larger than that of the control LED.

Fig. 5.1 Process flow of a GaN-based LED with a microhole array incorporated in the MQW active region.
Since the plasma-induced damage on sidewalls was substantially removed during the contact annealing [10-12], we exposed the LEDs to an Ar ICP plasma (300 W ICP power, 100 W RIE power, 20 mTorr) for 30 s so as to enhance the effects of plasma damage. The electrical characteristics of the LEDs after plasma etching were recorded using an Agilent 4156C semiconductor parameter analyzer. Light emission was detected using a silicon photodiode-array fiber-optic spectrometer under pulsed operation with a frequency of 1 kHz and a duty cycle of 1%.

Figure 5.3 compares the forward and reverse $I$-$V$ characteristics of LEDs with and without microholes. The total sidewall areas of the LEDs are normalized to that of the control LED and are shown in the legends. As expected, both the reverse-bias and low forward-bias leakage currents increase sharply in the perforated LEDs, by many orders of magnitude. The leakage current increases as the total sidewall area increases, suggesting the dominance of surface currents in the plasma-damaged layer. However, it does not scale up with the sidewall area, presumably due to nonuniform current spreading in the perforated region. The adverse effects of plasma damage on the optical characteristics are only seen at low and intermediate injection currents.
Fig. 5. I-V characteristics of perforated LEDs after plasma etching. The total sidewall surface areas are normalized to that of the LED without microholes and are shown in the legends.

Fig. 4. L-I characteristics of blue LEDs with and without a microhole array. The data are plotted on a log-log scale. The inset shows a microphotograph of light emission from the microhole array.
Figure 5.4 shows the light output power-current ($L$-$I$) curve for a LED with 3μm microholes in comparison with the control. A microphotograph of light emission from the microhole array is illustrated in the inset. Plasma-induced defects at the sidewall surfaces act as nonradiative recombination centers and significantly reduce the radiative efficiency in the low injection regime. As the defect states are saturated at elevated current densities, the influence of plasma damage diminishes. This is also evidenced by the overlapped forward $I$-$V$ curves above 1 mA in Fig. 5.3. At 20 mA, the LEDs with microholes are ~21% brighter due to enhanced light extraction. Since the holes are at the micron scale, we do not expect that there exist any photonic bandgap effects.

5.3. Leakage suppression by thermal treatment and sulfide passivation

After the plasma etching, the samples were then divided into two sets and subjected to different treatments. The first set was annealed in flowing N$_2$ at 400-800 °C for 30 s. The second set was immersed in a diluted (NH$_4$)$_2$S solution (C$_3$H$_7$OH: (NH$_4$)$_2$S=1:1) for 10-60 min at room temperature. The electrical characteristics of the LEDs before and after the treatments were recorded using an Agilent 4156C semiconductor parameter analyzer.

Our previous studies showed that thermal annealing can effectively remove plasma damage in GaN and restore the electronic properties of plasma-etched GaN surfaces [13-14]. Figure 5.5 shows the forward and reverse $I$-$V$ characteristics of the LEDs with 3μm microholes after annealing in N$_2$ at 400–800 °C. As the temperature is raised, the reverse leakage is increasingly suppressed and the $I$-$V$ curve approaches the control. Annealing at 700 °C leads to a nearly complete recovery of the reverse characteristics. As the temperature is further increased to 800 °C, the LED becomes leakier. This is due to the creation of thermal damage on the sidewalls as a result of a preferential loss of N during the annealing [13-15]. A substantial recovery of the forward characteristics is also seen upon annealing. However, after 700 °C annealing, the surface leakage at low forward bias (<2 V) is still significantly higher compared to...
the control LED. This finding suggests that the forward-bias leakage currents may originate from carrier tunneling or recombination assisted by multiple bandgap states. The remaining forward leakage currents may be associated with N vacancies at the immediate surface generated during the plasma as well as annealing processes.

![Graph](image)

*Fig.5.5 I-V characteristics of perforated LEDs after annealing in N₂ at different temperatures.*

The microperforated LEDs were immersed in various acidic and base solutions which are commonly used in microelectronic fabrication. It has been found that boiled KOH can slowly etch plasma-damaged GaN, and led to a full recovery of the electrical characteristics of the LEDs after a treatment for over 40 min, during which, several tens of nanometers of damaged materials were presumably etched off [8]. Unfortunately, the KOH etch also resulted in a significant increase in the forward voltage of the LEDs due to its destructiveness to the metal contacts. In an effort to seek a less aggressive wet chemical treatment, we have found that (NH₄)₂S treatment can significantly reduce the surface leakage and yet does not compromise the performance of the LEDs. Sulfide treatment has been used to remove the unstable native oxides as well as the associated surface states in conventional III-V
semiconductors such as GaAs and InP [16-18], and form a monolayer of sulfides, which can physically and electronically passivate the semiconductor surfaces. As a result, nonradiative surface recombination velocities are significantly reduced. Similar effects of sulfide passivation have also been observed on GaN surfaces, leading to $4-6\times$ increase in photoluminescence intensity [19]. Figure 5.6 shows the forward I-V characteristics of the LEDs with 3 $\mu$m microholes after being soaked in $(\text{NH}_4)_2\text{S} : \text{C}_3\text{H}_7\text{OH}$ (1:1) for different lengths of time. As the process proceeds, the I-V curves are gradually recovered. This corresponds to a slow removal of surface oxides and probably a thin GaN layer which was severely damaged as well. While a nearly full recovery of the reverse-bias characteristics is obtained after 30 min, the forward I-V characteristics are only partially restored. A significant amount of surface leakage remains in the low and intermediate injection regimes. Prolonged treatment did not further suppress the leakage. This is explained by the fact that the $(\text{NH}_4)_2\text{S}$ can only passivate the defect states in the immediate surface layer but cannot remove all the plasma damage which may be tens of nanometer deep.

