Optical investigations of InGaN heterostructures and GeSn nanocrystals for photonic and phononic applications: light emitting diodes and phonon cavities

Shopan d. Hafiz

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Optical investigations of InGaN heterostructures and GeSn nanocrystals for photonic and phononic applications: light emitting diodes and phonon cavities

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Electrical and Computer Engineering at Virginia Commonwealth University

by

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May 2016
Acknowledgement

First of all, I would like to express my gratitude to my advisor, Professor Ümit Özgür. It has been a privilege to have been educated by him, not only for providing precious ideas, comments, and critiques with his profound knowledge in nitride optoelectronics but also for his exceptional ability to elucidate any complex topic. Without his invaluable help, guidance, encouragement and his endless patience, this thesis would not have been possible. I am very much thankful to him for all the efforts that he has made for my personal development as a researcher. I am also grateful to Professor Hadis Morkoç for his valuable suggestions and constant support. I would like to acknowledge Prof. Vitaliy Avrutin and Dr. Natalia Izyumskaya for their help and guidance during my research. I also appreciate the helpful comments and contributions from my other committee members, Prof. Shiv Khanna and Prof. Michael Reschikov. Special thanks to Professor Kestutis Jarasiunas, Dr. Ryoko Shimada, Dr. Emilis Sermuksnis, and Dr. János Volk. I learnt a lot from the discussions I had with them during their visit to VCU.

I would like to thank all the collaborators with whom I had the opportunity to work with; Richard J Alan Esteves, Lamia Nahar, and Prof. Indika Arachchige from Dept. of Chemistry, VCU, Prof. Denis Demchenko from Dept. of Physics, VCU, Prof. Bernard Gil from University of Montpellier, Dr. Sebastian Metzner, Prof. Frank Bertram, and Prof. Juergen Christen from University of Magdeburg.

I am grateful to my colleague, Serdal Okur, for his mentoring and guidance during my first two years of graduate study. Thanks to my other colleagues in the lab, Xing Li, Huiyong Liu, Congyong Zhu, Fan Zhang, Romualdo Ferreyra, Nicolas Andrade, Mykyta Toporkov, Morteza Monavarian, Barkat Ullah, Saikat Das, and Tanner Nakagawara for their help with experiments.

Finally, and most importantly, I would like to thank my parents, brother, and my wife for their love, support and motivation.
Table of Contents

List of Figures .................................................................................................................. v
List of Tables .................................................................................................................... xii
Abstract .............................................................................................................................. xiii

Chapter 1. Introduction ......................................................................................................... 1
  1.1. Efficiency loss mechanisms in InGaN LEDs ............................................................... 4
      1.1.1. Auger recombination .......................................................................................... 6
      1.1.2. Electron overflow ............................................................................................. 9
      1.1.3. Reduced polarization fields in semi-polar LEDs ............................................. 14
  1.2. Coherent acoustic phonons in InGaN heterostructures ............................................ 15
  1.3. Prospect of Ge\textsubscript{1-x}Sn\textsubscript{x} QDs and BeMgZnO thin films in optoelectronics ........ 17
  1.4. Organization of the thesis ....................................................................................... 19

Chapter 2. Efficiency enhancement in InGaN LEDs .......................................................... 21
  2.1. Determination of diffusion length in GaN .................................................................. 21
      2.1.1. Diffusion length in p-GaN from PL spectroscopy ............................................ 22
      2.1.2. Diffusion length in n-GaN from PL spectroscopy ............................................ 25
      2.1.3. Diffusion length in n-GaN from CL spectroscopy .......................................... 27
      2.1.4. Comparison of PL and CL measurements ....................................................... 29
  2.2. Determination of electron escape rate in InGaN LEDs ............................................ 30
  2.3. Optimization of active region thickness in InGaN LEDs ......................................... 34
  2.4. Optimization of electron injector layer in InGaN LEDs .......................................... 37
  2.5. Improvement of carrier injection symmetry using delta doped barriers in InGaN MQW LEDs ........................................................................................................... 43
2.6. Enhancement of Indium incorporation to InGaN MQWs on AlN/GaN periodic multilayers ................................................................. 50

2.7. Near-field optical microscopy of extended defect distribution in semipolar InGaN LEDs ........................................................................................................ 60

Chapter 3. Generation and amplification of coherent acoustic phonons in InGaN heterostructures ................................................................. 68

3.1. Phonon dispersion in bulk and in superlattices ........................................ 68

3.2. Generation and detection of coherent acoustic phonons .......................... 74

3.3. Design of a phonon cavity for coherent acoustic phonon amplification ........ 80

Chapter 4. Optical properties and carrier dynamics in GeSn nanocrystals and quaternary alloy BeMgZnO ........................................................................................................ 84

4.1. Optical gap engineering and carrier dynamics in Ge_{1-x}Sn_{x} QDs .............. 84

4.2. Optical investigation of BeMgZnO quaternary alloys ............................... 90

Chapter 5. Conclusions and outlook ................................................................ 100

References ......................................................................................................... 104

Curriculum Vitae ............................................................................................... 110
List of Figures

Figure 1: Room temperature bandgap energy versus In composition for InGaN ternary within visible spectrum energy range ................................................................. 1

Figure 2: Typical techniques of white light generation .......................................................... 2

Figure 3: Simplified schematic for different types of carrier recombination mechanisms in semiconductors. There are other possible radiative and nonradiative processes not shown here. ........................................................................................................ 5

Figure 4. Typical (a) direct and (b) indirect Auger recombination. There are other varieties of Auger processes not shown in this figure. ................................................................. 6

Figure 5. Simplified conduction band schematic of the two color LED structure ................. 8

Figure 6: With 425 nm excitation at 15 K, only the PL peak from low energy blue QW (460 nm) can be observed at an excitation density corresponding to $10^{19} \text{cm}^{-3}$ photo-generated carrier concentration. No emission from the larger bandgap UV QW (400 nm) was observed. The spectral range near the excitation laser line is blocked. ......................... 9

Figure 7: Schematic of electron overflow caused by ballistic or quasi-ballistic electron transport across the InGaN active region. .................................................................................. 10

Figure 8. Illustration of increasing active region volume, (a) by increasing thickness of single a DH layer, (b) by employing multiple thin DH layers separated by barriers.............. 11

Figure 9. Illustration of EBL and EI in a simplified conduction band diagram .................... 12

Figure 10: (Top) Crystallographic representation of polar c-plane (0001), semi-polar (11$ar{2}$2), and (10$ar{1}$1) plane. (Bottom) Piezoelectric polarization (left axis) and electron-hole wavefunction overlap (right axis) as function of the angle between substrate normal
and the nitride c-axis in a 3 nm wide Ga_{0.75}In_{0.25}N quantum well pseudomorphically strained with respect to GaN barriers.

Figure 11: Cross-sectional schematic of the InGaN-based DH samples investigated. The steps of different height are generated by ICP etching.

Figure 12: Integrated PL intensities from underlying GaN, In_{0.01}GaN layer, and the active region at 15 K and 295 K as a function of p-GaN thickness. The lines are exponential fits to the data for the active region. Data at 295 K and 15 K are shifted vertically for clarity. Error bars apply to all respective points for a given thickness. The inset shows a representative PL spectrum for the region with 100 nm thick p-GaN at 295 K.

Figure 13: Integrated PL from the active region at 15 K and 295 K as a function of n-GaN thickness. The lines are exponential fits to the data for the active region. Data at 295 K and 15 K are shifted vertically for clarity.

Figure 14: CL intensity profile for the GaN and the spectrally integrated InGaN luminescence from 366 nm to 474 nm along the cross-section of the sample at 6 K.

Figure 15: (a) I-V curve and, (b) electron leakage percentage at different photo-generated carrier density.

Figure 16. Measured IE in 6 nm DH LEDs. Multiple devices were measured and the data for a representative LED is presented.

Figure 17. Relative PL efficiency of multi-3 nm DHs vs. injected carrier concentration at room temperature.

Figure 18. Relative EL efficiency of multi-3 nm DHs vs. injected carrier concentration at room temperature.
Figure 19: Simplified conduction band schematic of quad 3 nm DH LED structures investigated.

Figure 20: (a) The integrated EL intensity dependence on current density for single and quad 3 nm DH LEDs with varied SEI thickness. (b) The relative EL efficiency vs. injected current density.

Figure 21: The integrated PL intensity dependence on optical excitation density at (a) 15 K and (b) 295 K for single and quad 3 nm DH LEDs with varied SEI thickness.

Figure 22: $B_{eff}$ coefficients of (a) single-DH and (b) multi-DH LEDs calculated using squared overlap integrals of electron and hole wavefunctions (proportional to radiative recombination rate) within the active region as a function of current density obtained from SILVACO Atlas simulations.

Figure 23: Simplified conduction band schematic of hex 3 nm DH LEDs. The Mg $\delta$-doping is employed for either only the first or the first and the second 6 nm thick $\text{In}_{0.06}\text{Ga}_{0.94}\text{N}$ barriers located near the $n$-GaN side. The rest of the barriers are undoped and are 3 nm thick. A third sample with no $\delta$-doping in the barriers is used for reference.

Figure 24: (a) Electron and (b) hole concentrations and (c) the corresponding energy band structures for the reference LED (black) and LEDs with one (red) or two (blue) Mg $\delta$-doped barriers simulated at a current injection of 35 A/cm$^2$ with SILVACO Atlas. The dashed lines in (c) indicate the quasi-Fermi levels. Left side is n-GaN with 15+15 nm-thick SEI. The horizontal dotted line represents the energy corresponding to the valence band maximum in p-GaN.

Figure 25: (a) The integrated EL intensities and (b) the relative EQE vs. injected current density for the LEDs investigated.
Figure 26. Schematics of the InGaN MQWs structures with nominal compositions grown on (a) relaxed GaN and (b) strained AlN/GaN multilayers................................................................. 51

Figure 27 (a) ω-2θ HRXRD patterns from both AlN/GaN periodic multilayers. Large number of satellite peaks is indicative of relatively smooth interfaces between the AlN and GaN layers. The simulation results and fitting curves for the structure ML₁ (b) ML₂ (c) indicate degree of relaxation of 100%/60% and 100%/0.0% for AlN/GaN in ML₁ and ML₂, respectively................................................................. 53

Figure 28. Room temperature PL spectra of InGaN MQWs grown on GaN (A and B) and AlN/GaN multilayers (C and D). The thicknesses of GaN in the multilayer are 4.5nm (C) and 2.5nm (D)........................................................................................................ 55

Figure 29. Room temperature PL transient of InGaN multi-quantum well structures grown on GaN (A and B) and AlN/GaN multilayers (C and D). The solid lines indicate the single exponential (A and B) and bi-exponential (C and D) fitting of the data. The thicknesses of GaN in the multilayer structures are 4.5nm (for layer C on ML₁) and 2.5nm (for layer D on ML₂)........................................................................................................ 56

Figure 30. Room temperature PL spectra for the highest and the lowest photo-generated carrier density in InGaN MQWs on relaxed GaN (A and B) and AlN/GaN MLs (C on ML₁ and D on ML₂) recorded using ultra-fast optical spectroscopy. The PL spectrum tends to shift to longer wavelengths with increasing delay time. This shift is much more pronounced for MQWs on MLs (C and D) compared to those on relaxed GaN (A and B)........................................................................................................ 58

Figure 31: Cross-sectional schematic of the LED structures grown on semipolar (1101) and (1122) GaN templates. ........................................................................................................ 62
Figure 32: (a) Angled-view SEM image, (b) Macroscopic PL spectra (D\textsuperscript{10}X, BSF, and DAP emission peaks are marked), and (c) NSOM PL intensity map of semipolar (1\overline{1}01) GaN. (d) Local PL spectra for the points indicated in (c). ………………………………………………………………………………………………………… 63

Figure 33: (a) Angled-view SEM image, and (b) NSOM PL intensity maps of semipolar (1\overline{1}01) LEDs. (c) Local PL spectra for the two points indicated in (b). ………………………………………………………………………………………………………… 65

Figure 34: (a) AFM image and (b) NSOM PL intensity map (15 K) of semipolar (1\overline{1}22) InGaN LEDs. (c) Local PL spectra for the points indicated in (b). ………………………………………………………………………………………………………… 66

Figure 35: A diatomic crystal structure with masses M\textsubscript{1}, M\textsubscript{2} connected by force constant C between adjacent planes. ……………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………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Figure 44. (a) Calculated phonon dispersion curves for sample A3 and AlN (11.8 nm)/GaN (2.9 nm) phonon mirror, (b) calculated reflectivity of the phonon cavity structure .......... 83

Figure 45. (a) PL spectra of the Ge$_{1-x}$Sn$_x$ QDs with varying Sn content investigated at 15 K, (b) Experimental (PL peak) and theoretical transition energies as a function of % Sn in 2.1 nm and 2.7 nm QDs. Inset shows the size histogram of Ge$_{0.77}$Sn$_{0.23}$ QDs sample, representative of QDs with different Sn compositions, obtained from TEM analysis without any postsynthetic size selection ................................................................. 85

Figure 46. PL transients of the Ge$_{1-x}$Sn$_x$ QD samples of different composition at 15 K .......... 87

Figure 47. Experimental PL decay times at (a) 15 K and (b) 295 K as a function of %Sn in Ge$_{1-x}$Sn$_x$ QDs. Fast decay components are shown in the insets of (a) and (b). .................. 88

Figure 49. Schematic of carrier localization .................................................................................. 90

Figure 50. The schematic diagram of Zn-polar (0001) and O-polar (000$\bar{1}$) BeMgZnO samples grown on GaN templates ................................................................. 91

Figure 51. Low temperature and room temperature PL spectra of O-polar BeMgZnO samples grown on GaN. Sample B1 is Be$_{0.04}$Mg$_{0.17}$Zn$_{0.79}$O, sample B2 is Be$_{0.11}$Mg$_{0.15}$Zn$_{0.74}$O, sample B3 is Be$_{0.10}$Mg$_{0.25}$Zn$_{0.65}$O and sample Z is Be$_{0.03}$Mg$_{0.18}$Zn$_{0.79}$O .................. 93

Figure 52. PL decay time dependence on the emission energy at 15 K and time integrated PL for a) sample B1: Be$_{0.04}$Mg$_{0.17}$Zn$_{0.79}$O; b) sample B2: Be$_{0.11}$Mg$_{0.15}$Zn$_{0.74}$O; c) sample B3: Be$_{0.10}$Mg$_{0.25}$Zn$_{0.65}$O; d) sample Z: Be$_{0.03}$Mg$_{0.18}$Zn$_{0.79}$O. The spectral sampling width is 1nm. The localization parameters are determined from the fit with Equation (23).... 95

Figure 53. Temporal dependence of PL peak position of O-polar BeMgZnO samples grown on GaN at 15 K. Delay time equal to zero corresponds to the moment of pulse excitation. Note, vertical scales are different ................................................................. 97
Figure 54. The dependence of the degree of localization depth $\Delta_0$ (top) and the temporal redshift of the PL peak $\Delta E_t$ (bottom) on $r_{\text{Mg/Be}}$ content ratio.
List of Tables

Table 1. Descriptions of samples used in the investigation of the effects of strain on Indium incorporation ................................................................. 52

Table 2. Calculated strain in GaN for the templates used ................................................................. 54

Table 3. PL characteristics, and calculated indium contents for the structures used in this investigations emitting from purple to cyan ................................................................. 59

Table 4. Composition, Mg to Be content ratio (r_{Mg/Be}), out-of-plane lattice parameter (c), PL peak position (E_{PL}), characteristic energy (E_0), the exciton recombination time in the absence of the energy transfer ($\tau_0$), PL transients ($\tau$), degree of localization depth determined from the fit with Equation (23) to the spectral dependence of the decay time ($\Delta_0$), and $\Delta E_t$ is the observed temporal redshift of the PL peak position ................................................................. 96
Abstract

InGaN heterostructures are at the core of blue light emitting diodes (LEDs) which are the basic building blocks for energy efficient and environment friendly modern white light generating sources. Through quantum confinement and electronic band structure tuning on the opposite end of the spectrum, Ge$_{1-x}$Sn$_x$ alloys have recently attracted significant interest due to its potential role as a silicon compatible infra-red (IR) optical material for photodetectors and LEDs owing to transition to direct bandgap with increasing Sn. This thesis is dedicated to establishing an understanding of the optical processes and carrier dynamics in InGaN heterostructures for achieving more efficient visible light emitters and terahertz generating nanocavities and in colloidal Ge$_{1-x}$Sn$_x$ quantum dots (QDs) for developing efficient silicon compatible optoelectronics.