![Figure 5.6](image.png)

*Fig. 5.6* I-V characteristics of microperforated LEDs after soak in a $(\text{NH}_4)_2\text{S} : \text{C}_3\text{H}_7\text{OH}(1:1)$ solution for different times.
It is clear that thermal annealing and sulfide passivation remove defects in different regions of the plasma damaged GaN, i.e. the near-surface bulk and the immediate surface, respectively. The former may induce new surface defects (N vacancies) whereas the latter cannot remove bulk damage. Therefore, the best strategy for damage removal in GaN-based LEDs may be thermal annealing used in conjunction with sulfide passivation or a brief KOH. To validate this, we conducted the following experiment: a microperforated LED sample was annealed in N$_2$ at 700 °C for 30 s, and then was immersed in (NH$_4$)$_2$S for 10 or 60 min. I-V characteristics before and after the treatments are shown in Fig. 5.7. As seen, both the forward and reverse I-V characteristics are fully recovered after annealing followed by 60 min (NH$_4$)$_2$S passivation, supporting our hypothesis above. It is worthy to note that sulfide passivation on GaN is expected to be more stable than that on GaAs and InP due to the greater strength of N-S bonds compared to As-S and P-S bonds [19]. We retested the passivated samples after exposure to air for one month, no noticeable degradation was observed.

Fig. 5.7: I-V characteristics of microperforated LEDs after annealing at 700 °C followed by treatment in (NH$_4$)$_2$S for 60 min.
5.4. Summary

In summary, we have investigated the effects of thermal annealing and sulfide passivation on the electrical characteristic of InGaN/GaN MQW LEDs integrated with a microhole array resembling a 2D photonic crystal structure. Both thermal annealing and (NH₄)₂S treatment can only partially recover the reverse I-V characteristics. The former is effective in removing bulk damage whereas the latter can only passivate surface states. A complete removal of plasma damage in microperforated GaN-based LEDs is realized by a combination of these two techniques. This work is a significant step toward developing high-efficiency LEDs with the active region integrated with 2D PhC structures.

5.5 References


CHAPTER 6
Enhancement of Light Extraction from nitride LEDs using Photonic Crystals

6.1 Photonic Crystals for LED light extraction

Photonic crystals (PhC) are periodic dielectric structures with periods that are of the order of wavelength of light in material $\left(\frac{\lambda}{n}\right)$ [1]. In the optical regime, a PhC plays the same role as an electronic crystal. The periodic potential in the PhC is originated from a lattice of dielectric media instead of atoms. The difference in dielectric constants of the materials in the crystal creates the similar phenomena for light waves as the atomic potential does for electron waves. Thus, we can manipulate light propagation by designing and constructing PhCs with photonic band gaps to prevent light from traveling in certain directions with some specified energies. Depending on the number of dimensions in which there exists a periodic change in dielectric constant, PhCs can be classified into 1D, 2D and 3D PhCs as shown in Fig 6.1.

![Fig. 6.1 Geometry of one-, two-, and three- dimensional photonic crystals.](image)

Although 3D PhCs seem to be the best candidate to completely mold light propagation in all directions, the 2D PhC slab platform is the most popular structure that most devices are based on due to its simple fabrication and easy modeling [3]. The slab is surrounded by a low-index material which is usually air so that light confinement in the third direction is realized by total internal reflection (TIR) at the interface of the slab and air. The optical properties of 2D PhCs are influenced by several parameters including hole size, slab thickness, and the refractive indices of
both slab and cladding materials.

Figure 6.2 shows the calculated band diagram of a GaN 2D triangular PhC in a thin membrane suspended in air. Parameters used for this calculation are: refractive index of GaN $n=2.4$, lattice constant $a$, hole radius $r = 0.3a$, and membrane thickness $d=0.5a$. The vertical axis is the normalized frequency. The horizontal axis is in-plane Bloch wave vector. Every point on the solid curves represents a quasi-TM electromagnetic mode propagating along the membrane plane. The shaded region is where the amplitude of the in-plane Bloch wave vector is smaller than the amplitude of the $k$ vector of plane waves in air at the same frequency. Therefore the shaded region indicates where the normal-to the-plane $k$ vector has a real part and the mode is leaky in the vertical direction. The boundary of the shaded region is the dispersion relation for a plane wave propagating in the air cladding in an in-plane direction, and is called light line. Thus the light line is used to distinguish leaky modes from guided modes within the slab. There is a complete band gap for the guided modes around the normalized frequency of 0.4 which are located under the light cone. Quasi-TM light waves cannot propagate along the membrane within this band gap because of the absence of in-plane modes.

![Figure 6.2 Photonic band diagrams in TE polarization for 2D GaN PhC slabs.](image-url)
It is well known that in a planar LED, a large fraction of light emitted from the active region is waveguided light trapped inside the chip due to TIR at the semiconductor/air interfaces. The resultant low light extraction efficiency is a primary limitation to producing high-power LEDs required for SSL [4]. For GaN-based LEDs grown on sapphire, light outside the escape cones is trapped within a thin epitaxial structure. The extraction efficiency is limited to $\sim 1/4n^2 = 4\%$ per GaN/air interface, and the overall extraction efficiency of a planar LED is found to be $\sim 12\%$ by ray-tracing calculation [4]. Because the GaN LED structure acts as an asymmetric slab waveguide, trapped light is distributed in a series of so-called guided modes as seen in Fig 6.3. The relative intensity ratio of the higher-order modes becomes weak due to the poor field overlap with the MQW emission regions. Therefore, the guided mode energy is mainly carried by the lower-order modes.

The fact that light of wavelength in the PhC band gap is forbidden from propagating in the plane of the slabs and only radiates into air can be used to improve the light extraction efficiency of LEDs. The integration of PhCs is one of the most promising approaches that are being explored to improve light extraction [5]. Comparing to conventional light extraction strategies, PhCs have the advantages of being prone to interaction with guided light and modify spontaneous emission in
LEDs. When PhC airholes penetrate the light-emitting layer, the band gap inhibits light emission into guided modes, whereas emission into radiative modes is enhanced due to the increased density of electromagnetic states. It has been predicted that over 90% light can be extracted from a GaAs-based PhC-integrated LED [6]. Unfortunately, PhC-integrated LEDs would suffer from strong nonradiative surface recombination at room temperature, which will hinder its use in actual devices [7]. In addition, a free-standing membrane geometry must be employed in order to obtain a complete photonic bandgap in GaN due to its relatively low refractive index. It is a significant challenge to incorporate a LED structure into a thin membrane and realize electrical pumping. To date, photonic bandgap effects have only been observed through optical pumping [8], and the first electrically-driven GaN PhC LED is yet to be demonstrated.

![Fig. 6.4.Schematic of using PhC for diffraction of guided light: Light is generated in the PhC region (left) and light is generated in an injection region and guided modes are extracted after reaching the PhC region (right).](image)

Most research efforts have therefore focused on another approach which uses PhCs as diffraction gratings [9]. In this scheme, spontaneous emission into guided modes is allowed but these modes are subsequently diffracted into air by the PhC (see Fig 6.4). Several groups have demonstrated GaN-based LEDs with a PhCs diffractive structure fabricated on the surface, showing a significant improvement in light extraction and modification of the radiation pattern [10-11]. This approach offers the advantage of being compatible with current fabrication technologies and amenable to implantation in real LED devices. However, because each guided mode propagates at
a different angle and interacts with the PhCs differently, it is difficult to control and extract all the guided modes. In addition, the incorporation of PhCs into the p-GaN layer presents a couple of processing challenges: First, plasma damage can increases surface recombination and reduce the hole concentration in GaN. Second, the p-contact area is significantly reduced due to the presence of airholes, giving rise to a higher contact resistance. To overcome these problems, in this work, PhCs will be built into the ITO transparent electrode on top of blue LEDs as diffraction gratings. The ITO PhCs are expected to enhance light outcoupling, whereas cause little damage to the LED structures.

6.2 Optimization of ITO transparent contact on InGaN LEDs

Conventional nitride-based LEDs use semi-transparent Ni/Au on Mg-doped GaN as the p-contact material. It could provide good adhesion to P-GaN and form ohmic contact. However, attributing to the semi-transparency property of metal thin films, the transmittance of such semi-transparent Ni/Au contact at 450–470nm (blue light region) is confined to be around 60–75%, and is even lower (around 65–67%) in the wavelength region of 380–410nm (near UV). We could increase the transmittance by reducing Ni/Au metal layer thickness, but the contact reliability could become an issue when the contact layer thickness becomes too small. Therefore, the overall LED output power is not fully maximized when Ni/Au is used a p-contact. One possible way to solve this problem is to use transparent indium tin oxide (ITO), instead of Ni/Au, as the p-contact material. In fact, ITO has already been used in Al-GaInP-based LEDs as the transparent upper p-contact material and it could achieve > 90% transmittance at near UV/Blue region [12].

Ni (6nm)/Au (6nm), which were prepared by the electron beam evaporation method, were deposited on top of glass substrates and went through post rapid thermal annealing (RTA) in air under different temperature from 450°C to 600 °C for 3 minutes. 150 nm ITO films on glass substrates were also prepared by electron beam evaporation from highly pure (99.999%) ITO sources. The concentration of SnO₂ in
ITO was 10 wt%. For electron beam evaporation, the base pressure in the chamber was $1 \times 10^{-5}$ Torr. The oxygen flow rate was ranging from 2 to 20 sccm, and the deposition rate of ITO was ~1 Å/s. After deposition, the ITO films were annealed in N$_2$ at temperatures at 600°C for 3 min. The optical properties of both Ni/Au and ITO samples were then investigated over 200-800 nm using a white light ellipsometer.

As shown in Fig 6.5 (a), the highest value of transmittance for Ni/Au films was measured to be 72% at the wavelength of 470 nm for the sample annealed at 550°C. In sharp contrast, the best optical transmittance for the annealed ITO film was ~ 95% at the same wavelength as presented in Fig. 6.5 (b). Compared to ITO contact, the smaller transmittance observed from Ni (6 nm)/Au (6 nm) contact could be attributed to the larger Ni layer thickness and the more opaque nature of Au layer. On the other hand, the high 95% transmittance observed from ITO contact suggests ITO is indeed suitable optically to serve as the upper p-contact for nitride-based LEDs. In order to improve light extraction efficiency of blue LEDs with ITO PhC, the optimized ITO deposition condition and annealing temperature would be used throughout this work.