To alleviate the electron overflow, which through strong experimental evidence is revealed to be the dominating mechanism responsible for efficiency degradation at high injection in InGaN based blue LEDs, different strategies involving electron injectors and optimized active regions have been developed. Effectiveness of optimum electron injector (EI) layers in reducing electron overflow and increasing quantum efficiency of InGaN based LEDs was demonstrated by photoluminescence (PL) and electroluminescence spectroscopy along with numerical simulations. Increasing the two-layer EI thickness in double heterostructure LEDs substantially reduced the electron overflow and increased external quantum efficiency (EQE) by three fold. By incorporating δ p-doped InGaN barriers in multiple quantum well (MQW) LEDs, 20% enhancement in EQE was achieved due to improved hole injection without degrading the layer quality. Carrier diffusion length, an important physical parameter that directly affects the performance of optoelectronic devices, was measured in epitaxial GaN using PL spectroscopy.
The obtained diffusion lengths at room temperature in p- and n-type GaN were 93±7 nm and 432±30 nm, respectively. Moreover, near field scanning optical microscopy was employed to investigate the spatial variations of extended defects and their effects on the optical quality of semipolar (11\(\overline{2}\)2) and (1\(\overline{1}\)01) InGaN heterostructures, which are promoted for higher efficiency light emitters owing to reduced internal polarization fields. The near-field PL from the c+ wings in (1\(\overline{1}\)01) heterostructures was found to be relatively strong and uniform across the sample but the emission from the c- wings was substantially weaker due to the presence of high density of threading dislocations and basal plane stacking faults. In case of (11\(\overline{2}\)2) heterostructures, striated regions had weaker PL intensities compared to other regions and the meeting fronts of different facets were characterized by higher Indium content due to the varying internal field.

Apart from being the part and parcel of blue LEDs, InGaN heterostructures can be utilized in generation of coherent lattice vibrations at terahertz frequencies. In analogy to LASERs based on photon cavities where light intensity is amplified, acoustic nanocavity devices can be realized for sustaining terahertz phonon oscillations which could potentially be used in acoustic imaging at the nanoscale and ultrafast acousto-optic modulation. Using \(\text{In}_{0.03}\text{Ga}_{0.97}\text{N/In}_{x}\text{Ga}_{1-x}\text{N MQWs}\) with varying \(x\), coherent phonon oscillations at frequencies of 0.69-0.80 THz were generated, where changing the MQW period (11.5 nm -10 nm) provided frequency tuning. The magnitude of phonon oscillations was found to increase with indium content in quantum wells, as demonstrated by time resolved differential transmission spectroscopy. Design of an acoustic nanocavity structure was proposed based on the abovementioned experimental findings and also supported by full cavity simulations.
Optical gap engineering and carrier dynamics in colloidal Ge$_{1-x}$Sn$_x$ QDs were investigated in order to explore their potential in optoelectronics. By changing the Sn content from 5% to 23% in 2 nm-QDs, band-gap tunability from 1.88 eV to 1.61 eV, respectively, was demonstrated at 15 K, consistent with theoretical calculations. At 15 K, time resolved PL spectroscopy revealed slow decay (3 – 27 μs) of luminescence, due to surface traps and recombination of spin-forbidden dark excitons. Increase in temperature to 295 K led to three orders of magnitude faster decay (9 – 28 ns) owing to the thermal activation of bright excitons. These findings on the effect of Sn incorporation on optical properties and carrier relaxation and recombination processes are important for future design of efficient Ge$_{1-x}$Sn$_x$ QDs based optoelectronic devices.

This thesis work represents a comprehensive optical study of InGaN heterostructures and colloidal Ge$_{1-x}$Sn$_x$ QDs which would pave the way for more efficient InGaN based LEDs, realization of terahertz generating nanocavities, and efficient Ge$_{1-x}$Sn$_x$ based silicon compatible optoelectronic devices.
Chapter 1. Introduction

InGaN heterostructures are at the core of light emitting devices working in short wavelength region of the visible spectrum and extensive research has been undertaken for improving the performance of these devices in the past three decades. The advantage of the InGaN ternary alloy is that it can be used as the light emitting layer (commonly known as the active region) in violet, blue or even green light emitting diodes (LEDs) by varying only the mole fraction of Indium as the direct bandgaps for the wurtzite GaN and InN are 3.4 eV and 0.7 eV, respectively (Figure 1).

![Figure 1: Room temperature bandgap energy versus In composition for InGaN ternary within visible spectrum energy range](image)

Red, yellow and green LEDs, utilizing phosphide and arsenide materials, had been around since 1960s; however, without blue light, white LEDs could not have been produced.\textsuperscript{1,2,3} Despite considerable efforts, both in the scientific community and in industry, the blue LED had remained
a challenge for three decades. In early 1990s, contributions of Dr. Isamu Akasaki, Dr. Hiroshi Amano and Dr. Shuji Nakamura finally resulted in the demonstration of GaN-based high brightness blue LEDs and as a recognition of their revolutionary achievement, they were jointly awarded the Nobel Prize in Physics in 2014.\textsuperscript{4,5} Consequently, the invention of GaN-based efficient blue LEDs enabled the realization of efficient white light sources, which could be produced in two different ways. The most practical way that is dominantly employed today is by exciting a combination of yellow/green and red phosphors with blue LEDs, which results in red and green emission and when combined with blue produces white light. The alternative way is by mixing the light from individual red, green and blue LEDs (Figure 2), which increases the cost and brings about complexities associated with individual control of three different sources.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{white_light_generation.png}
\caption{Typical techniques of white light generation}
\end{figure}

Lighting by LEDs is by far the most energy efficient, ecologically friendly way of illumination with a very long operational lifetime. In addition to significant energy savings, high efficiency together with the long lifetime of LEDs ultimately results in much higher cost efficiency compared to conventional lighting. However, loss of electroluminescence (EL) efficiency in InGaN based blue LEDs at high injection currents limits full utilization of these advantages and the origin of this efficiency loss still remains to be a topic of debate. Therefore, identifying and characterizing
the principle mechanism responsible for efficiency degradation of InGaN based blue LEDs is critical in finding a way to minimize its effect and thereby improve the efficiency. This thesis primarily focuses on the enhancement of quantum efficiency in InGaN LEDs by reducing electron overflow, which based on a plethora of experimental evidence is suggested to be the dominating mechanism responsible for efficiency degradation, as well as on experimental techniques to quantify electron overflow.

Apart from being the part and parcel of blue and green light emitting devices, InGaN heterostructures can be used in generation of coherent acoustic phonons at terahertz frequencies. Coherent acoustic phonons provide a means to study electron-phonon interactions in semiconductor heterostructures and can be used in realizing acoustic phonon cavities. In analogy to LASER based on coherent light, phonon cavities would ultimately result in sound amplification by stimulated emission of radiation (SASER) devices. Potential applications of these devices include sources for acoustic nanoscopy, generation and manipulation of THz electromagnetic signals and ultrafast acousto-optic modulation. Phonon cavities using GaAs-based multilayer structures have already been demonstrated and are well established. However, III-nitride materials such as InGaN are preferred over GaAs for phonon cavities because the electron-phonon interaction in piezoelectric InGaN MQWs is much stronger than the deformation potential coupling in the GaAs material system. Therefore, as a big stride towards implementation of InGaN based SASER, design of an InGaN based acoustic cavity has been presented in this thesis.

Finally, investigation of optical properties and carrier dynamics in other semiconductor material systems such as colloidal Ge$_{1-x}$Sn$_x$ QDs, and epitaxial thin films of BeMgZnO quaternary has been carried out to explore their potential in optoelectronics.
1.1. Efficiency loss mechanisms in InGaN LEDs

In InGaN based LEDs, external quantum efficiency (EQE) reaches a peak value at relatively low current densities, typically below 50 Acm\(^{-2}\) (in some cases, as low as 1 Acm\(^{-2}\)), and then decreases dramatically with increasing injection current. This phenomenon is widely known as efficiency droop. Different mechanisms such as Auger recombination\(^9,10,11\), polarization and bias-enhanced electron overflow\(^12,13,14,15,16\), carrier delocalization and nonradiative recombination at defects, defect generation under high injection\(^17,18\) and junction heating\(^19\) have been proposed to be responsible for efficiency droop. Among these, Auger recombination and electron overflow received the most attention as the primary cause of efficiency degradation and therefore discussion in this dissertation will be focused on these two mechanisms. Before going into details of these two mechanisms, different types of carrier recombination processes in LEDs would be introduced first.

There are three types of carrier recombination: Shockley-Read-Hall (SRH) recombination, radiative recombination, and Auger recombination (Figure 3). In SRH recombination, an electron from the conduction band is trapped by an intermediate energy state, introduced through defects, and recombines with a hole which moves to the same energy state from the valence band. This is a non-radiative recombination process and is dominant in indirect bandgap semiconductors and at low level injection in LEDs. In radiative recombination, an electron from the conduction band directly recombines with a hole in the valence band producing a photon having an energy similar to the band gap. Auger recombination is a process in which an electron and a hole recombine and the resulting energy is given off to another electron or hole. As this process involves three or more carriers, Auger recombination becomes important at high injection levels.
Figure 3: Simplified schematic for different types of carrier recombination mechanisms in semiconductors. There are other possible radiative and nonradiative processes not shown here.

In order to better understand the carrier recombination and efficiency droop phenomenon in blue LEDs, simplified ABC model assuming no carrier overflow can be invoked. Within the framework of ABC model, the total recombination rate at high injection level can be written as

$$\frac{dn}{dt} = An + Bn^2 + Cn^3 - \left( G + \frac{J}{qd} \right)$$  \hspace{1cm} (1)

Here A, B, and C represent the SRH, radiative, and Auger recombination coefficients, respectively, and n is the carrier density. This equation has been derived under the assumption that A, B, and C coefficients are temperature, structure design, and injection level independent. The last term (inside bracket) in Equation (1) is included if there is generation by photo excitation or/and by injection current. G is the generation rate by optical excitation, J is the injection current density, q is the elementary charge, and d is the thickness of the active region.
1.1.1. Auger recombination

There are two types of Auger recombination, direct and indirect. In the direct variety, as defined earlier, the energy given off by an electron dropping to the valence band from the conduction band is consumed to excite another electron or hole to higher states satisfying energy and momentum conservations (Figure 4a). The indirect Auger recombination, which can occur in parallel to the direct variety, includes phonon-assisted, alloy scattering assisted and/or defect assisted processes (Figure 4b).

![Figure 4. Typical (a) direct and (b) indirect Auger recombination. There are other varieties of Auger processes not shown in this figure.](image)

It has been reported that the direct Auger recombination coefficient \( C \) in InGaN layers is almost an order of magnitude smaller than that associated with indirect Auger recombination. Considering that the direct Auger process is less likely in wider gap materials such as InGaN and yet the Auger process is assumed to be taking place to an extent as to account solely for the efficiency loss, one must then evoke the notion that the Auger process that is taking place must be
the indirect Auger variety, which would be more likely in relatively low quality material if alloy and compositional fluctuations are involved.

Recently, Iveland et al.\textsuperscript{20} reported detection of Auger electron under electrical carrier injection in an InGaN LED by using electron emission spectroscopy and concluded that droop phenomenon originates from Auger recombination. However their spectroscopic analysis of Auger induced hot electrons as they traverse through the $\Gamma$ and L bands before being emitted into the vacuum by means of cesiated surface, challenges the existing theories and some experiments regarding carrier scattering and $\Gamma$-L valley energy separation.\textsuperscript{21} A simple and direct way to see the effect of Auger recombination is through photoluminescence (PL) under below barrier resonant excitation, in which the photons are absorbed only in the InGaN active region with ensuing photo excitation of equal number of electrons and holes followed by their thermalization and either radiative or nonradiative recombination only in the same region. In most of the resonant PL experiments, no Auger induced hot electrons were observed to exist and the internal quantum efficiency (IQE) degradation has not been noted at photo carrier generation rates comparable to the electrical injection levels where the EL efficiency shows degradation.\textsuperscript{13,15} If the Auger process came into the picture at the injection levels of the order of hundreds of $\text{A/cm}^2$, this should be observable in resonant PL experiments at high excitation densities.

Contradicting the above mentioned observations, Binder et al.\textsuperscript{22} investigated two color structures wherein when the lower bandgap layer (green) is resonantly excited, the higher bandgap (UV) region emits light, which was attributed to hot electrons created by the Auger process in the lower bandgap layer (green) traversing to the higher bandgap one (UV) followed by radiative recombination. This report, however, is void of quantum well (QW) thicknesses and excitation power density levels used. Moreover, Hader et al.,\textsuperscript{23} using a fully microscopic model to emulate
this particular experiment, reported that a resonant laser tuned to create carriers only in the green region does also create carriers in the UV region even in the absence of any Auger process. The reason provided is that the polarization excited by the spectrally narrow optical pulse dephases in a few tens of femtoseconds due to electron–electron and electron–phonon scattering. In this scenario, the free carriers are generated through coupling between the optical pulse and the associated material polarization, causing the total spectral width of the excitation to be dominated by dephasing time of the polarization, not by that of the optical pulse. The resulting spectral width is argued to be sufficiently wide to excite the UV QW as well. Due to the very small coupling between the states in the green region and those of the UV region, the carriers generated in the UV region do not relax to states in the green region, which paves the way for UV emission.

Moreover, a two color LED structure (Figure 5) having a blue and an UV quantum well (QW) was investigated in order to detect Auger recombination experimentally. The idea was similar to that of Binder et al; the longer wavelength QW (blue) would be resonantly excited to see emission from shorter wavelength QW (UV) which would then be attributed to hot electrons created by the Auger process in the blue QW traversing to the UV QW followed by radiative recombination.

![Figure 5. Simplified conduction band schematic of the two color LED structure](image)

However, the resonant excitation of the blue QW region using a frequency doubled Ti:Sapphire laser of ~ 100 fs pulse width and 80 MHz repetition rate did not result in any detectable
emission from the UV QWs (400 nm) even at a laser excitation density corresponding to a carrier density of $10^{19} \text{ cm}^{-3}$, much larger than the injection densities employed in LEDs (Figure 6).

![Graph showing emission from UV QWs](image)

**Figure 6:** With 425 nm excitation at 15 K, only the PL peak from low energy blue QW (460 nm) can be observed at an excitation density corresponding to $10^{19} \text{ cm}^{-3}$ photo-generated carrier concentration. No emission from the larger bandgap UV QW (400 nm) was observed. The spectral range near the excitation laser line is blocked.

Finally, if Auger recombination was the dominant factor responsible for the efficiency degradation then InGaN-based lasers which require high injection levels would be hurt even more, which is obviously not the case. So it is reasonable to conclude that Auger recombination cannot be the dominating factor responsible for efficiency droop.

1.1.2. Electron overflow

The escape of electrons from the active region (quantum well) in forward bias and thereby escape from radiative recombination inside active region is referred to as electron overflow. Two
mechanisms are mainly responsible for electron overflow in InGaN heterostructures: (1) thermionic emission of electrons thermalized in the active region over the barrier into the p-layer; (2) ballistic and quasi-ballistic transport of the injected electrons across the active region. Ballistic and quasi-ballistic electrons refer to those that experience no scattering and one (either longitudinal optical (LO) phonon emission or absorption) or two scattering events in the active region, respectively (Figure 7).

![Figure 7: Schematic of electron overflow caused by ballistic or quasi-ballistic electron transport across the InGaN active region.](image)

Thermionic emission contribution to the electron overflow is very small in the InGaN system due to the large band discontinuities\(^{24}\) and therefore, ballistic and quasi-ballistic transport of hot electrons is the dominating factor for electron overflow. So far, extensive experimental results suggest that the electron overflow is the most likely cause for the efficiency degradation in InGaN-based LEDs under high current injection.\(^{16,25}\) Therefore, estimation of electron overflow and exploring the effects of LED design in reducing the overflow are pivotal for improving the performance of InGaN LEDs. Calculation of electron overflow from band structure simulation has already been reported.\(^{26}\) However, experimental estimation of electron overflow in InGaN LEDs
has hardly been employed so far. Experimental estimation of electron leakage, escape of electron from active region in reverse bias, can be obtained from I-V measurements of LEDs performed with and without optical excitation. The difference in measured current corresponds to the electrons escaped from active region. Both below (resonant excitation) and above (non-resonant excitation) GaN bandedge optical excitation can be used. However in case of non-resonant excitation, absorption in top p-layer has to be taken into account and the fraction of photons absorbed in the active region can only be determined if the minority carrier diffusion length in top p-GaN is known.