![Fig.6.5](image)

**Fig.6.5 (a)** Transmittance of Ni (6nm)/Au (6nm) on Glass substrates under different annealing temperature. **(b)** Transmittance of 150nm ITO on Glass substrates deposited at different oxygen flow rates.
6.3 Modeling and fabrication of 2D GaN PhCs

6.3.1 Frequency and time-domain modeling of GaN PhCs

MPB, a freely available Linux software tool, was to solve Maxwell’s Equations in the frequency domain [13]. Eigenstates and eigenvalues were calculated using the plane-wave-expansion (PWE) method so as to determine the allowable TE and TM mode frequencies of a 2D triangular PhC lattice and the photonic band structure. The output of the simulation will be band diagrams, highlighting guided bands beneath the light cone, radiation modes within the background above the light cone, and the photonic band gap range for guided bands. In the case of blue LEDs on sapphire substrates, the guided modes are localized in the nitride epilayer. To suppress the guided modes and promote radiation modes, the emission must fall into a band gap of the PhC slab. After establishing a PhC lattice with a desirable photonic band structure, finite-difference time domain (FDTD) simulations was performed to compute the electromagnetic field changing in time in the computational domain. For each value of the wave vector \( \mathbf{k} \), the Maxwell’s equations are solved and the field is observed at certain points in the unit cell. MIT Electromagnetic Equation Propagation (MEEP) is a free software tool capable of such calculations [14].

![Fig. 6.6 Photonic band diagrams in TE polarization for 2D GaN PhC slabs suspended in air with a thickness of (a) 0.6\( a \), (b) 1.0\( a \) and (c) 1.4\( a \). \( r=0.3a \) in all cases.](image)

Figure 6.6 shows the TE mode band structures of triangular lattices of airholes in symmetric GaN slabs with different thicknesses calculated using MPB. The discrete bands below the light line are guided TE modes which are extended within the plane
of the slabs but decay exponentially into the background. There is a band gap between the first and second guided modes below the line cone. The results in Fig. 6.6 also show that, for a fixed r/a ratio, the band gap is a strong function of the slab thickness and there exists an optimal slab thickness. If the slab is too thin, the modes are weakly guided. As the slab thickness increases, the gap initially increases. However, at a certain critical thickness (~1.4a), higher order modes with more vertical nodes are pulled down and populate the gap, leading to a sharp decrease in the gap. For a 0.6a-thick slab with a r/a ratio of 0.3, the mid bandgap frequency falls into the blue wavelength range (~470 nm) when the lattice constant a is set to be ~ 190 nm. The photonic bandgap is also distinguished from the transmission spectrum calculated by FDTD. The bandgap is clearly visible as the range of very low transmission, which is located in the range of normalized frequency from 0.36 to 0.42 as shown in Fig 6.7.

![Transmission spectrum for 2D GaN PhC slabs in TE polarization with a thickness of 0.6a and r=0.3a.](image)

Symmetric PhC slabs are realized by a perforated membrane freely suspended in air. However, due to its fabrication difficulty and mechanical instability, this type of structures is typically size-limited. More importantly, it is difficult to incorporate them into real devices where current injection is required. PhC slabs with a solid substrate support are more realistic from standpoints of both fabrication and photonic
integration. Nevertheless, most of such structures are asymmetric. It has been suggested that the PhC bandgap effects are ostensibly lost in asymmetric structures due to the lack of translational symmetry with respect to the plane bisecting the slabs [15]. Our calculations showed that when the PhC slab is built on a GaN or sapphire template, the bandgap shrinks as the background index pulls down high-order guided modes as well the light cone states into the band gap region. However, some reported calculations and experimental results have indicated that complete or partial photonic band gaps still exist in asymmetric structures [16]. One interpretation is that if the guided modes have no wave-vector components in the vertical direction and are sufficiently localized within the slabs, the substrate may only be a small perturbation, particularly when its refractive index is small. In this case, the guided modes may still be classified as TE-like or TM-like and some effects of the photonic bandgap will persist.

6.3.2 Fabrication of 2D GaN PhC Slab

6.3.2.1 Process description

2D PhCs will be fabricated using electron beam lithography (EBL) and plasma etching. Once the critical dimensions for PhC structures are determined, these geometries will be transferred to CAD software to create writing files used for e-beam pattern writing in a negative tone resist (ma-N 2403). However, the etch resistance of the e-beam resist alone has proven to be insufficient for transferring the pattern into the underlying GaN substrate via inductively coupled plasma (ICP) etching using a Cl₂-based chemistry. A metal hard mask, such as Ni or Cr which has high etch resistance in Cl plasmas, is required to achieve good pattern transfer. To produce a nano-patterned metal etch mask, a lift-off process employing a negative e-beam resist has been conceived. An outline of this process is given in Fig. 6.8.

GaN wafers were cleaned with acetone, methanol, and DI water for 5 minutes each in ultrasonic bath. The samples were etched in HCl:H₂O (1:1) solution and Buffer Oxide Etchant (BOE) for 1 minutes, respectively. Dehydration bake was held on a hot plate at 110°C for 5 minutes. The ma-N 2403 negative resist was then spun
onto the GaN substrate at a thickness of ~300 nm. Next, Phc patterns were written by EBL using the JEOL 7600 system operating at 30 kV and a beam current of 40 pA. The optimum dosage range was 40-80 μC/cm$^2$. Subsequent pattern development in maD-525 solution for 65s was performed to produce a negative image of the PhC lattice, which exists as an array of cylindrical pillars arranged in a triangular lattice. A thin metal layer of Ni ~65 nm was then deposited by e-beam evaporation. After this, the metal on top of the resist pillars was lifted off in acetone, leaving behind a positive metal mask of the PhC lattice on the substrate. Finally, the sample was etched by ICP plasma etching for 120 seconds at a pressure of 15 mTorr, RIE power 150W, ICP power 400W, and BCl$_3$/Cl$_2$ 3/27 sccm, and the remaining metal was removed by dipping in Ni etchant for 1 minute.

6.3.2.2 Dose optimization and modification on Phc structures

One of the issues of electron beam lithography is the so-called proximity effect. This effect is depicted in Fig. 6.9 (a). As the electron beam exposes the resist, secondary electrons are produced in the resist and in the substrate. These electrons are scattered in every direction, thereby exposing the vicinity of the desired feature. For close enough features, the dose due to secondary electrons builds up producing undesired exposure. In the case of 2D Phc, this effect is particularly notorious at the edges of the device, where the dose build up is much less than in the bulk, as shown in
Fig. 6.9 (b). Even though the same dose is applied to the entire structure, the holes in the bulk receive a higher dose due to the build-up generated by the surrounding holes. On the other hand, the holes at the edges of the structure receive a lower electron dose. To compensate for this effect, the electron beam dosage should be gradually increased towards the periphery of the device.

As seen from previous section, for a 0.6a-thick slab with a r/a ratio of 0.25~0.3, the mid bandgap frequency falls into the blue wavelength range (~470 nm) when the lattice constant a is set to be ~ 200 nm. The experiment was applied in the same way as used for EBL on GaN. In this case, the lattice parameters were designed to be a =
200nm, r = 50nm, and an optimized dose of 65 μC/cm$^2$. Figure 6.10 shows the Top-view and 45$^\circ$-view SEM images of the EBL results on ma-N 2403.

![Fig. 6.10 (a) Top-view and (b) 45$^\circ$-view SEM images of EBL for ma-N 2403 of PhC pattern (r/a=0.25 r=50nm a=200nm) on GaN (65 μC/cm$^2$).](image)

As shown in Fig. 6.10, the negative resist ma-N 2403 shows poor resolution on the PhC patterns (r/a=0.25, a = 200nm, and r = 50nm). This result can be attributed to the fact that proximity effect are more noticeable in close enough features, especially in thick negative tone resists on GaN, which leads to secondary electrons builds-up producing undesired exposure.

In order to mitigate the proximity effect in closed features of GaN PhC structures, which have a r/a = 0.3, all the GaN PhC structures written on the negative resist were redesigned as a = 333 nm and r = 100 nm. To obtain the optimal resolution with such feature size with the negative resist on GaN, PhC patterns with doses varied from 40 to 80μC/cm$^2$ were exposed in the ma-N 2403 resist and the results are depicted in Fig. 6.11. As seen in Fig 6.11 (d), the cross-link of photoresist due to the proximity effect is less noticeable at the edges compared to the center, which might lead to the difficulty of Ni lift-off issues in the following step. In contrast, the dose of 60μC/cm$^2$ appeared to achieve the best feature resolution on GaN and was to be applied throughout this work.
6.3.2.3 Fabrication of 2D PhC GaN slab using lift-off and etch-back process

Figure 6.12 shows SEM images representing the summary of each fabrication step using lift-off and etch-back techniques as described in section 6.3.2.1. The top-view of metal mask after the liftoff is shown in Fig. 6.12 (a) and (b). Figure 6.12 (c) and (d) displays the PhC pattern transferred into a GaN substrate after an ICP etch using BCl₃/Cl₂ plasma for 120s. Figure 6.12 (e) and (f) shows the final 2D PhC structure on GaN after Ni removal.

Fig. 6.11 45°-view SEM images of dose characterization with EBL for maN-2403 on GaN: (a) and (b) Optimal exposed pattern of 60μC/cm²; (c) underexposed pattern of 40μC/cm² (d) overexposed pattern of 90μC/cm², r=100nm and  a=333 nm in all cases.
The sidewall angle was measured as ~ 82° and etch selectivity (~16:1) of GaN over Ni hard masks have been obtained. One of the problems of ICP is the mask erosion. As the ICP etching proceeds, the edge of the Ni mask tend to etch faster, and thus, the veins in the mask assume a triangular cross-section. This creates a window for skew rays in the ion beam that would be screened out otherwise. These rays severely affect the quality of the fabricated devices as they attack the walls of the structure and create roughness on the surfaces. To obtain better side wall etching profile, a thicker Ni mask (~ 85nm) were to be used in next section.

Fig. 6.12 SEM micrographs of the PhC structure on GaN: (a) and (b) top view of Ni metal mask after lift-off; (c), (d) 45° and cross-section view of PhC pattern transfer from Ni mask into GaN; (e), (f) 45° and cross-section view of final PhC structure on GaN after Ni removal.
6.4 Fabrication and characterization of blue LEDs with ITO PhCs

6.4.1 Introduction

To date, studies of light extraction in blue LEDs by means of PhCs have focused on 2D PhCs separated from the active regions of LEDs, i.e. the PhCs were built around or atop the light emitting regions [17-19], where they actually act as diffraction gratings. For PhCs integrated in the top p-GaN layer, it is obvious that the etch depth is an important parameter affecting light extraction. If the etch depth is too shallow, the low-order guided modes will have limited interaction with the PhC. However, a deeply-etched PhC will be seen by guided modes as an intermediate layer with a low effective refractive index. The field distribution of the guided modes will be shifted downward, limiting the interaction between the PhC and guided light.