1.1.2.1. Active region volume

A simple and straightforward way to reduce electron overflow and increase quantum efficiency is to increase active region volume which would result in accommodation of more carriers for radiative recombination. This can be achieved either by increasing the thickness of a single double-heterostructure (DH) or by employing multiple DH separated by barriers (Figure 8).

![Figure 8. Illustration of increasing active region volume, (a) by increasing thickness of single a DH layer, (b) by employing multiple thin DH layers separated by barriers](image)

However, in thick single DH LEDs, electron and hole wavefunctions are widely separated particularly at low injection levels, which results in reduced radiative recombination rate and low
quantum efficiency.\textsuperscript{27,28} Moreover, large peak emission energy shifts are observed with injection when the single DH thickness is increased.\textsuperscript{27}

1.1.2.2. Electron blocking layer

In order to reduce electron overflow, an AlGaN electron blocking layer (EBL) is commonly employed in InGaN LEDs. EBL is inserted between InGaN active region and $p$-GaN layer to prevent electron leakage from the active region. However, there are several disadvantages of using EBL. First of all, the EBL impedes hole injection due to the barrier it introduces in the valence band after $p$-GaN. Using numerical simulations, the reduced IQE in InGaN-based LEDs with EBL due to poor hole transport has been demonstrated by Ryu and Lee.\textsuperscript{29} Moreover, the AlGaN EBL is located on top of the InGaN barrier of the active region, and the lattice mismatch between AlGaN and InGaN generates a piezoelectric polarization field in addition to differential spontaneous polarization field. These two fields together pull down the conduction band at the AlGaN/GaN interface. As a result, the effective barrier height of the AlGaN EBL is compromised, and the electron overflow is not effectively suppressed.\textsuperscript{14}

![Figure 9. Illustration of EBL and EI in a simplified conduction band diagram](image-url)
1.1.2.3. Electron injector layer

Another way to minimize overflow is employing electron injector (EI) layer inserted between $n$-GaN layer and InGaN active region which acts as an electron cooler by promoting the interaction of ballistic and quasi-ballistic electrons with LO phonons to reduce the gained kinetic energy of the injected electrons. It was demonstrated that the electron overflow and the associated efficiency loss can be effectively reduced without hampering hole transport by incorporating staircase electron injector (SEI), stepwise indium composition increased InGaN layers inserted between $n$-GaN layer and InGaN active region, in the LED design. Two layer SEI with intermediate layer compositions of $\text{In}_{0.04}\text{Ga}_{0.96}\text{N}$ and $\text{In}_{0.08}\text{Ga}_{0.92}\text{N}$ has been reported to be effective in reducing electron overflow in LEDs having active region of $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$. Indium contents in the SEI layers are chosen in such a way that each of the two steps are greater than the LO phonon energy of 88 meV.

1.1.2.4. Carrier injection symmetry

Electron overflow and subsequently efficiency degradation also occurs because of asymmetrical doping in GaN, resulting in an insufficient supply of holes to the active region under electrical injection. Since hole injection lags behind electron injection, the radiative recombination cannot keep up with increasing carrier injection. This results in either electron escape to $p$-GaN without recombination or electron accumulation in the active region causing internal bias which opposes further carrier injection and thereby reduces radiative recombination efficiency. To address the problem of asymmetric carrier injection, the efforts have focused on either increasing hole concentration in $p$-GaN or $p$-type doping of the barriers in the multi-well LED structures. Regarding the second approach, presence of Mg in the active region has a
detrimental effect on LED efficiency manifested as diminishing band edge emission with increasing Mg content.\textsuperscript{33} However, incorporation of a $\delta$ p-doped barrier can overcome that problem of active region quality degradation.

1.1.3. Reduced polarization fields in semi-polar LEDs

Conventional InGaN-based LEDs are usually grown with the crystal structure in a c-plane orientation due to its well-established technology even though polarization inherent to this orientation limits the device performance. Polarization fields cause spatial separation of electron and hole wave functions in the active region and reduce the radiative recombination rate especially at low injections as well as worsen the electron overflow scenario. This is the well-known quantum confined Stark effect (QCSE). This effect is more severe in longer wavelength devices, significantly reducing the quantum efficiency of green/yellow LEDs. Theoretical calculations predict that the piezoelectric field across InGaN/GaN heterostructures would be considerably reduced in semipolar orientations.\textsuperscript{34} Figure 10 shows piezoelectric polarization and wavefunction overlap of the electrons and the holes in the conduction and valence bands in a 3 nm wide Ga$_{0.75}$In$_{0.25}$N quantum well.\textsuperscript{35} It is obvious that semipolar orientations (vertical lines around 60°; (1101), (1122)) has increased electron and hole wavefunctions overlap and reduced polarization charge compared to c-plane.
1.2. Coherent acoustic phonons in InGaN heterostructures

As mentioned previously, InGaN heterostructures can be used in generation of coherent acoustic phonons at terahertz frequencies. Different methods such as impulsive stimulated Raman scattering (ISRS) and the displacive excitation of coherent phonons (DECP) have been proposed for explaining the generation of coherent phonons in semiconductors. In ISRS, the excitation pulse is only present for a fraction of the vibrational oscillation period. This short pulse impulsively
excites the vibrational mode, initiating coherent oscillations that continue after the pulse is gone. The coherent atomic motion is induced on the ground electronic state and because of that the atoms start to move from their equilibrium position and therefore the resulting oscillation should be a sine function of time. In case of DECP, the equilibrium coordinates of the ions experience a sudden shift as they couple to the photoexcited carriers induced by the optical pulse. After the excitation, the lattice abruptly tries to adjust to the new electronic state by moving toward and oscillating about a new equilibrium position. In this case the coherent atomic motion is induced on the excited electronic state with the phonon amplitude maximum at photo-excitation and therefore the resulting oscillation should be a cosine function of time. It has been proposed that the coherent phonon generation mechanism in InGaN MQWs is similar to the DECP and strain induced piezoelectric field plays an important role in it. The carriers generated by an optical pulse shorter than the vibrational period partially screen the built-in piezoelectric field. This results in an immediate change in the material stress and excitation of the vibrational mode.

Generation and direct observation of coherent oscillation of phonon modes have been made possible by the tremendous progress in femtosecond lasers and ultrafast optical spectroscopy. The optical investigation of acoustic phonons in bulk semiconductors is challenging because the phonon dispersion relation permits only low frequency Brillouin scattering. However in semiconductor superlattices, nonzero frequency acoustic phonons can be observed at the Brillouin zone (BZ) center. Additional periodicity of the superlattice along the confinement direction results in the folding of the bulk acoustic dispersion relation into a smaller superlattice BZ. This folding of the acoustic branches gives rise to additional optical phonon-like modes of the superlattice, termed as zone folded longitudinal acoustic phonons (ZFLAPs), with non-zero frequencies at the center of the BZ. Optical excitation using sub-picosecond pulses has been shown to generate low
frequency coherent acoustic phonons in bulk semiconductors. Zone-folding has allowed the observation of higher frequency coherent acoustic phonons near the zone center in superlattices.

1.3. Prospect of GeSn QDs and BeMgZnO thin films in optoelectronics

One of the better choices as possible alternatives to conventional materials used in light emitting devices are group IV semiconductors such as Silicon and Germanium, because of their well-established technology, large natural abundance, and low cost of elemental components. Germanium has attracted significant interest as an infra-red (IR) optical material in photodetectors, thermal imaging cameras, phosphors, and light emitting diodes. However, the major limitation for efficient use of Ge in optical/optoelectronic applications is its indirect band structure, which makes its interactions with light (i.e. absorption/emission) much less efficient than those of direct bandgap semiconductors. Theoretical studies suggest that the band structures of Ge can be modified by alloying with Sn to reduce the energy difference between the first direct and indirect transitions, and beyond a certain Sn concentration even purely direct gap transition is achievable. As the incorporation of Sn (bandgap, $E_g = 0.08$ eV) makes the fundamental energy gaps of such alloys narrower and closer to metallic behavior, the use of semiconductor quantum dots (QDs) can offer the advantage of wider bandgap tunability, due to the effects of quantum confinement, in addition to enhanced optical efficiency. Thin films of Ge$_{1-x}$Sn$_x$ alloys produced via chemical vapor deposition and molecular beam epitaxy are well-studied and exhibit tunable band gap energies in the mid-IR region. However, growth of homogenous Ge$_{1-x}$Sn$_x$ thin film alloys is challenging due to the emergence of phase segregation in high temperature growth and
because of poor crystallinity and presence of high density of defects in case of low temperature growth.\textsuperscript{54,55} Colloidal synthesis is a low cost alternative approach to attain high quality, solution-processable Ge\textsubscript{1-x}Sn\textsubscript{x} QDs avoiding phase segregation of Sn.\textsuperscript{56,57} The synthesis of phase-pure Ge\textsubscript{1-x}Sn\textsubscript{x} nanoalloys with sizes in the range of 15 −23 nm and 3.4−4.6 nm with Sn compositions up to x = 0.279, have been demonstrated.\textsuperscript{56} Therefore, optical properties and carrier dynamics in colloidally synthesized Ge\textsubscript{1-x}Sn\textsubscript{x} QDs of sub-3 nm size would be worth investigating due to the presence strong quantum confinement effect.

ZnO based materials are attractive for optoelectronic applications due to their large bandgaps (3.3 eV for ZnO) and large exciton binding energies (60 meV for ZnO).\textsuperscript{58,59} Particularly attractive is quaternary Be\textsubscript{x}Mg\textsubscript{y}Zn\textsubscript{1-x-y}O alloy for UV and solar blind applications, and intersubband transition devices, owing to its wide bandgap, lattice tunability and its matching to ZnO. Wide band-gap tunability can be achieved in Be\textsubscript{x}Mg\textsubscript{y}Zn\textsubscript{1-x-y}O by changing the compositions of BeO and MgO, which also allows for suppression of strain-induced phase separation. The performance of heterostructure devices is highly sensitive to the material quality, which in turn is governed by defects. Carrier lifetimes, which are extremely sensitive to the type and quality of defects, are strongly affected by carrier localization, which is well pronounced in wide-bandgap semiconductor alloys due to large differences in metal covalent radii and the lattice constants of the binaries. Therefore, study of carrier dynamics is imperative in order to evaluate material quality and possibly to correlate it with carrier localization.
1.4. Organization of the thesis

This thesis represents a comprehensive optical study focused on InGaN heterostructures, for both photonic and phononic applications, and nanostructures based on Ge$_{1-x}$Sn$_x$ and BeMgZnO quaternary alloys as potential candidates for optoelectronics. A set of experimental techniques such as photoluminescence (PL), time-resolved PL, near-field scanning optical microscopy (NSOM), time-resolved differential transmission (TRDT) were used to evaluate and optimize the active region quality of light emitting devices and acoustic cavities based on polar InGaN heterostructures and to explore recombination dynamics and defect related luminescence in semipolar InGaN heterostructures, Ge$_{1-x}$Sn$_x$ QDs, and BeMgZnO thin films. Silvaco Atlas software was used to simulate the electronic energy bands, carrier concentration and radiative efficiency in InGaN based LED structures and these results were consistent with what observed experimentally and also helped to better understand the device physics.

Chapter 2 reports on improvement of quantum efficiency of InGaN heterostructure based light emitting devices. This chapter starts with a discussion on the determination of carrier diffusion length in GaN by PL and CL spectroscopy followed by the estimation of electron leakage by photocurrent technique using non-resonant optical excitation where the obtained diffusion length value was used. A technique for determining carrier injection efficiency will be presented from which electron overflow can be deduced. Next, different techniques such as employing multiple double heterostructure active region, optimizing electron injector layers, and introducing delta p-doped barriers will be discussed that were applied to improve the quantum efficiency (up to four fold increase) of InGaN based LEDs at high injection current. Enhancement of Indium incorporation, useful property for efficient long wavelength light emitters, to InGaN MQWs on
AlN/GaN periodic multilayers will be presented next followed by the near-field scanning optical microscopy of semipolar (1\bar{1}01) and (11\bar{2}2) oriented GaN and InGaN heterostructures.

In Chapter 3, basic theory of phonon dispersion in bulk and superlattice structures is presented first. Next, generation and detection of ZFLAPs in InGaN heterostructures by TRDT technique will be discussed along with the optimization of phonon generating active region. Finally design of an acoustic nanocavity will be proposed based on the theoretical calculation of phonon dispersion relation and reflectivity and experimental results of optimized active region.

Chapter 4 will discuss the prospect of colloidal Ge\textsubscript{1-x}Sn\textsubscript{x} QDs and BeMgZnO quaternary thin films in optoelectronic applications. Experimental demonstration of optical gap engineering and investigation on carrier dynamics in Ge\textsubscript{1-x}Sn\textsubscript{x} QDs, supported by theoretical calculation will be presented first. SSPL and TRPL measurements to investigate the effect of Mg/Be ratio on carrier localization and optical performance of BeMgZnO quaternary alloys will follow. All the results are summarized and overall conclusions and outlook are provided in Chapter 5.
Chapter 2. Efficiency enhancement in InGaN LEDs

Different processes are responsible for efficiency loss in InGaN LEDs and two major mechanisms, Auger recombination and electron overflow, have been discussed in Chapter 1. However, as alluded earlier, electron overflow is arguably the leading mechanism for efficiency degradation in InGaN based blue LEDs. Therefore it is imperative to devise overflow measurement techniques as well as to figure out various strategies to improve efficiency by reducing overflow and other deleterious processes in LEDs. Before discussing different efficiency improvement strategies, determination of electron leakage will be presented followed by a technique for estimating electron injection efficiency, which is another representation of electron overflow.

2.1. Determination of diffusion length in GaN

As alluded in Chapter 1, in order to determine electron leakage in InGaN LEDs using non-resonant excitation, carrier diffusion length in p-GaN needs to be known to take the absorption in top p-GaN in to account. To this end, diffusion length in p-GaN was determined using PL measurements. In order to explore the effect of doping, diffusion length in n-GaN was also measured using the same technique. Various experimental techniques such as electron beam induced current (EBIC), junction based photocurrent, time resolved four wave mixing, light induced transient grating (LITG), and surface photo-voltage spectroscopy have been devised for determination of carrier diffusion length in GaN and a wide range of values ranging from 50 nm to 3.4 µm have been reported depending on the material quality, sample thickness, doping levels, and the techniques used. All these methods require either advanced non-linear optical techniques or electrical contacts and therefore diffusion length in GaN was determined using a simple technique.
2.1.1. Diffusion length in p-GaN from PL spectroscopy

The samples used for the determination of carrier diffusion length in p-GaN was c-plane 6 nm thick In$_{0.15}$Ga$_{0.85}$N double heterostructure (DH) active region grown on a ~3.7 µm-thick n-type GaN template on sapphire in a vertical low-pressure metalorganic chemical vapor deposition (MOCVD) system. A 60 nm Si-doped (2×10$^{18}$ cm$^{-3}$) In$_{0.01}$Ga$_{0.99}$N underlying layer was inserted just beneath the active region for improving the quality of the overgrown layers. The structures were completed with Mg-doped (chemical doping concentration ~ 10$^{19}$ cm$^{-3}$) p-GaN layer of 500-nm thickness (Figure 11). Hole concentration in p-GaN (after activation) was determined to be 5×10$^{17}$ cm$^{-3}$ from Hall measurements on a separate calibration sample. To mitigate the effect of any Mg out-diffusion from p-GaN on the optical quality of the active region, a 20 nm thick In$_{0.01}$Ga$_{0.99}$N spacer layer was grown in between.