The incorporation of diffracting PhCs into the p-GaN layer would suffer from a couple of drawbacks. First, plasma damage can increases surface recombination and reduce the hole concentration in GaN. Second, the p-contact area is significantly reduced due to the presence of airholes, giving rise to a higher contact resistance. To overcome these problems, we will incorporate the diffracting PhC into an ITO layer which is deposited atop p-GaN as ohmic contact. The refractive index of ITO matches well with that of GaN, ensuring a good light coupling. An ITO layer ~ 150 nm will be deposited and PhCs will then be produced. We have optimized the deposition of ITO films using e-beam evaporation. The best films were obtained by e-beam evaporation of an ITO source under an oxygen partial pressure. The post-deposition annealing was found to have remarkable impact on both the electrical and optical properties of the films. After annealing at 600 °C in N₂, the ITO contact exhibited transmittance ~ 95% at 470 nm.

6.4.2 Fabrication of blue LEDs with ITO PhCs as diffraction gratings

The blue LED wafer grown by MOCVD consisted of a 2.5 μm Si-doped n-GaN layer, MQW active region comprising 10 pairs of undoped InGaN well (~3 nm) and
Si-doped GaN barrier layers (~10 nm) emitting at ~470 nm, a 0.05 μm p-type AlGaN electron-blocking layer and a 0.2 μm p-GaN contact layer. A thin film of ITO ~ 150 nm was first deposited on LED wafer using e-beam evaporation and followed by post annealing at 600 °C in N₂ for 3 minutes. A total 300 x 300 μm² area of Phc patterns, which exists as 3 x 3 array of 100 μm² or 4 x 4 array of 80 μm², were then written by EBL using the JEOL 7600 system operating at 30 kV, a beam current of 40 pA and the optimal dosage was 60µC/cm². The similar lift-off process described in previous section was carried out to form PhC pattern (a = 333 nm and r = 100 nm) on ITO surface except that a thicker Ni film (85nm) was deposited by e-beam evaporation instead of 65nm. After this, the sample was etched by ICP plasma etching for 90s at a pressure of 10 mTorr, RIE power 150W, ICP power 400W, and BCl₃/Cl₂/CF₄ gas flow rate of 15/12/3 sccm. The etch depth was ~ 180 nm to ensure that the nanoholes were etched through the ITO region down to the P-GaN layer. The remaining Ni hard mask was removed by dipping in Ni etchant for 1 minute. 300 μm × 300 μm LED mesas were then formed using photolithography and ICP etching. The Ti/Al/Ti/Au n-type metallization was deposited by e-beam evaporation. Finally, the PhC LED fabrication was completed after the deposition of Ni/Au (20/200 nm) bonding pads. An outline of this process is given in Fig. 6.13.

Fig. 6.13 Fabrication process flow of a blue LED with ITO PhCs
Figure 6.14 (a) and (b) displays the PhC pattern transferred into ITO/GaN interface after an ICP etch using BCl$_3$/Cl$_2$/CF4 plasma for 90s. The sidewall angle and etch depth as measured were ~ 87° and 180nm, respectively. Figure 6.14 (c) and (d) shows the final 2D PhC structure on ITO/GaN after Ni removal. Figure 6.14 (e) illustrates the formation of 3 x 3 array of 100 μm$^2$ PhC pattern after Ni liftoff. The 45° view of a completed ITO PhCs blue LEDs with or 4 x 4 array of 80 μm$^2$ is shown in Fig. 6.14 (f). To minimize nonradiative carrier recombination at air hole surfaces, and to retain all the active material in the structure, the holes do not penetrate the InGaN QW. The asymmetry of the active region, however, allows the etched hole of the PhC to be deep enough (~ 30nm into P-GaN) to cause strong Bragg scattering of the index-guided light.

Fig. 6.14 SEM micrographs of the ITO PhC structure on blue LED: (a), (b) 45° and cross-section view of PhC pattern transfer from Ni mask into ITO/GaN; (c), (d) 45° view of final PhC structure on ITO/GaN after Ni removal; (e) top view of PhC pattern on ITO/GaN with 3 x 3 array of 100 μm$^2$ after Ni liftoff; (f) 45° view of completed ITO PhCs blue LEDs with or 4 x 4 array of 80 μm$^2$. 
Table 6.1 shows final measurements of the holes in the PhC structure on GaN and ITO and its respective error compared with the dimensions of the CAD design file.