![Figure 11: Cross-sectional schematic of the InGaN-based DH samples investigated. The steps of different height are generated by ICP etching.](image)

To achieve p-type layers with different thicknesses, selective area inductively coupled plasma (ICP) etching was used in multiple steps. ICP etching introduces surface damage which modifies the PL intensity. To minimize this effect, a two-step etching procedure, a high power, i.e. physical
etch step followed by a low power, i.e. chemical etch, was employed. This two-step etching process was found to help with the surface recovery so that the effect of etching on PL intensity could be neglected. Etched thickness of the top layer was determined after each etching step using a surface profiler (errors bars indicated in Figure 12 are representative of thickness variations). PL measurements were carried out on regions with different p-GaN thickness using He-Cd laser (325 nm wavelength) excitation with resulting photogenerated carrier concentrations ($n$) from $1.2 \times 10^{18}$ cm$^{-3}$ to $3.9 \times 10^{18}$ cm$^{-3}$. At a given excitation power, the carrier density was determined from the generation rate at steady state, $G = An + Bn^2 + Cn^3$, assuming that electron and hole capture cross-sections are equal, and $n$ is much higher than the background carrier concentration, which is justified (background concentration $\sim 10^{17}$ cm$^{-3}$). The Shockley-Read-Hall, bimolecular, and Auger recombination coefficients of $A = 5 \times 10^7$ s$^{-1}$, $B = 5 \times 10^{-11}$ cm$^3$s$^{-1}$, and $C = 10^{-31}$ cm$^6$s$^{-1}$, respectively, were used.\textsuperscript{71} The carrier generation rate, $G$, was calculated using $G = [P\alpha(1-R)]/(Sh\nu)$, where $P$ is the excitation laser power incident on the sample, $\alpha$ is the absorption coefficient at the excitation photon energy $h\nu$, $R$ is the Fresnel reflection coefficient for the sample/air surface, $S$ is the laser spot size on the sample surface. Due to the large absorption coefficient ($1.2 \times 10^5$ cm$^{-1}$)\textsuperscript{72} at the excitation wavelength, carrier photogeneration takes place near the surface region of the sample, and upon diffusion of carriers away from the surface the PL emanating from the active region, spacer layer, underlying InGaN and underlying n-GaN is measured. The thicker the top layer, the less intense the PL is from the underlying layers. The PL intensity of the etched region was compared with that from the corresponding un-etched reference region to minimize the effect of any variation across the sample. It should be noted that as the top GaN layer is made thinner, more of the excitation light penetrates into the active region and the underlying layers and gets absorbed there. The resulting PL is then due to recombination of both
the directly photogenerated carriers and those diffusing from the top GaN. Figure 12 shows the integrated PL intensity of the active region plotted as a function of the p-GaN layer thickness at 295 K and at 15 K, taking into account the absorption of incident laser power in the top p-GaN and In_{0.01}GaN spacer layer. With increasing p-GaN layer thickness, the normalized PL intensity exhibits an exponential decay of the form $e^{-x/L_{\text{diff}}}$, where $x$ is the p-GaN thickness and $L_{\text{diff}}$ is the diffusion length. The diffusion lengths in p-GaN extracted from the fits are 93±7 nm and 70±7 nm at 295 K and 15 K, respectively. The error in the diffusion length measurements by PL originates mainly from the thickness nonuniformity across the sample introduced by multiple ICP etching steps. The same values within the error bars were obtained from the fits to the integrated PL intensities emanating from the underlying n-GaN as well as the spacer and underlying In_{0.01}GaN layer, the individual contributions from which cannot be identified due to their identical bandgap. In case of underlying n-GaN PL intensity data, the effect of absorption of n-GaN emission in the top p-GaN was taken into account. It is worth mentioning that as the penetration depth of the exciting laser is 83 nm in GaN, this 93±7 nm of diffusion length in p-GaN represents only the upper limit for this parameter. A typical PL spectrum (region with 100 nm thick p-GaN) is shown in the inset of Figure 12. As is often the case, it should be noted that due to high Mg doping, there is nearly no near band edge emission from the p-GaN layer.
2.1.2. Diffusion length in n-GaN from PL spectroscopy

For determination of diffusion length in n-type GaN, a sample with a 1.5 μm thick top n-GaN layer, instead of 500 nm p-GaN, was used. Rest of the layers were the same as depicted in Figure 11. As the emission from the underlying n-GaN layer cannot be differentiated, intensities of PL from the \text{In}_{0.01}\text{GaN} layer and the active region were monitored to determine the diffusion length. In Figure 13, integrated active region and \text{In}_{0.01}\text{GaN} layer PL intensities are plotted as a function of the top n-GaN thickness. Exponential decay fits to active region data in Figure 13 revealed diffusion lengths of 432±30 nm at 295 K and 316±30 nm at 15 K in n-GaN. It should be noted that the internal absorption in InGaN region does not affect the diffusion length values deduced from
PL data. As the regions with different top GaN layer thicknesses contain the same underlying InGaN and the InGaN active region, the percentage of light emitted from GaN that is absorbed in the InGaN layers is the same for all these regions. Underlying InGaN PL spectra could not be used for diffusion length estimation particularly at 15 K as the emission from the InGaN layer could not be distinguished from that emanating from n-GaN for top n-GaN thickness of 450 nm or more.

![Figure 13: Integrated PL from the active region at 15 K and 295 K as a function of n-GaN thickness. The lines are exponential fits to the data for the active region. Data at 295 K and 15 K are shifted vertically for clarity.](image)

Carrier diffusion length in p-GaN is smaller than in n-GaN, which is expected because a large concentration of Mg tends to degrade sample quality and these substitutional Mg atoms act as traps for carriers and give rise to trap assisted recombination which eventually becomes the dominant recombination mechanism. This observation is consistent with literature as the diffusion length has been reported,\(^{69}\) using EBIC method, to decrease drastically from 950 nm to 220 nm with increasing Mg doping from \(4\times10^{18}\) cm\(^{-3}\) to \(3\times10^{19}\) cm\(^{-3}\) for low dislocation densities below \(10^8\).
The decrease in diffusion length at low temperature in both n- and p-GaN is mainly due to the increased ionized impurity scattering which is dominant at low temperatures. As the thermal velocity of the carriers reduce, the effect of long-range Coulomb interactions on their motion increases. Moreover, radiative recombination rate increases with decreasing temperature, and consequently, shorter recombination lifetime reduces the diffusion length.

2.1.3. Diffusion length in n-GaN from CL spectroscopy

To augment the PL data, carrier diffusion lengths in n-GaN were also determined by CL in a scanning electron microscope using samples prepared in cross-section to allow direct access to the vertical layer stack. For excitation, an acceleration voltage of 5 kV was used for electrons and the beam current was set to 500 pA. Under these conditions, the excess carrier concentration was calculated to be $\sim 10^{17}$ cm$^{-3}$, which is more than one order of magnitude lower than the lowest carrier concentration in effect in our PL measurements ($1.2 \times 10^{18}$ cm$^{-3}$). The excited area was 50 nm in diameter. As the electron beam scans across the layers, a CL linescan is obtained by correlating the position of excitation beam and the spectral emission from the sample. The InGaN active region, and spacer and underlying layers, spectrally separated from GaN, are used as a position marker. As the area excited by the electron beam approaches the position of the InGaN layers, an increasing number of carriers are able to reach these layers by diffusion and recombine there radiatively, which manifests itself as increased CL intensity. The CL profile spectrally integrated over the InGaN layers, inclusive of the active region, is shown in Figure 14. Under the assumption that the CL intensity is proportional to the number of carriers that reach the InGaN layers, the exponential increase in the profile provides the diffusion length of the carriers as in the case of PL experiments discussed above. As the excitation spot further approaches the exact
position of the InGaN layers, a stronger increase in CL intensity is observed in the CL profiles. Here the luminescence is not only generated by diffusion of carriers, but also by the excitation range of the electron beam gradually reaching the InGaN layers and generating electron-hole pairs directly within the InGaN layer. The related peak in the InGaN profile as well as the dip in the GaN profile (also shown in Figure 14) between 1.9 and 2.3 \( \mu m \) is thus associated with the direct photoexcitation range of the electron beam. The diffusion length determined from the CL cross-sectional linescan in Figure 14 is 525±6 nm at 6 K for the unintentionally doped n-GaN.

Figure 14: CL intensity profile for the GaN and the spectrally integrated InGaN luminescence from 366 nm to 474 nm along the cross-section of the sample at 6 K.

CL measurements at room temperature were not conclusive due to a low signal to noise ratio. Moreover, diffusion length in p-GaN could not be determined from the CL measurements. The thickness of the p-GaN cap is 500 nm, which was found to be the upper limit to maintain a good quality active region underneath due to the much higher growth temperature of p-GaN and the
associated degradation of the active region due to Mg out-diffusion. As shown in Figure 14, the diffusion length in n-GaN could be deduced from the InGaN CL intensity profile in the electron beam excitation range of ~250 nm away from the surface to ~350 nm away from the active region to account for only the diffusion contribution to CL intensity. Therefore, the thickness of a sample has to be more than 600 nm to determine the diffusion length by the CL technique.

2.1.4. Comparison of PL and CL measurements

Diffusion length measured by PL in unintentionally doped n-GaN at low temperature is 40% lower than that measured by CL. This change mainly stems from the difference in excitation densities employed and thus the difference in resulting photogenerated carrier densities in the two methods. The lowest photogenerated carrier density that could be possible in our PL measurements ($1.2 \times 10^{18}$ cm$^{-3}$) is an order of magnitude higher than that in CL measurements ($10^{17}$ cm$^{-3}$). As the photo-generated carrier concentration increases from $10^{17}$ cm$^{-3}$ to $10^{18}$ cm$^{-3}$, carrier recombination rate (both radiative and non-radiative) increases and thereby lifetime decreases but carrier diffusivity remains nearly constant ($D \approx 1.5$ cm$^2$s$^{-1}$).\textsuperscript{73,74} Therefore, diffusion length, which is the square root of the product of carrier lifetime and diffusivity, decreases with increasing photogenerated carrier concentration. However when the photo-generated carrier density goes beyond $10^{18}$ cm$^{-3}$, diffusivity starts increasing,\textsuperscript{73} compensating for the decrease in lifetime, which is why the diffusion length was found independent of photo-excited carrier densities within the range employed in PL measurements: $1.2 \times 10^{18}$ cm$^{-3}$ to $3.9 \times 10^{18}$ cm$^{-3}$. For PL, only the results for the highest excitation density used are presented above. Lin \textit{et al.}\textsuperscript{66} have reported a 40% decrease in carrier diffusion length when excitation density was changed by two orders of magnitude. Using the LITG technique, in-plane diffusion lengths of 1.7 μm and 1 μm have been measured at photo-
excited carrier concentrations of $10^{16}$ cm$^{-3}$ and $5\times10^{18}$ cm$^{-3}$, respectively, in a 400 µm thick bulk c-GaN sample. Along the c-direction these numbers correspond to 1.57 µm and 0.92 µm, calculated using an anisotropy ratio of 1.17 for diffusivity perpendicular and parallel to the c-axis.$^{74}$ This longer diffusion length in bulk GaN compared to the epitaxial layer used here is expected due to its better structural quality. For a 1.7 µm thick n-type GaN film grown on sapphire by MOCVD, using the time-integrated photoluminescence method Lutsenko et al.$^{64}$ reported a diffusion length of 200 nm, which is much smaller than the value reported here due to the much higher excitation density used (200 kW/cm$^2$ with a corresponding $\sim10^{19}$ cm$^{-3}$ photo-generated carrier density).

The carrier diffusion length of 93±7 nm in p-type GaN has been used in the determination of carrier leakage with non-resonant excitation which is discussed in the following section.

2.2. Determination of electron escape rate in InGaN LEDs

For experimental determination of electron leakage, a c-plane InGaN LED structure, emitting at ~430 nm, was grown on ~3.7 µm-thick n-type GaN templates on sapphire in a vertical low-pressure MOCVD system. The active region was composed of 6 nm-thick In$_{0.15}$Ga$_{0.85}$N and a 60-nm Si-doped (2×10$^{18}$ cm$^{-3}$) In$_{0.01}$Ga$_{0.99}$N underlying layer was grown just beneath the active region for improving the quality of the overgrown layers. A 10 nm EBL of Al$_{0.2}$Ga$_{0.8}$N was deposited on top of the active layer. The LED structure was completed with Mg-doped p-GaN layer of 100-nm thickness having 4×10$^{17}$ cm$^{-3}$ hole density, as determined by Hall measurements on a separate calibration sample. For devices, square mesa patterns (400×400 µm$^2$) were formed by conventional lithography and Chlorine-based inductively coupled plasma (ICP) etching. Ti/Al/Ni/Au (30/100/40/50 nm) metallization annealed at 800°C for 60 s was used for n-type ohmic contacts,
and 5 nm/5 nm Ni/Au electrodes served as the semi-transparent p-contact. Finally, 40/50 nm Ni/Au electrodes were deposited on part of the mesas for contact pads. I-V measurements were carried out for the LED structure with and without optical excitation. A CW HeCd (wavelength 325 nm) laser was used for optical excitation. Multiple devices were measured for the LED sample and no significant variation was observed across the sample. The representative data are presented in Figure 15 (a). As the excitation density increases from 0 to 280 Wcm⁻² (photo-excited carrier density, \( n \sim 9 \times 10^{17} \text{cm}^{-3} \)), reverse current also increases due to increased photo-current (as a result of electron leakage). Moreover, with increasing reverse bias, band bending increases resulting in higher electron leakage percentile.

![Figure 15: (a) I-V curve and, (b) electron leakage percentage at different photo-generated carrier density.](image)

Under forward bias, hot electrons travel from n-GaN to p-GaN escaping recombination in the active region. In this experiment, reverse biased LED was illuminated with HeCd excitation which resulted in generation of electron-hole pairs not only in the active region but throughout the whole
structure depending on the penetration depth (83 nm). Carriers were created mostly in the top p-GaN and electrons diffused from p-GaN to n-GaN. Electron leakage rate was calculated from photo-current while the injected carrier rate was calculated using absorption and minority carrier diffusion profile of top p-GaN using the diffusion length value calculated in the previous section. The ratio of electron escape (leakage) to generation rate as a function of reverse bias is plotted in Figure 15 (b) for different photo-generated carrier density.

Moreover, carrier injection efficiency (IE) was measured in LEDs to deduce electron overflow from it. The technique of IE determination is as follows. First the electroluminescence (EL) intensity, $I_{EL}(J)$ was measured at a certain current density $J$ and the corresponding generated carriers can be denoted as $n_{EL}(J)$. Then optical excitation $\Delta n_{pl}(J)$ was applied in addition to $n_{EL}(J)$ and the resultant luminescence intensity $[I_{EL}(J) + I_{pl}(J)]$ was recorded. Next, the optical excitation was removed and the forward current was increased until the total EL intensity $(I_{EL}(J + \Delta J))$ reaches the same intensity as $[I_{EL}(J) + I_{pl}(J)]$. The current required to reach this intensity was denoted as $\Delta n_{EL}(J)$. This measurement process was repeated for different forward current densities. It was found that the required electrical current $\Delta n_{EL}(J)$ to reach $[I_{EL}(J) + I_{pl}(J)]$ was always larger than $\Delta n_{pl}(J)$, which means the some portion of electrically injected carriers did not participate in the recombination process and escaped from the active region. The injection efficiency at the given $J$ per small carrier density increase can be determined to be

$$\eta(J) = \Delta n_{pl}(J) / \Delta n_{EL}(J)$$

And the IE $(J)$ therefore can be obtained by
\[ IE(J) = \frac{1}{J} \int_{0}^{J} \eta(J) dJ \] (3)

Figure 16 shows the measured IE vs. injection current density plot for 6-nm DH LEDs. IE is high at low current density and reaches peak at around 10-20 Acm\(^{-2}\). Beyond 30 Acm\(^{-2}\), IE starts to decrease. This observation can be explained with electron overflow phenomenon. As the injection current density increases, more hot electrons escape from the radiative recombination in the active region. Quantitatively, at 52 Acm\(^{-2}\), the electron overflow percentile is \(\sim 22\%\) for this LED structure.