**6.4.3 Electrical and optical characterization of blue LEDs with ITO PhCs**

The electrical characteristics of the ITO PhCs blue LEDs were recorded using an Agilent 4156C semiconductor parameter analyzer. Light emission was detected using a silicon photodiode-array fiber-optic spectrometer under continuous wave operation. Figure 6.15 shows the microphotograph image of uniform light emission from an ITO PhCs blue LED. Figure 6.16 compares the forward $I-V$ characteristics of LEDs with and without PhCs in logscale. As expected, in low forward-bias region leakage currents increase sharply in the PhC LEDs, suggesting the dominance of surface currents in the plasma-damaged layer. This finding indicates that the forward-bias leakage currents may originate from carrier tunneling or recombination assisted by multiple bandgap states induced by plasma etching [20]. In addition, the forward voltage (20mA) of LEDs with ITO PhC is ~0.6V higher than that of LEDs without PhC. This degradation of forward voltage can be attributed to the reduction of the effective ohmic contact area due to the 2D etch hole array, which in turn increases the series resistance of the device.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Designed (nm)</th>
<th>Measured (nm)</th>
<th>Error Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>200</td>
<td>196</td>
<td>2</td>
</tr>
<tr>
<td>ITO</td>
<td>200</td>
<td>195</td>
<td>2.5</td>
</tr>
</tbody>
</table>

*Table 6.1 Experimental errors of hole diameter for PhC structure of GaN and ITO*
Figure 6.17 (a) shows the light output power-current ($L-I$) curve for a LED with ITO PhC in comparison with the control. Regardless of the reduced ITO contact area and plasma-induced nonradiative recombination, the PhC LED exhibited significant improvements in output power with no anomalies in the $L-I$ characteristics, such as an abrupt slope change or rapid power saturation. The integrated light intensity of the PhC LED at the injection current of $I = 20mA$ is 1.5 times that of LED without PhC integration. A further improvement of light diffraction would be expected if 2D hole array is etched into ITO or a thicker ITO is applied. As shown in Fig 6.17 (b),
emission spectra taken at 20mA are almost identical. This indicates that the integration of 2D-PhC does not affect the MQW quality.

![Graphs showing L-I characteristics and EL spectra of blue LEDs with and without ITO PhC.](image)

**Fig. 6.18** (a) L-I characteristics of blue LEDs with and without ITO PhC (b) EL spectra of blue LEDs with and without ITO PhC.

### 6.5 Summary

In summary, time and frequency-domain modeling of GaN PhC with triangular lattices was carried out to determine the allowable TE modes of two dimensional (2D) PhC lattice and the photonic band structure. 2D PhC GaN slab with airhole diameters in the range of 100-200 nm were fabricated using pattern transfers by lift-off process. Finally, we integrated triangular-lattice 2D ITO PhC structure in GaN-based blue LED devices emitting at 470 nm. The resultant LEDs exhibited significant improvements in light extraction up to 1.5 times that of planar LEDs without PhC integration. This improvement results from the efficient diffraction in the surface-normal direction by the integrated 2D ITO PhC structure.

### 6.6 References


Chapter 7

Conclusions and Future Work

7.1 Conclusions

The objective of this work is to improve the external quantum efficiencies of InGaN-based green and blue LEDs by reducing the QE droop and improving the light outcoupling efficiencies. In this dissertation, we have observed that carrier overflow from localized states and loss at interfacial misfit defects appears to be the nonthermal mechanism of the efficiency droop in InGaN-based blue and green LEDs. Green LEDs grown on free-standing GaN showed substantially reduced microstructural defects and significantly higher internal quantum efficiencies (IQE) compared to their counterparts on sapphire. However, it suffered from even more dramatic efficiency droop which occurs at a current density as low as 0.3 A/cm². Reduction of misfit defects in green LEDs by using a train-compensated InGaN/InGaN MQW structure was proven to be an effective way to reduce the QE droop. Furthermore, based on frequency and time-domain simulations of 2D PhC GaN slabs, we designed and integrated triangular-lattice 2D ITO PhC structure with GaN-based blue LED devices emitting at 470 nm. The PhC LEDs exhibited 1.5x improvements in light extraction. To minimize the adverse effects of sidewall plasma damage which lead to increased junction leakage and nonradiative recombination rates, we developed a new post-etching treatment technique which combined thermal annealing and sulfide passivation. Blue PhC LEDs subjected to annealing at 700 °C followed by (NH₄)₂S passivation exhibited a complete restoration of the electrical characteristics.

7.2 Future Work

Further studies of the QE droop of InGaN-based blue and green LEDs should focus on the reduction of excessivestrain and misfit defects in InGaN/GaN QWs through design and growth optimization. Strain engineering, as a promising solution
to the droop problem, has been briefly studied, and should be further explored. Although the achieved droop reduction can be explained by a lower density of misfit defects in the InGaN/InGaN MQW LED as a result of strain compensation, the fundamental mechanism of strain-induced formation of misfit defects is worth further investigation at an atomic level using high-resolution transmission electron microscopy. Additional efforts should be made to gain insight into the strain relief mechanisms in different strain-engineered InGaN-based heterostructures.

In the study of 2D PhC integration as a means to improve the light outcouping efficiency of InGaN LEDs, the fabrication process needs to be further optimized. The proximity effect must be reduced during e-beam lithography in order to create sub 100 nm PhC features in negative resists. The influence of the PhC geometry, including the lattice constant, slab thickness, airhole size, on the light extraction efficiency should be further investigated. The interaction between PhCs and light may be greatly enhanced by integrating PhCs with the active region of the LEDs. Finally, a suspended and symmetrical PhC LED structure may be fabricated by growing the LED on top of a thin InGaN sacrificial layer, which is subsequently removed by photoelectrochemical etching (PEC). This will allow us to study EL enhancement by the photonic bandgap effect in true PhC structures.