![Figure 16. Measured IE in 6 nm DH LEDs. Multiple devices were measured and the data for a representative LED is presented.](image)
2.3. Optimization of active region thickness in InGaN LEDs

As increasing the thickness of a single DH active region results in poor electron-hole wavefunction overlap and large shift in PL peak with increasing injection, effect of employing multiple DH (MDH) active region was investigated for improving quantum efficiency and reduction of electron overflow in InGaN LEDs. The c-plane InGaN LED structures were grown on ~4 μm-thick n-type GaN templates on sapphire substrate in a vertical low-pressure MOCVD system. An \textit{in situ} SiN\textsubscript{x} nanonetwork was employed to reduce dislocation density in the GaN templates down to mid-10\textsuperscript{8} cm\textsuperscript{-3}.\textsuperscript{75} The active regions contained one to eight 3 nm-thick In\textsubscript{0.15}Ga\textsubscript{0.85}N DH active layers separated by 3 nm In\textsubscript{0.06}Ga\textsubscript{0.94}N barriers. All the structures incorporate EI layer for efficient thermalization of hot carriers prior to injection into the active region, and a 60-nm Si-doped (2×10\textsuperscript{18} cm\textsuperscript{-3}) In\textsubscript{0.01}Ga\textsubscript{0.99}N underlying layer for improving the quality of overgrown layers. The EI consists of two 5 nm InGaN layers with step-increased In compositions of 4% and 8%, inserted in the given order below the active region. The SEI steps have conduction band potential energy drop more than one LO phonon energy (92 meV for GaN) and thus enhance electron thermalization through LO-phonon emission. The LED structures were completed with 100 nm-thick Mg-doped \textit{p}-GaN layers having 6×10\textsuperscript{17} cm\textsuperscript{-3} hole density, as determined by Hall measurements on a separate calibration sample. The same device fabrication procedures using standard photolithography processes as described in section 2.2 were employed.

To evaluate the optical quality of MDHs, excitation power dependent resonant PL measurements were performed with a frequency doubled Ti:Sapphire laser of excitation wavelength 385 nm ensuring photo-injection of carriers only into the LED active regions. Figure 17 depicts PL efficiencies defined as the collected integrated PL intensity normalized to the incident laser power.
Figure 17. Relative PL efficiency of multi-3 nm DHs vs. injected carrier concentration at room temperature.

The injected carrier density was estimated from incident PL power on the samples according to Ref. 76 but invoking different absorbed laser power for various samples from transmission and reflectance measurements. Notably, the saturated PL efficiencies nearly scaled with the number of DH layers up to 6, showing ~ 2, 4 and 6.5 fold increase for dual, quad and hex DHs compared to single DH under carrier density $10^{18}$ cm$^{-3}$. Saturation of PL efficiency takes place for octal DH LED probably due to degradation of active region induced by strain relaxation resulting in enhanced non-radiative recombination at this active region thickness.

In order to study the impact of carrier overflow and other carrier transport features, EL efficiencies were measured on-wafer with light output collected primarily normal to the sample surface into an optical fiber (Figure 18).
As presented in Figure 18, the EL efficiency for the MDH structures with number of DH layers up to 4 increases at a fast rate with current injection and reaches its maximum at ~ 37 A/cm². The observed increase of peak EL efficiencies by 1.6 and 3.5 times that of single 3 nm DH is consistent with data of resonant PL efficiency shown in Figure 17. This significant improvement on EL efficiency by increasing the number of 3 nm DH layers (from 1 to 4) indicates that the amount of injected carriers captured by the active region is increased considerably, while further increase of layers introduces more nonradiative recombination centers. It should be noted that employment of low and thin InGaN barriers is essential for enhancing hole transport across the active region as demonstrated in literature. With continuously increasing the number of DHs, the EL efficiency of hex 3 nm DH LED did not scale to ~6 times that of the single 3 nm DH but is slightly larger than that from the quad 3 nm DH, which indicates that the injected holes are mostly consumed in the first four DHs. Further increasing the number of DH layers to 8 lowered the EQE
by ~20% compared to the hex 3 nm DH at a current density of 350 A/cm², which is an indicative of the layer quality degradation confirmed by PL measurements.

It is worth mentioning that the EL efficiency for all the DH LEDs except the hex and octal 3 nm DH show negligible degradation with increasing injection current density up to 500 A/cm². Thus the increase of DH layer up to four confirms the optimized DHs solution. In addition, the quad 3 nm DH LED structure outperforms a typical MQW LED having the same total active layer thickness (6×2 nm well) and a slightly thinner single 9 nm-thick DH, which was reported to have 1.25 and 3.8 times higher relative EL efficiency than that of 6 nm and 11 nm-thick DH LEDs, respectively, under current density ~ 300 A/cm². Therefore, it is apparent that multi-3 nm DH layer design is a superior approach for increasing the active region volume and enhancement of LED external efficiency.

2.4. Optimization of electron injector layer in InGaN LEDs

Use of electron injector layers in lieu of electron blocking layers, which hampers efficient hole injection, has been proven beneficial in reducing electron overflow and improving efficiency. To investigate the effect of EI thickness on carrier overflow and efficiency droop, the integrated electroluminescence (EL) intensity vs. current injection for DH LEDs with varied SEI thickness was measured. The c-plane InGaN LED structures, emitting at ~430 nm, were grown on ~3.7 µm-thick n-type GaN templates on sapphire in a vertical low-pressure MOCVD system. The structures feature either single or quad 3 nm In₀.₁₅Ga₀.₈₅N DH active regions separated by 3 nm In₀.₀₆Ga₀.₉₄N low energy barriers to help reduce adverse effects on hole transport. Situated below the active region is a two-layer varied thickness (4+4 nm, 20+20 nm and 30+30 nm) stair-case EI
(SEI) consisting of In$_{0.04}$GaN and In$_{0.08}$GaN layers of the same thickness grown in the given order on a 60-nm In$_{0.01}$Ga$_{0.99}$N underlying layer intended for improving materials quality. The LED structures (Figure 19) were completed with 100 nm-thick Mg-doped $p$-GaN layers having 6×10$^{17}$ cm$^{-3}$ hole density, determined from Hall measurements in separate samples.

![Simplified conduction band schematic of quad 3 nm DH LED structures investigated.](image)

Figure 19: Simplified conduction band schematic of quad 3 nm DH LED structures investigated.

For devices, the same fabrication method as described in section 2.2 was used. Figure 20(a) demonstrates that for the LEDs with 4 + 4 nm SEI, the EL efficiency of quad 3 nm DH LED is ~3.5 times higher than that of single 3 nm DH LED which is an indication that the low EQE of the single 3 nm DH structure is due to higher carrier overflow in the thinner active layer facilitating ballistic and/or quasi-ballistic electron transport across the active layer without recombination. The SEI thickness should be larger for single 3 nm DH to provide hot electrons more time to sufficiently thermalize before being injected into the active region. However, regardless of the active layer design, the total SEI thickness must be kept below the critical thickness above which the active region material quality would degrade noticeably due to strain relaxation.
Increase of the SEI thickness from 4 + 4 nm to 20 + 20 nm for the single 3 nm DH LED resulted in an enhancement in the peak EL efficiency by nearly 3.5 times, making it comparable to those of the quad 3 nm DH LEDs [Figure 20(a)]. This significant improvement indicates that the electrically injected hot electrons are cooled more efficiently within the thicker SEI. The more visible efficiency roll off in the single DH LED both with 20 + 20 and 30 + 30 nm-thick SEIs compared to the quad 3 nm DH LEDs [Figure 20(b)] suggests larger electron overflow in the thinner active region, which increases at higher injection levels. At the highest injection level employed (550 A/cm², which corresponds to an average carrier density around 5 x 10^{18} cm⁻³, estimated using \(A = 10^7\) s⁻¹ and \(B = 10^{-10}\) cm⁻³s⁻¹), the efficiency for the single 3 nm DH LED with 20 + 20 nm SEI is nearly twice that for the single DH LED with 4 + 4 nm SEI and 70% of quad 3 nm DH LEDs. Note that thicker, multi-DH or MQW active regions would serve as efficient
electron coolers. Accordingly, the quad 3 nm DH LEDs with 20+20 nm SEI show only a moderate increase of 15–20% in the peak EQE compared to those for the LEDs with 4+4 nm SEIs. To demonstrate further that the loss of efficiency at high injection is due to carrier overflow, the single and quad 3 nm DH LED structures were investigated under resonant optical excitation. The data shown in Figure 21 (a) and (b) also demonstrate that the PL intensity nearly scales with the number of 3 nm active layers. The variation in intensity with SEI thickness is due in part to unintentional variations in the active layers thickness, absorption in the SEI layers, and improvement in the active layer quality with the underlying SEI.

![Figure 21](image-url)

**Figure 21:** The integrated PL intensity dependence on optical excitation density at (a) 15 K and (b) 295 K for single and quad 3 nm DH LEDs with varied SEI thickness.

So, SEI thickness plays an important role in quantum efficiency of LED structures through reduction of electron overflow. Increasing the two-layer SEI thickness from 4+4 nm up to 20+20 nm did not degrade the material quality, as suggested by the high optical efficiency observed from 15 K and room temperature PL measurements, but substantially reduced the electron overflow at
low injection. The improvement in quad 3 nm DH LEDs with increasing SEI thickness is not that obvious, as the influence of SEI is less in effectively thicker active regions, which also naturally thermalize carriers during their transport. Consequently, although the peak EL efficiencies are similar for single and quad 3 nm DH LEDs with thicker SEIs, at high injection, single 3 nm DH LEDs suffer more from electron overflow due to the thinner active region. However, even at the highest excitation density employed (550 A/cm²) the EL efficiency of the single 3 nm DH LED with 20+20 nm or 30+30 nm SEI is nearly doubled when compared to that with a much thinner 4+4 nm SEI. These results indicate that the two-layer SEI with optimum thickness significantly reduces the electron overflow, and the optimum SEI design depends on the active region structure employed.

Moreover, the effect of SEI thickness on radiative recombination coefficient (B coefficient) has also been explored with numerical simulation using SILVACO Atlas software. Figure 22 presents the simulated effective bimolecular recombination coefficients, \( B_{\text{eff}} \), derived from the transition matrix element and thus the simulated squared overlap integrals of the electron and hole wavefunctions within the single and multi-DH active regions.
Figure 22: $B_{\text{eff}}$ coefficients of (a) single-DH and (b) multi-DH LEDs calculated using squared overlap integrals of electron and hole wavefunctions (proportional to radiative recombination rate) within the active region as a function of current density obtained from SILVACO Atlas simulations.

It is evident that LEDs with wider SEI regions have higher $B_{\text{eff}}$ values which indicates that SEI clearly improves the electron-hole wavefunction overlap. This effect is even stronger for LEDs with active regions composed of wider DHs. Additionally, thinner active layers have relatively larger spatial overlap of the electron and hole distribution functions that results in larger $B_{\text{eff}}$ values at low injection and faster rate of increase with injection current. Relatively lower $B_{\text{eff}}$ coefficient in wider active regions are due to the increased spatial separation of electrons and holes by the larger impact of the polarization field.
2.5. Improvement of carrier injection symmetry using delta doped barriers in InGaN MQW LEDs

Carrier injection symmetry is vital in order to achieve improved efficiency retention at high current injection and reduced electron overflow. To demonstrate the effect of Mg delta (δ) doping of barrier on carrier injection asymmetry problem, three c-plane InGaN LED structures emitting at ~430 nm were grown on ~4 μm-thick n-type GaN templates on sapphire in a vertical low-pressure MOCVD system. A 15+15 nm-thick staircase electron injector (SEI) consisting of In$_{0.04}$GaN and In$_{0.08}$GaN layers is situated beneath the active region to efficiently cool the injected hot electrons.$^{80,81}$ Placed below the SEI, a 60-nm n-type ($2\times10^{18}$ cm$^{-3}$) In$_{0.01}$Ga$_{0.99}$N underlying layer was employed to reduce the probability of strain relaxation in the active region owing to its compliance action provided by its softer lattice compared to GaN. As shown in Figure 23, all three LED structures feature hex (6x) 3-nm In$_{0.15}$Ga$_{0.85}$N double heterostructure (DH) active regions separated by relatively low energy In$_{0.06}$Ga$_{0.94}$N barriers, meant to help with the hole transport across the active region. The first two In$_{0.06}$Ga$_{0.94}$N barriers near n-GaN are 6 nm-thick and the remaining three are 3 nm-thick. In two of the LED structures, δ-doping with Mg was employed in either one or both of the 6 nm-thick barriers. The third LED sample (reference) was grown without any Mg doping in the barriers. The first two barriers closest to n-GaN were made thicker than the others to prevent possible Mg out-diffusion from p-doped barriers into the active regions. The δ-doping with Mg was implemented as follows: after the first 3 nm growth of the 6 nm-thick barrier (applied to either only the first or the group of first two of the barriers), the growth was interrupted, and the Cp$_2$Mg source was supplied to the growth chamber for 20 s, followed by the growth of remaining 3 nm of the 6 nm barrier. The hole concentration in the doped barrier was estimated to be $4\times10^{17}$ cm$^{-3}$ from measurements on δ-doped p-GaN deposited in separate experiments. The
LED structures were completed with 100 nm-thick Mg-doped $p$-GaN layers with $6 \times 10^{17}$ cm$^{-3}$ hole concentration, as determined from Hall measurements performed on separate samples. Square mesa patterns (400×400 µm$^2$) were formed by conventional photolithography and chlorine based Inductively Coupled Plasma (ICP) etching. Ti/Al/Ni/Au (30/100/40/50 nm) metallization annealed at 860 °C for 60 seconds was used for $n$-type Ohmic contacts, and semitransparent 5nm/5nm thick Ni/Au with 40nm/50nm Ni/Au contact pads served as $p$-contacts.

![Diagram](image)

Figure 23: Simplified conduction band schematic of hex 3 nm DH LEDs. The Mg δ-doping is employed for either only the first or the first and the second 6 nm thick $\text{In}_{0.06}\text{Ga}_{0.94}$N barriers located near the $n$-GaN side. The rest of the barriers are undoped and are 3 nm thick. A third sample with no δ-doping in the barriers is used for reference.

In order to verify the effectiveness of Mg δ-doping of barriers in improving hole injection, electron and hole distributions were simulated using the Silvaco Atlas commercial software with simulation parameters appropriate for nitride materials (Shockley-Read-Hall recombination coefficient $A = 10^7$ s$^{-1}$, bimolecular recombination coefficient $B = 10^{-10}$ cm$^{-3}$s$^{-1}$, Auger recombination coefficient $C = 10^{-30}$ cm$^6$s$^{-1}$, electron and hole mobility 250 and 5 cm$^2$/Vs, and 40% of the theoretical polarization charge). Figure 24(a) shows the distribution of electrons in the active regions of the three LED structures under investigation for an injection current density of 35 A/cm$^2$. As evidenced from the figure, due to efficient cooling of injected electrons in the SEI,
the electron distribution is relatively uniform in the reference LED. Although δ-doping of barriers
does not have any significant effect on the electron distribution in the active regions, it increases
substantially the hole concentrations in the wells near the n-side, as shown in Figure 24(b) and
discussed below.
Figure 24: (a) Electron and (b) hole concentrations and (c) the corresponding energy band structures for the reference LED (black) and LEDs with one (red) or two (blue) Mg δ-doped barriers simulated at a current injection of 35 A/cm² with SILVACO Atlas. The dashed lines in (c) indicate the quasi-Fermi levels. Left side is n-GaN with 15+15 nm-thick SEI. The horizontal dotted line represents the energy corresponding to the valence band maximum in p-GaN.
Transport of holes deeper across the multilayer active region is hampered due to their relatively large effective mass and low mobility. Therefore, even without hot electron overflow, radiative recombination is limited by the concentration of holes, which are the minority carriers in the active region under bias. Under these circumstances, as shown in Figure 24(b) for the reference sample, the hole distribution across the active region is very non-uniform. The hole concentration is the highest in the InGaN well closest to $p$-GaN, and it decreases rapidly towards the $n$-side of the LED structure. Therefore, for multi-well LEDs, electron and hole recombination occurs mainly in the active layers adjacent to $p$-GaN, while the rest of the active region lacks sufficient number of holes for efficient recombination with the existing electrons. When the InGaN barrier closest to $n$-GaN is $\delta$-doped with Mg, the hole concentration in the nearby active regions increases by nearly an order of magnitude [Figure 24(b)], greatly reducing the asymmetry of electron and hole concentrations and thus enhancing the recombination efficiency. When the two 6 nm-thick InGaN barriers are $\delta$-doped, the hole concentration in the active regions near $n$-GaN increases further [Figure 24(b)], particularly in the second well closest to $n$-GaN, which would enhance the LED output power even more. Moreover, $\delta$-doping of barriers near the n-side of LED gives rise to band bending that favors the hole transport across the active region. As seen from Figure 24(c), representing the simulated energy band structures for the three LEDs at a current density of 35 A/cm$^2$, $\delta$-doping of the In$_{0.06}$GaN barrier closest to $n$-GaN reduces the effective height of the last barrier for holes with respect to the valence band maximum of $p$-GaN from 120 meV in the reference LED to 50 meV. The doping of the first and the second barrier on the n-GaN side reduces the barrier further to -10 meV.
To demonstrate the effect of $p$-type $\delta$-doping of barriers on LED performance, integrated EL intensities and relative external quantum efficiencies (EQEs) were measured under pulsed excitation with 0.1 % duty cycle to eliminate heating effects. As shown in Figure 25(a), samples with $\delta$-doped barriers exhibit higher integrated EL intensities at high current injection levels (> 50 A/cm$^2$), indicating no notable material degradation associated with Mg incorporation to the active regions compared to the reference structure. As shown in Figure 25(b), the peak relative EQE for the LED with one $\delta$-doped barrier is ~20% higher than that for the reference LED. The $\delta$-doping of two barriers adjacent to the n-side of the structure results only in an insignificant increase of the peak EQE, probably due to slight degradation of the active region quality caused by higher amount of Mg, which partially cancels an additional improvement owing to enhanced hole injection resulting from $\delta$-doping. It should be noted that LEDs with $\delta$-doped barriers exhibit less efficiency degradation percentile (~14 % at 400 A/cm$^2$) with increasing injection compared to the reference LED (~23% at 400 A/cm$^2$), and the EQE roll over with $\delta$-doped barriers occurs at higher current injection (~120 A/cm$^2$ vs. ~80 A/cm$^2$ in the reference LED). For a given active-region structure, the increase in the roll-over current density is indicative of improved hole supply, because electrons start to escape from the active region reducing the efficiency when hole injection cannot keep up with the electron supply. These findings imply that, in addition to enhancing the peak EQE, improved hole injection partly suppresses the efficiency degradation at high injection.
δ-doping of barriers with Mg was found to significantly improve the quantum efficiency of multi-well LEDs. With Mg δ-doping of the first barrier on the $n$-GaN side, the relative peak EQE is increased by 20% compared with the reference structure due to enhanced hole injection and the reduction of carrier-injection asymmetry as supported by numerical simulations. Mg δ-doping of an additional barrier on the $n$-GaN side results in only a marginal increase in peak EQE despite what is suggested by simulations. It is likely that slight degradation of the active region quality caused by higher amount of Mg associated with δ-doping of two barriers partially cancels the additional improvement expected due to enhanced hole injection.
2.6. Enhancement of Indium incorporation to InGaN MQWs on AlN/GaN periodic multilayers

Strain engineering in InGaN heterostructures through modification of in-plane lattice parameter of buffer layers is a promising approach to improve In incorporation and thus efficiency of long wavelength InGaN emitters. GaN buffer layer under tensile strain reduces the total strain of the structure and thus improve radiative recombination efficiency of the InGaN active layers while the situation is opposite in case of compressively-strained GaN under-layer. On the other hand, amount and sign of strain in InGaN heterostructures has a strong effect on indium incorporation; tensile strain enhances while compressive strain reduces the incorporation efficiency.\textsuperscript{82,83} Even though increase in compressive strain could significantly improve performances for certain applications\textsuperscript{84}, in light emitting devices the increase in compressive strain reduces indium incorporation and enhance polarization-induced QCSE at the same time.\textsuperscript{83,85} Strain relaxations, on the other hand, improves the indium incorporation efficiency but at the expense of reduced radiative recombination efficiency due to defect generation. Therefore, it is imperative to explore the effect the strain in underlying layer on indium incorporation and polarization-induced QCSE in InGaN multi-quantum well (MQW) active regions.

The investigated structures were grown using a vertical design MOCVD. InGaN active regions were grown concurrently on the same holder on strained 10-pair AlN/GaN periodic multilayers and GaN templates, which were prepared by \textit{in situ} epitaxial later overgrowth through SiNx nanoporous mask\textsuperscript{75,86}. The GaN and the multilayer templates were located at the same radial positions to avoid any possibility of radial temperature non-uniformity affecting indium incorporation and to ensure fair comparison of indium incorporations. For these experiments, two different AlN/GaN templates were used with different strain conditions (Figure 26): (1) periodic
multilayer 1 (ML₁) composed of 14-nm AlN and 4.5-nm GaN and (2) multilayer 2 (ML₂) composed of 14-nm AlN and 2.5-nm GaN. The InGaN active regions consisted of ten 3-nm In₀.₁₅Ga₀.₈₅N QWs separated by 8-nm In₀.₀₂Ga₀.₉₈N barriers (the indicated compositions are nominal) have been grown side by side on the relaxed GaN and strained ML templates in two separate growth runs. Thus, four samples were investigated; the active regions of samples A and C were grown at substrate temperature of 810°C on relaxed GaN and strained ML₁, respectively, while samples B and D were deposited at substrate temperature of 790°C on relaxed GaN and strained ML₂ (See Table 1).

![Diagram](image)

**Figure 26.** Schematics of the InGaN MQWs structures with nominal compositions grown on (a) relaxed GaN and (b) strained AlN/GaN multilayers.
Table 1. Descriptions of samples used in the investigation of the effects of strain on Indium incorporation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>AlN/GaN thickness in MLs (nm)</th>
<th>InGaN growth temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Relaxed GaN</td>
<td>---</td>
<td>810</td>
</tr>
<tr>
<td>B</td>
<td>Relaxed GaN</td>
<td>---</td>
<td>790</td>
</tr>
<tr>
<td>C</td>
<td>ML1 (10 pairs)</td>
<td>14 / 4.5</td>
<td>810</td>
</tr>
<tr>
<td>D</td>
<td>ML2 (10 pairs)</td>
<td>14 / 2.5</td>
<td>790</td>
</tr>
</tbody>
</table>

High resolution X-ray diffractometry (XRD) was utilized to evaluate the interface quality and to verify layer thicknesses in the AlN/GaN periodic multilayers as well as to determine the degree of relaxation of GaN layers. The optical properties of the InGaN active layers were characterized using SSPL and TRPL spectroscopy using a frequency doubled Ti-sapphire laser (150 fs pulse width and 80 MHz repetition rate) as an excitation source. A Hamamatsu streak camera was used for the study of temporal evolution of emission lines and the QCSE induced shift in the emission wavelengths. The peak positions of the PL emission lines at the highest excitation (immediately after the pulsed excitation in time-dependent PL measurements) were used to assess the actual indium contents in the QWs.

The $\omega$-20 HRXRD scans (Figure 27) reveal multiple satellite peaks indicating smooth interfaces between the AlN and GaN multilayers. The ML period defined as $t_{\text{AlN}} + t_{\text{GaN}}$ (where $t_{\text{AlN}}$ and $t_{\text{GaN}}$ represent respectively the thickness of AlN and GaN) was found to be about 18.5 nm and 16.5 nm for ML1 and ML2 structures, respectively. The thicknesses of individual AlN and GaN were determined by fitting simulated HRXRD patterns to the measured ones. The results of simulations also indicate that the degree of relaxation of AlN and GaN layers are 100% and 60%, respectively, in ML1 (Figure 27b) and are 100% and 0.0% in ML2 (Figure 27c).
Figure 27 (a) $\omega$-2$\theta$ HRXRD patterns from both AlN/GaN periodic multilayers. Large number of satellite peaks is indicative of relatively smooth interfaces between the AlN and GaN layers. The simulation results and fitting curves for the structure ML$_1$ (b) ML$_2$ (c) indicate degree of relaxation of 100%/60% and 100%/0.0% for AlN/GaN in ML$_1$ and ML$_2$, respectively.

The in-plane lattice parameters, $a$, and amount of strain in GaN layers in the multilayers were calculated\textsuperscript{87} using the degrees of relaxation ($R$) obtained from the analysis of HRXRD patterns under assumption that the degree of relaxation in 14-nm AlN layers is 100%

$$R = \frac{a - a_s}{a_l - a_s} \times 100\%$$

(4)

where $a_{AlN}$, $a_{GaN}^b$, and $a_{GaN}^c$ are the in-plane lattice constants of AlN acting as a substrate for thin GaN layers, bulk GaN, and measured in-plane lattice constants of the layer (GaN), respectively. Therefore, strain in GaN layers can be calculated as follows\textsuperscript{87,88}

$$\varepsilon = \frac{a - a_l}{a_l} \times 100\%$$

(5)
The calculated values of strain in the periodic multilayer structures as well as the GaN template are summarized in Table 2.

**Table 2. Calculated strain in GaN for the templates used.**

<table>
<thead>
<tr>
<th>Structure design</th>
<th>GaN relaxation (%)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxed GaN</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>ML₁ (10 pairs)</td>
<td>60</td>
<td>1.11</td>
</tr>
<tr>
<td>ML₂ (10 pairs)</td>
<td>0</td>
<td>2.78</td>
</tr>
</tbody>
</table>

Room temperature PL spectra from the InGaN MQWs structures grown on relaxed (samples A and B) and compressively strained (samples C and D) templates are shown in Figure 28. It should be restated here that the active regions of A and C structures are grown at 20°C higher substrate temperatures (810 °C) compared to those of B and D (790 °C). Thus, the difference in observed PL peak positions for samples A and B is related to the difference in substrate temperatures. Nevertheless, the data clearly show longer emission wavelengths for the structures grown on AlN/GaN multilayers (C and D) compared to the ones on relaxed GaN (A and B). Moreover, significantly longer emission wavelength for sample D with thinner GaN layers in the multilayer template compared to sample C (2.5 nm vs. 4.5 nm) can be attributed to higher value of strain in the GaN causing higher degree of strain relaxation in InGaN layers. Another interesting finding is the comparable integrated PL intensities from InGaN MQWs of different emission wavelength on strained periodic multilayers and GaN templates.
Figure 28. Room temperature PL spectra of InGaN MQWs grown on GaN (A and B) and AlN/GaN multilayers (C and D). The thicknesses of GaN in the multilayer are 4.5nm (C) and 2.5nm (D).

Room temperature PL transients integrated over active region emission for the structures under investigation are displayed in Figure 29. The data indicate single exponential decay for InGaN MQWs grown on relaxed GaN templates (samples A and B), while the decay is bi-exponential for the structures grown on MLs (samples C and D). The longer decay times for the layers C and D compared to A and B can be attributed to larger spatial separation of electrons and holes wave function for the active regions with higher indium content. The double exponential decay behavior for InGaN MQWs on MLs (C and D) can be attributed to presence of localized states with different indium contents while the indium distribution is uniform in the MQWs grown on the smooth GaN templates. This observation is in agreement with the dot-like surface morphologies revealed by the AFM for the active regions grown on the periodic multilayer templates (not shown).
While the effect of strain on InGaN growth rate was found to be negligible based on HRXRD data, there are two main parameters contributing to the large difference in PL emission wavelengths: strain induced enhanced band bending and corresponding shift in the emission wavelength and increased indium incorporation. Therefore, a reliable separation of these contributions is imperative for the correct interpretation of the experimental findings.

In order to evaluate the above-mentioned contributions to the observed emission wavelengths, ultra-fast optical spectroscopy was performed on the layers using pulsed excitation and compared the emission wavelengths at pulse arrival and when photo-excited carrier concentration was significantly reduced through carrier recombination. For the used excitation power density and pulse width, the estimated density of photo-generated carriers at the peak is
\[ n = 4.54 \times 10^{19} \text{cm}^{-3} \] which results in complete screening of the polarization induced electric field. With time, the carrier density reduces due to recombination and thus, the screening effect gradually vanishes. As a result, the band bending and associated separation of electron and hole wavefunctions increase. Therefore, time evolution of PL spectra allows one to isolate the contribution to the redshift of emission lines associated with the presence of the polarization field. Figure 30 compares the 300-K PL spectra recorded for the highest and the lowest photo-excited carrier concentrations for all the samples investigated. The structures grown on MLs (samples C and D) exhibit significantly larger red shifts (\( \Delta E \)) with reducing photo-generated carrier density compared to the structures on the relaxed GaN templates (samples A and B). The calculated shift in PL peak might have contributions from band filling and bandgap renormalization effects in addition to polarization charge induced quantum confined stark effect (QCSE). However, the relative change in peak shift is purely due to screening of QCSE as the same excitation energy and excitation power density was used for all the measurements.
Figure 30. Room temperature PL spectra for the highest and the lowest photo-generated carrier density in InGaN MQWs on relaxed GaN (A and B) and AlN/GaN MLs (C on ML$_1$ and D on ML$_2$) recorded using ultra-fast optical spectroscopy. The PL spectrum tends to shift to longer wavelengths with increasing delay time. This shift is much more pronounced for MQWs on MLs (C and D) compared to those on relaxed GaN (A and B).

The average indium compositions in InGaN active regions were determined from the PL peak positions at the highest photo-generated carrier concentrations, which eliminated the contribution from the internal electric field. Considering the quantum confinement, the PL emission energy can be written as

\[ E_{PL} = E_{g}^{InGaN}(x) + E_{Confinement} \]  

(6)
Where $E_{PL}$ denotes the MQW PL peak emission energy, and $E_{g}^{InGaN}(x)$ is the InGaN bandgap calculated using\textsuperscript{89,90}

$$E_{g}^{InGaN}(x) = xE_{g}^{InN} + (1-x)E_{g}^{GaN} - b(x(1-x))$$ (7)

Where $b$ is the bowing parameter, $E_{g}^{InN}$ and $E_{g}^{GaN}$ are the room temperature bandgaps for InN and GaN, respectively. The bowing parameter ($b$) is assumed to be dependent on indium content as predicted by Moses et al.\textsuperscript{91} The bandgap values of 0.7 eV \textsuperscript{92} and 3.42 eV \textsuperscript{88} were used in the calculation for InN and GaN, respectively. The confinement component of the PL emission energy ($E_{Confinement}$) can be found considering solution for ground state energy of electrons and heavy holes in a finite rectangular potential well having width of $L = 3.0 \text{nm}$.\textsuperscript{93}

The calculated indium concentrations are shown in Table 3 together with the PL emission properties including the redshift associated with polarization-induced QCSE. It can be inferred from the data shown in Table 3 that high indium content (up to cyan emission) can be achieved with no significant drop in the integrated PL intensity by employing of AlN/GaN MLs. The results obtained for AlN/GaN periodic MLs with 60% and 0.0% relaxation GaN layers reveal 6.7 % and 14.5 % higher indium contents, respectively, for the structure grown on MLs compared to those grown side by side on relaxed GaN layers.

**Table 3.** PL characteristics, and calculated indium contents for the structures used in this investigations emitting from purple to cyan.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PL peak (nm)</th>
<th>Shift in PL peak (meV)</th>
<th>FWHM (meV)</th>
<th>Relative PL intensity</th>
<th>Indium content (%)</th>
<th>Emission color</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>425</td>
<td>15.0</td>
<td>126</td>
<td>0.38</td>
<td>14.4 ($\pm$0.2)</td>
<td>Purple</td>
</tr>
<tr>
<td>B</td>
<td>432</td>
<td>10.5</td>
<td>148</td>
<td>0.80</td>
<td>15.7 ($\pm$0.2)</td>
<td>Purple-Blue</td>
</tr>
<tr>
<td>C</td>
<td>458</td>
<td>46.5</td>
<td>218</td>
<td>1.00</td>
<td>21.1 ($\pm$0.3)</td>
<td>Blue</td>
</tr>
<tr>
<td>D</td>
<td>504</td>
<td>60.0</td>
<td>273</td>
<td>0.71</td>
<td>30.2 ($\pm$0.5)</td>
<td>Cyan</td>
</tr>
</tbody>
</table>
Employment of AlN/GaN periodic MLs is found to efficiently enhance indium incorporation efficiency in the InGaN MQWs by promoting the strain relaxations. The inhomogeneity of indium distribution cannot be ruled out. The indium contents in the active layers on the periodic multilayers with two different values of compressive strain in GaN (1.11% and 2.78 %) were found to be higher by absolute composition values of 6.7 % to 14.5 % compared to the layers grown side by side on relaxed GaN templates (0.0% strain). The enhanced indium incorporation could be originated from the role of AlN/GaN MLs as strain relaxation layer for the overgrown InGaN MQWs reducing the compressive strain. Presence of deep and shallow band-gap regions due to spatial non-uniformity of indium distribution could also be assumed due to bi-exponential decay behaviour of PL transients as well as surface undulation for active layers grown on MLs (C and D). The optical properties (integrated PL) of the structures containing high indium contents (> 20%) were not significantly degraded. Efficient PL emissions from purple to cyan was obtained using this approach which could be a potential candidate to alleviate the efficiency limitations for long wavelengths emitters.