Appendix

A.1 MPB frequency domain simulation code

(define-parameps-GaN 5.76) ; the dielectric constant of the GaN
(define-parameps-InGaN 6.29) ; the dielectric constant of the QW InGaN
(define-parameps-AlGaN 5.53) ; the dielectric constant of the AlGaN
(define-paramloweps 1.0) ; the dielectric constant of the superstrate
(define-param r 0.3) ; the radius of the holes
(define-paramsupercell-h 50) ; height of the supercell
(define-paramh_pGaN 0.6) ; thickness of sealing layer pGaN
(define-paramh_pAlGaN 0.1) ; thickness of the blocking layer PAlGaN
(define-paramh_qwInGaN 0.01) ; thickness of the QW InGaN layer
(define-paramh_qwGaN 0.04) ; thickness of the QW GaN layer
(define-paramh_nGaN 10) ; thickness of layer nGaN
(define-param m 10); periods of QW
; triangular lattice with vertical supercell:
(set! geometry-lattice (make lattice (size 1 1 supercell-h)

(basis1 (/ (sqrt 3) 2) 0.5)
(basis2 (/ (sqrt 3) 2) -0.5)))
(set! geometry

(list (make block (material air)

(center 0 0 (* 0.25 supercell-h))
(size infinity infinity (* 0.5 supercell-h)))
(make block (material air)
(center 0 0 (* -0.25 supercell-h))
(size infinity infinity (* 0.5 supercell-h)))
; sealing layer blocks - two, for defining asymmetric structures with diff
sealing
(make block (material (make dielectric (epsilon eps-GaN)))
(center 0 0 (/ (+ h_nGaN (* m (+ h_qwInGaNh_qwGaN)))) -2))
(size infinity infinity (+ h_nGaN (* m (+ h_qwInGaNh_qwGaN))))))
(make block (material (make dielectric (epsilon eps-GaN)))
(center 0 0 (/ (+ h_pAlGaN (pGaN) 2))
(size infinity infinity (+ h_pAlGaN (pGaN)))
(make cylinder (material air)
(center 0 0 (/ (- (+ h_pGaN (pAlGaN) (* (/ m 1) (+ h_qwInGaNh_qwGaN) 2)) (radius r) (height (+ h_pGaN (pAlGaN) (* (/ m 1) (+ h_qwInGaNh_qwGaN))))))
; 1st Brillouin zone of a triangular lattice:
(define Gamma (vector3 0 0 0))
(define M (vector3 0 0.5 0))
(define K (vector3 (-/3) (/3) 0))
(define-param only-K false) ; run with only-K=true to only do this k-point
(define-param k-interp 4)  ; the number of k points to interpolate
(if only-K
  (set! k-points (list K))
  (set! k-points (interpolate k-interp (list Gamma M K Gamma))))
(set-param! resolution (vector3 16 16 16))
(set-param! num-bands 9)

; Run even and odd bands, outputting fields only at the K point:
(run-zeven)
(display-eigensolver-stats)

A.2 MEEP time domain simulation code

(define-param h 0.6) ; the thickness of the slab
(define-parameps 5.76) ; the dielectric constant of the slab
(define-paramloweps 1.0) ; the dielectric constant of the substrate
(define-param r 0.3) ; the radius of the holes
(define-param w 1)
(define-paramsupercell-h 4) ; height of the supercell
(define-parmsx 12)
(define-parmsy 12)
(define-paramdpml 1)
; triangular lattice with vertical supercell:
(set! geometry-lattice (make lattice (size (+ sxdpml) (+ sydpml) supercell-h)
  (basis1 (/ (sqrt 3) 2) 0.5)
  (basis2 (/ (sqrt 3) 2) -0.5)))

(set! geometry
  (list (make block (material air)
    (center 0 0 0)
    (size infinity infinitysupercell-h))
  (make block (material (make dielectric (epsilon eps)))
    (center 0) (size infinity infinity
    h))))
(definecenter_x 0)
(definecenter_y 0)
; makes the finitely large photonic crystal by appending the holes
(do ((x -12 (+ x 1))) ((> x 12))
    (do ((y -12 (+ y 1))) ((> y 12))
        (set! center_x (* (+ x y) (/ (sqrt 3) 2)))
        (set! center_y (* (- x y) 0.5))
        (if (and (< (abs center_x) (abs (- (/ sx 2) r))) (< (abs center_y)
            (abs (- (/ sy 2) r))))
            (set! geometry (append geometry (list (make cylinder
                material (make dielectric (epsilon eps)))
                (center center_x center_y) (radius r) (height h)))))))
)

(set! pml-layers (list (make pml (thickness dpml))))
(set-param! resolution 10)
(define-paramfcen 0.3956) ; pulse center frequency
(define-paramdf 0.2) ; pulse width
(define-paramnfreq 500) ; number of frequencies at which to compute flux
(set! sources (list
    (make source
        (src (make gaussian-src (frequency fcen) (fwidth df)))
        (component Hz)
        (center -5.5 0 0)
        (size 0 w h))
    ))
(set! symmetries (list (make mirror-sym (direction Y) (phase -1))))
(define z1
    (add-fluxfcendfnfreq
        (make flux-region
            (center 5 0 0) (size 0 (* 2 w) h))))
)

(run-sources+ (stop-when-fields-decayed
    50 Hz
    (vector3 5 0 0)
    1e-3)
    (at-beginning output-epsilon)
    (during-sources
        (in-volume (volume (center 0 0 0) (size 12 0 h))
            (to-appended "hz-slice" (at-every 0.4 output-hfield-z))))
)

(display-fluxes z1)
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