2.7. Near-field optical microscopy of extended defect distribution in semipolar InGaN LEDs

Conventional GaN-based LEDs, grown with the polar c-plane orientation, suffers from QCSE resulting in injection-dependent emission wavelength and efficiency as well as overflow of electron particularly at low injection. In order to reduce the QCSE, semipolar GaN orientations on low-cost foreign substrates such as Si and sapphire have been proposed. Semipolar (1101)
InGaN LEDs grown on patterned Si substrates have been shown to exhibit reduced efficiency loss compared to their polar counterparts on sapphire.\textsuperscript{98} Moreover, semipolar $(11\overline{2}2)$ InGaN LEDs grown on m-sapphire have been reported to show higher indium incorporation rate which would be beneficial for attaining efficient emission at longer wavelengths.\textsuperscript{99} However, semipolar GaN growth often suffers from high density of extended defects such as threading dislocations and stacking faults, resulting in lower crystal quality.\textsuperscript{100} So, material quality needs to be improved further to take full advantage of semipolar orientation of GaN and comprehensive studies of effects of extended defects are required. Therefore, correlations between microscopic optical and structural properties in semipolar InGaN LEDs were investigated by means of spatially and spectrally resolved near-field scanning optical microscopy (NSOM).

Semipolar $(1\overline{1}01)$ GaN layers and InGaN LEDs were grown on patterned Si substrates in a low-pressure vertical MOCVD system. Si (001) substrates with an offcut by $7^\circ$ toward the Si$\langle 110\rangle$ direction were patterned to form grooves of 10 $\mu$m width separated by 3 $\mu$m terraces, the sidewalls of which were $\{111\}$ facets. The 3 $\mu$m x 10 $\mu$m pattern was chosen to prevent the coalescence of the growing wings which would result in inferior optical quality of the layers. The patterning procedure and initiation of GaN growth on the Si (111) facets exposed within the grooves have been described elsewhere.\textsuperscript{101} Semipolar $(11\overline{2}2)$ oriented GaN layers were grown on m-sapphire substrates by means of nano-epitaxial lateral overgrowth (ELO), details of which have been reported in Ref. 102.
LED structures incorporate, as shown schematically in Figure 31, a Si-doped In$_{0.01}$Ga$_{0.99}$N underlying layer for improving the quality of overgrown layers, electron injectors composed of In$_{0.04}$GaN and In$_{0.08}$GaN layers for efficient thermalization of hot carriers prior to injection into the active region, six periods of 3 nm-thick In$_{0.16}$GaN wells separated by 3 nm-thick In$_{0.06}$GaN barriers as the active region, and a 100 nm-thick Mg-doped p-type GaN, grown in the given order on top of (1$\bar{1}$01) and (11$\bar{2}$2) GaN templates. NSOM measurements were performed at 85 K using a Cryoview 2000 NSOM system (Nanonics Imaging Ltd) in the illumination mode where HeCd (3.81 eV or 325 nm wavelength) and InGaN (3.06 eV or 405 nm wavelength) laser excitation were used through a Cr-Al coated cantilevered optical fiber probe with 350 nm aperture.

Angled-view scanning electron microscope (SEM) image of a semipolar (1$\bar{1}$01) GaN layer on patterned Si is shown in Figure 32(a). One of the \{111\} Si sidewalls was coated with SiO$_2$ to prevent nucleation and growth of GaN started from the other sidewall and continued in the GaN
[0001] c+ direction (c+ wing). Growth in the [0001] c- direction (c- wing) is very limited due to the given geometry. It is evident that the layers did not coalesce and roughly 13 µm-wide GaN stripes formed on patterned Si. Using 3.81 eV excitation, steady-state macroscopic (incident laser beam diameter of 100 µm) PL spectrum was measured at 85K and is presented in Figure 32(b). Peaks at 3.457 eV, 3.406 eV and 3.296 eV correspond to the donor-bound exciton (D0X), basal-plane stacking fault (BSF), and donor-acceptor pair (DAP) emission, respectively. Longitudinal optical (LO) phonon replicas of D0X emission as well as the yellow emission band of GaN are also observed as indicated in the figure.

Figure 32: (a) Angled-view SEM image, (b) Macroscopic PL spectra (D0X, BSF, and DAP emission peaks are marked), and (c) NSOM PL intensity map of semipolar (1 101) GaN. (d) Local PL spectra for the points indicated in (c).
Figure 32(c) shows the 85K NSOM PL intensity map where the PL spectra were integrated up to 3.54 eV (i.e. above 350 nm). It is evident that the intensity of PL emission from the c+ wings is stronger than the emission from c- wings. For the particular section mapped, the darker regions observed in the bottom left and top right corner of the figure are due to presence of high density of threading dislocations and point defects which act as nonradiative recombination centers. Local PL spectra were collected at different points along and across the c+ and c- wings. PL spectra of two representative points, A in the c+ wing and B in the c- wing, are shown in Figure 32(d). D\textsuperscript{0}X peak intensity at point B is lower than that at point A. Moreover, B shows clear BSF emission peak at 3.41 eV whereas at point A, phonon replica of D\textsuperscript{0}X dominates at 3.397 eV and BSF emission is not very clear. This implies that stacking fault density at point B, located on the c- wing, is higher than at point A, on c+ wing. Using spatially and spectrally resolved cathodoluminescence (CL) technique, Okur et al.\textsuperscript{103} also reported that the optical quality of c- wings was much lower than c+ wings because of the presence of higher density of TDs and BSFs.

Angled-view SEM image of the semipolar (1\textsuperscript{1}01) LEDs is shown in Figure 33(a). Coating of one of the sidewalls with SiO\textsubscript{2} was not employed for this particular sample, which led to growth of GaN on both sidewalls. After establishing the lateral extension as shown in the SEM image, the LED active region and the p-GaN layers were grown. NSOM PL measurements were carried out using below GaN bandgap excitation (3.06 eV) to avoid influence of the top p-GaN layer.
Figure 33: (a) Angled-view SEM image, and (b) NSOM PL intensity maps of semipolar (1\bar{1}01) LEDs. (c) Local PL spectra for the two points indicated in (b).

NSOM PL map [Figure 33(b)] shows that c+ wings are dominated by strong active region emission whereas emission from c- wings are relatively weaker. Local PL spectra were collected at multiple points along and across the c+ and c- wings and two representative spectra are shown in Figure 33(c). It is evident that the PL intensity of c+ wing (point A) is stronger than that of c- wing (point B), consistent with the observation in (1\bar{1}01) GaN layers. Moreover the emission peak of c- wing is 15 meV red-shifted compared to that of c+ wing indicating higher Indium incorporation in the c- wing which could be induced by the presence of high density of stacking faults.
The atomic force microscopy (AFM) image of (11\(\bar{2}2\)) LED structure in Figure 34(a) shows striations along the [11\(\bar{2}3\)] direction of GaN. Such morphology is characteristic of the (11\(\bar{2}2\)) GaN surface.\textsuperscript{104,105,106} Using cross-sectional SEM image, S. Y. Bae \textit{et al.}\textsuperscript{106} reported that the striated pattern consists of a “ridge-and-valley” shape which is formed due to the intersection of \{10\(\bar{1}1\)\} planes. Moreover, from cross-sectional AFM image, the angle between the faceted and the flat surfaces was found to be \(\sim 26^\circ\), which is the angle between the \{10\(\bar{1}1\)\} and \{11\(\bar{2}2\)\} family of planes.

Figure 34: (a) AFM image and (b) NSOM PL intensity map (15 K) of semipolar (11\(\bar{2}2\)) InGaN LEDs. (c) Local PL spectra for the points indicated in (b).
The spatial NSOM PL intensity map presented in Figure 34(b) shows similar surface features as observed in the AFM image. The striations are in general characterized by lower PL intensity, most likely due to the presence of threading dislocations and the associated defects, compared to the other regions. Local PL spectra were collected at multiple points on the sample and three representative spectra are shown in the figure. Point A located in a relatively flat region shows strong active region emission whereas point B located on one of the striations has weaker PL intensity. Point C located near the edge of the striation is characterized by intermediate PL intensity. In addition, appearance of an additional peak on the lower energy side as well as the red-shift of the main peak indicates higher indium content near the edge of the striations, where faceted surface meets the flat surface. Changes in the local strain may be the reason for different Indium incorporation efficiency and variations in the emission wavelength. Investigations of the (11\(\bar{2}2\)) GaN templates are in progress in order to shed light on the effects of stacking faults on emission characteristics.

The spatial variations of extended defects, stacking faults and threading dislocations, and their effects on the optical quality for semi-polar [(1\(\bar{1}01\) and (11\(\bar{2}2\))] InGaN light emitting diodes (LEDs) were investigated by near-field scanning optical microscopy at 85 K. In case of (1\(\bar{1}01\)) GaN layers, the near-field PL from the c+ wings was found to be relatively strong and uniform across the sample but the emission from the c- wings was substantially weaker due to the presence of high density of threading dislocations and basal plane stacking faults as shown by the local PL spectra. Similarly, in (1\(\bar{1}01\)) LED structures, c+ wings showed comparatively stronger active region emission than c- wings. For (11\(\bar{2}2\)) LED structures, striated regions had weaker PL intensities compared to other regions and the meeting fronts of different facets were characterized by higher Indium content due to the varying internal field.
Chapter 3. Generation and amplification of coherent acoustic phonons in InGaN heterostructures

Before moving on to the discussion of acoustic phonons generation in semiconductor periodic structure and design of an acoustic cavity, phonon dispersion relation in bulk using a simple one-dimensional linear chain of atoms will be presented followed by the description of how folding of the acoustic dispersion relation arises due to artificial periodicity in a superlattice structure.

3.1. Phonon dispersion in bulk and in superlattices

Consider a crystal structure where atoms of masses $M_1$ and $M_2$ are connected by force (spring) constant $C$ between adjacent planes (Figure 35). The period of the crystal is $a$ (distance between nearest identical planes, not nearest-neighbor planes) and for simplicity it is assumed that the masses are constrained to move in the direction of the chain (longitudinal vibrations).

![Figure 35: A diatomic crystal structure with masses $M_1$, $M_2$ connected by force constant $C$ between adjacent planes.](image)

The equations of motion under the assumption that each plane interacts only with its nearest-neighbor planes and that the force constants are identical between all pairs of nearest-neighbor planes can be written as follows.\textsuperscript{107}
\[ M_1 \frac{d^2 u_s}{dt^2} = C \left( v_s + v_{s-1} - 2u_s \right) \quad (8) \]

\[ M_2 \frac{d^2 v_s}{dt^2} = C \left( u_{s+1} + u_s - 2v_s \right) \]

Where \( u_s \) and \( v_s \) denote the displacements of atoms \( M_1 \) and \( M_2 \), respectively.

To find the eigenmodes, a Bloch solution of the following form can be assumed.

\[ u_s = u \exp(iska) \exp(-i\omega t) \]
\[ v_s = v \exp(iska) \exp(-i\omega t) \quad (9) \]

Where \( K \) and \( \omega \) are the wavevector and frequency of the corresponding eigenmode.

On substitution of (9) in (8),

\[-\omega^2 M_1 u = C \left[ 1 + \exp(-ika) \right] - 2Cu \]
\[-\omega^2 M_2 v = C \left[ \exp(ika) + 1 \right] - 2Cv \quad (10) \]

These homogeneous linear equations have a solution only if the determinant of the coefficients of the unknown \( u, v \) vanishes:

\[ \begin{vmatrix} 2C - M_1 \omega^2 & -C \left[ 1 + \exp(ika) \right] \\ -C \left[ 1 + \exp(ika) \right] & 2C - M_2 \omega^2 \end{vmatrix} = 0 \quad (11) \]

Or,

\[ M_1 M_2 \omega^4 - 2C \left( M_1 + M_2 \right) \omega^2 + 4C^2 \sin \left( \frac{Ka}{2} \right) = 0 \quad (12) \]

The solutions are:

\[ \omega^2(K) = C \left( \frac{M_1 + M_2}{M_1 M_2} \right) \pm \sqrt{C \left( \frac{M_1 + M_2}{M_1 M_2} \right)^2 - 4C^2 \sin \left( \frac{Ka}{2} \right)} \quad (13) \]

This is the dispersion relation of the waves in the one-dimensional crystal. The two solutions represent two different branches of the vibrational modes of the chain. The upper curve is the \( \omega^+ \) solution and is called the optical branch while the lower curve is the \( \omega^- \) solution and is called the acoustic branch. A consequence of the translational symmetry of the crystal is that the function \( \omega \)
$(K)$ is periodic in $K$ with period $2\pi/a$. This means that all the information of the vibrational modes of the lattice is contained in $-\pi/a < K < \pi/a$, as illustrated in Figure 36. This is the one-dimensional, first Brillouin zone of the linear chain; any wavevector outside is equivalent to a wavevector inside by a translation of $2\pi/a$.

In case of acoustic mode, at $K = 0$, $\omega_1 = 0$, and at $K = \pi/a$, $\omega_1 = \pm \sqrt{2C/M_1}$ ($m_1>m_2$)

In case of optical mode, at $K = 0$, $\omega_2 = \pm \sqrt{2C \left( \frac{1}{M_1} + \frac{1}{M_2} \right)}$, and at $K = \pi/a$, $\omega_2 = \pm \sqrt{2C/M_2}$

Modes with frequencies between $\omega_1$ and $\omega_2$ have a purely imaginary wavevector and therefore do not propagate

![Figure 36: Optical and acoustical branches of the dispersion relation for a diatomic linear lattice](image)

Acoustic phonon branch can be modified by artificially introducing an additional (longer) periodicity in the system by using a periodic multi-layered/superlattice structures. This leads to the term “zone folded acoustic phonons” because the acoustic branch is folded into a smaller first
Brillouin zone determined by the artificial period. As we are interested in longitudinal waves propagating in the $z$ direction, perpendicular to the interfaces, these phonons are referred to as zone folded longitudinal acoustic phonons (ZFLAPs). Dispersion relation for ZFLAPs in a superlattice can be obtained using Elastic Continuum model which described next.

The propagation of longitudinal acoustic phonons along the $z$-axis ($c$-axis) in a periodic bi-layer structure is described by the following equation

$$\rho_{A,B} \frac{\partial^2 u_{A,B}(z,t)}{\partial t^2} = C_{A,B} \frac{\partial^2 u_{A,B}(z,t)}{\partial z^2}$$  \hspace{1cm} (14)

where $\rho_{A,B}$, $C_{A,B}$ ($C_{33}$) and $u_{A,B}(z,t)$ are the material densities, elastic constants and atomic displacements, respectively (in each layer A and B). The solution of the above equation has the form

$$u(z,t) = \phi(z) e^{i\epsilon t}$$  \hspace{1cm} (15)

Within each layer, $\phi(z)$ is given by a linear combination of counter propagating waves,

$$\phi_A(z) = a_A e^{ik_Az} + b_A e^{-ik_Az} = \phi_A^+(z) + \phi_A^-(z)$$  \hspace{1cm} (16)

that has to satisfy the boundary conditions related to the continuity of atomic displacement and stress, $u_A(z_1) = u_B(z_1)$ and $C_A \left. \frac{\partial u_A(z_1)}{\partial z} \right|_{z_1} = C_B \left. \frac{\partial u_B(z_1)}{\partial z} \right|_{z_1}$, respectively. Here, $z_1$ defines the position of the interface between layers A and B. The oscillation frequency of the acoustic wave is related to its wave vector by $k_A \nu_A = \omega$, with $\nu_A$ being the sound velocity in layer A.

The dispersion relation between the phonon frequency $\omega$ and the phonon wave vector $q$ can then be obtained as (assuming, $z_1 = 0$)
\[
\cos(qd) = \cos \left( \omega \left( \frac{d_A}{v_A} + \frac{d_B}{v_B} \right) \right) - \frac{\varepsilon^2}{2} \sin \left( \omega \frac{d_A}{v_A} \right) \sin \left( \omega \frac{d_B}{v_B} \right)
\]

(17)

Here \(d_{A,B}\) are the thicknesses and \(v_{A,B} = \sqrt{C_{A,B} / \rho_{A,B}}\) are the sound velocities along the c-axis for layers A and B, \(d = d_A + d_B\) is the period of the structure and \(\varepsilon = \frac{(\rho_B v_B - \rho_A v_A)}{\sqrt{\rho_B v_B \rho_A v_A}}\). \(\varepsilon\) describes the acoustic modulation through the relative difference between the acoustic impedances \(\rho_i v_i\) of both bulk constituents. Figure 37 shows the zone folding of bulk acoustic phonon dispersion to reduced-zone in a periodic bi-layered structure.

![Image](image.png)

**Figure 37:** Representation of zone-folding for the LA phonon branch of a superlattice with period \(d\) and lattice constant \(a\). The LA phonon branch is folded into the reduced Brillouin zone, which has its edge at \(\pi/d\).

For the available superlattices of III-V compounds, the acoustic modulation is usually small, and this suggests, to a first approximation, that the second right hand term in Equation (17) can be
neglected. This results in a simple form which corresponds to the folding of the average elastic dispersion curve, introducing degeneracies at the zone center and edges at angular frequencies

\[ \Omega_n = \frac{n v_r \pi}{d} \]  

where \( n \) is an even (odd) integer at the zone center (edge), and the average sound velocity is given by

\[ v_s = \frac{d}{\frac{d_A + d_B}{d_A v_B + d_B v_A}} = \frac{d v_A v_B}{v_A + v_B} \]  

The double degeneracies appearing at the zone center are lifted when the finite magnitude of the modulation through the second term in Equation (17) is taken into account. The upper and the lower frequencies of these gaps at the zone center and the edge correspond to the eigen-displacements with equal amplitudes of the backward and forward propagating components. Thus, these modes do not transport energy.

The splitting of the zone center and edge frequencies can be obtained by expanding the exact frequency \( \Omega \) to second order in \( \Delta \Omega = \omega - \Omega_n \):

\[ \eta - \cos \left[ \left( \omega + \Omega_n \right) \frac{d}{v_s} \right] = \frac{\varepsilon^2}{2} \sin \left[ \left( \omega + \Omega_n \right) \frac{d_A}{v_A} \right] \sin \left[ \left( \omega + \Omega_n \right) \frac{d_B}{v_B} \right] \]  

where \( \eta = +1(-1) \) at the zone center (edge). Keeping only the second order terms in \( \Delta \Omega_n \) on the left hand side and the zeroth order terms on the right hand side, the shift of the zone center phonon frequencies can be obtained as

\[ \Delta \Omega_n \approx \pm \varepsilon \frac{n}{d} \sin \left[ \frac{n \pi (1-\alpha) v_B - \alpha v_A}{2 (1-\alpha) v_B + \alpha v_A} \right] \]
where \( \alpha = \nu_b / (\nu_A + \nu_B) \), and \( n \) is an even (odd) integer at the zone center (edge). It is clear from Equation (21) that the acoustic gap is negligible if the acoustic impedance mismatch for the two alternating layers \( \varepsilon \) is small.

3.2. Generation and detection of coherent acoustic phonons

ZFLAP dispersion has been calculated for three different InGaN MQWs using equation (17) presented in the previous section. Three 10 period In\(_x\)Ga\(_{1-x}\)N/In\(_y\)Ga\(_{1-y}\)N MQW samples with different layer thicknesses and Indium compositions have been considered for phonon dispersion calculation. Samples A1, A2, and A3 contain In\(_{0.09}\)Ga\(_{0.91}\)N (2 nm)/ In\(_{0.03}\)Ga\(_{0.97}\)N (8 nm) (MQW period, \( d = 10.0 \) nm), In\(_{0.11}\)Ga\(_{0.89}\)N (3 nm)/In\(_{0.03}\)Ga\(_{0.97}\)N (8 nm) (\( d = 11.0 \) nm), and In\(_{0.14}\)Ga\(_{0.86}\)N (3 nm)/In\(_{0.03}\)Ga\(_{0.97}\)N (8.5 nm) (\( d = 11.5 \) nm) MQWs respectively. Using Equation (17), ZFLAP dispersion for sample A1, A2, and A3 were calculated as shown in Figure 38. Phonon mode frequency at zone center for sample A1, A2, and A3 are 0.80 THz, 0.73 THz and 0.69 THz respectively.
Figure 38: Calculated phonon dispersion curves for three InGaN MQW samples A1, A2, and A3 with different layer thicknesses and Indium compositions.

For experimental investigation of ZFLAPs generation and detection, samples A1, A2, and A3 were grown on a ~4 μm-thick n-type GaN template on sapphire in a vertical low-pressure MOCVD system. Layer thicknesses and compositions were confirmed from high resolution XRD simulations and photoluminescence (PL) measurements.

Wavelength degenerate TRDT technique has been used to generate and detect coherent acoustic phonons. Figure 39 shows the schematic of set-up for TRDT experiment. Each pulse emitted by frequency doubled mode-locked Ti:Sapphire laser is split into two pulses, the pump and the probe, where the pump is usually at least 10 times stronger than the probe. Pump pulse is reflected from a retro-reflector mounted on a translational stage. The time delay between the pump and the probe is varied by changing the path length of the pump pulse using the translational stage. Both pump and probe pulses are focused by a lens and overlapped on the sample. The transmitted
probe pulse is spatially selected with an iris and sent to a photodetector. To eliminate the stray pump light on the detector, pump and probe beams are cross-polarized. In order to increase the signal-to-noise ratio, the pump pulse is modulated using a mechanical chopper, and the pump induced transmission change of the probe ($\Delta T$) is measured by lock-in amplifier. To compute the differential transmission ($DT \equiv \Delta T/T_0$), the bare probe transmission ($T_0$) is also measured by chopping the probe beam and using the lock-in amplifier when the pump beam is blocked. The sensitivity of this system ($\Delta T/T_0 \approx 10^{-6}$) depends on the pulse repetition rate (80 MHz), while the temporal resolution ($\sim 150$ fs) depends on the input pulse width.

![Figure 39. TRDT experimental setup](image)

Differential transmission transients for the samples are shown in Figure 40. Incident pump and probe power levels were 20 mW and 1 mW, respectively. Before $t = 0$, there is no transmission as the probe hits the sample before the pump and gets absorbed. After $t = 0$, the probe beam reaches the sample after the pump, which fills all the excited states, and therefore, results in reduced
absorption or increased transmission of the probe. A biexponential decay having damped oscillation is observed. The DT transient can be fit by the functional form

\[
DT(t) = A_fe^{-t/\tau_f} + A_se^{-t/\tau_s} + Ce^{-t/\tau} \cos(2\pi ft + \pi)
\]  

(22)

The damped oscillations start at the peak of the pump pulse \((t = 0)\) and are described by the third term in Equation (22), whose phase term \(\pi\) signifies that the oscillations are always observed to start at a minimum. These oscillations are the manifestation of coherent ZFLAPs. When carriers are captured into the wells, electrons and holes are separated by the strong piezoelectric field and partially screen it, resulting in instantaneous change in the material stress and thereby, impulsively inducing ZFLAP oscillations with wavelength corresponding to the MQW period. The first and the second terms in Equation (22) describe the fast and the slow relaxation, respectively, of the DT signal.

![DT transients of sample A1, A2 and A3 for pump/probe energy of 3.307 eV (375 nm)](image)

Figure 40: DT transients of sample A1, A2 and A3 for pump/probe energy of 3.307 eV (375 nm)
The fast and the slow decay components of the DT fits given by the first two terms in Equation (22) were subtracted from the DT, then fast Fourier transform (FFT) analysis was performed on the residual to obtain the coherent phonon oscillation frequency of 0.80 THz, 0.73 THz and 0.69 THz for samples A1, A2, and A3, respectively which are in very good agreement with calculated values presented earlier. The oscillation frequency increases with decreasing MQW period as 

\[ f = \frac{v_s}{d}, \]

where \( v_s \) is the sound velocity and \( d \) is the MQW period (phonon wavelength). Moreover, the number of oscillations observed as well as the oscillation amplitude increased with increasing QW depth. As the QW In content was increased from 9% in Sample A1 to 14% in sample A3 while keeping the barrier In content fixed at 3%, piezoelectric field in the QWs increased resulting in stronger ZFLAP phonon oscillations. Further enhancement of ZFLAP oscillations and decay times can be achieved by employing an acoustic phonon cavity resonator which is comprised of a phonon generating active region placed between two phonon mirrors.

TRDT measurements at different pump/probe energies were performed on sample A1. As evident from Figure 41, coherent ZFLAP oscillations were strongest when excitation energy (3.307 eV) is closer to the barrier energy (3.28 eV) because electrons are most efficiently captured from 3D barrier states to 2D confined QW states when the electron-hole pairs are generated closer to the barrier.\(^4\) FFT was taken to confirm that 0.8 THz frequency oscillation is present in all the transients.
Dependence of ZFLAP phonon amplitude on pump intensity was investigated for pump intensities varying from 63 Wcm\(^{-2}\) to 318 Wcm\(^{-2}\) (Figure 42). Oscillation amplitude was found to increase linearly with pump intensity due to increased screening of the electric field in the QWs. The sublinear dependence toward the maximum intensity employed suggests that the oscillation amplitude would saturate in the case of full screening. Within the range of pump intensities used no change of oscillation frequency was observed.
Figure 42. ZFLAP oscillation amplitude as a function of pump intensity for sample A2

Terahertz ZFLAP oscillations have been studied in InGaN MQWs with different In content separated by InGaN barriers containing 3% In. The amplitude of ZFLAP oscillations was observed to increase with increasing piezoelectric field (i.e. In content) in the InGaN QWs as well as with increasing excitation (pump) power density. Oscillation frequency, independent of excitation power density, was confirmed to reduce with increasing MQW period.

3.3. Design of a phonon cavity for coherent acoustic phonon amplification

As mentioned earlier, enhancement of ZFLAP oscillations and decay times can be achieved by using a phonon cavity comprised of a phonon generating active region placed between two phonon mirrors. Optimization of InGaN MQWs active region for phonon cavities has already been discussed in the previous section. In analogy to distributed Bragg reflectors for vertical photon
cavities, phonon mirrors can be formed with acoustic gaps at the BZ center by using a stack of two materials with sufficiently large acoustic mismatch (large $\mathcal{E}$). The conditions for layer thickness of an acoustic cavity are $l_1 = \frac{3\lambda_1}{4}$, $l_2 = \frac{\lambda_2}{4}$ where $l_j$ and $\lambda_j$ are the thickness and acoustic wavelength of the respective material. Such a structure reflects sound within stop bands defined around multiples of the basic frequency, $\omega = \nu/\lambda$. This basic block optimizes the stop-band width and reflectivity corresponding, in an infinite stack, to the first minigap at the Brillouin zone center. The reflectivity at the center of the optimized stop band is given by $R = 1 - 4Z^{-2N} + O(Z^{-4N})$ where $Z = \rho_1\nu_1/\rho_2\nu_2$ is the acoustic impedance mismatch between the two materials.

By choosing appropriate thicknesses for the constituent layers, the acoustic gap of the phonon mirror can be adjusted so that the folded acoustic phonon mode frequency of the active region falls into the gap, which would result in total reflection of phonons at the corresponding frequency.

![Figure 43. Cross-sectional schematic of the proposed phonon cavity](image)
Based on the results obtained from TRDT measurements on the InGaN MQWs presented earlier, sample A3 would be the best choice as the active region for the phonon cavity because of its stronger ZFLAP oscillation compared to other two samples. In order to choose a suitable bilayer stack for phonon mirror, acoustic impedance mismatch of different pairs of layers were considered. Acoustic impedance is defined as \( z = \sqrt{\rho c_{33}} \), where \( \rho \) and \( c_{33} \) represent the mass density and the elastic constant, respectively. Using typical values of \( \rho \) and \( c_{33} \), acoustic impedances of GaN, AlN and InN binaries can be obtained as \( 48.6 \times 10^6 \text{ kg m}^{-2} \text{s}^{-1} \), \( 35.3 \times 10^6 \text{ kg m}^{-2} \text{s}^{-1} \) and \( 37.1 \times 10^6 \text{ kg m}^{-2} \text{s}^{-1} \) respectively. Due to the largest acoustic mismatch it provides, the AlN/GaN multilayer structure would be the best choice for the phonon mirror. By choosing appropriate thicknesses for the constituent layers, the acoustic gap of the phonon mirror can be adjusted so that the folded acoustic phonon mode frequency of the active region falls into the gap, which would result in total reflection of phonons at the corresponding frequency. The thicknesses of AlN and GaN layers that would provide the maximum stop band width at the zone center corresponding to the 0.69 THz central frequency are 11.8 nm (\( 3\lambda_1/4 \)) and 2.9 nm (\( \lambda_2/4 \)).
Using the Equation 17, ZFLAP dispersion was calculated for sample C and a phonon mirror comprised of AlN/GaN multilayer structure (Figure 44a). The phonon mode frequency of sample A3 is 0.69 THz at zone center, consistent with experimental observation. The acoustic gap of phonon mirror at the Brillouin zone center was obtained between 0.65 - 0.73 THz. Reflectivity of the full cavity structure is showed in Figure 44b.
Chapter 4. Optical properties and carrier dynamics in GeSn nanocrystals and quaternary alloy BeMgZnO

4.1. Optical gap engineering and carrier dynamics in Ge$_{1-x}$Sn$_x$ QDs

Energy gap tuning and carrier dynamics in Ge$_{1-x}$Sn$_x$ QDs were explored using SSPL and TRPL and the experimental results were compared with theory. A wet-colloidal strategy was used to produce high quality Ge$_{1-x}$Sn$_x$ QDs with a diameter of 2.0±0.7 nm and Sn compositions of x = 0.05, 0.07, 0.12, and 0.23. Details of the synthesis procedures have been discussed elsewhere. Theoretical calculations were done using Heyd-Scuseria-Ernzerhof (HSE) hybrid functional theory. In a hybrid functional, the standard generalized gradient approximation (GGA) exchange correlation part of the density functional is mixed with a Fock-type exchange in varying proportions. The amount of exact exchange can be tuned for a particular material to obtain the best agreement of computed $E_g$ and effective masses with experiment.

For optical measurements, QD samples were spin-coated on sapphire or silicon substrates and mounted on a closed cycle He cryostat. Steady-state PL and TRPL measurements were performed using a frequency doubled Ti:sapphire laser (385 nm wavelength, 150 fs pulse width, 8 kHz to 80 MHz repetition rate) as the excitation source. A liquid N$_2$ cooled charge coupled device (CCD) camera connected to a spectrometer was employed to collect the steady-state PL spectra, and a Hamamatsu streak camera with 25 ps temporal resolution was used to analyze the PL transients. Hitachi FE-SEM Su-70 model scanning electron microscope (SEM) operating at 20 keV, coupled with an in situ EDAX energy dispersive x-ray spectroscopy (EDS) detector unit was employed for the elemental analysis. Transmission electron microscopy (TEM) images were collected on a Zeiss Libra 120 model microscope operating at 120 kV. Samples for TEM analysis were prepared by
drop casting the NPs in hexane onto carbon coated copper grids, followed by evaporation of the solvent.

Figure 45(a) shows the SSPL spectra of all four samples measured at 15 K. The PL peaks exhibit a red-shift from 1.88 eV for the sample with 5% Sn content to 1.61 eV for that with 23% Sn content. As these alloy QDs have the same nearly spherical shape and average particle size, hence the systematic red-shift in PL can be attributed to the decrease of bulk bandgap due to increasing Sn content. Moreover, strong quantum confinement effects are evident in this ultra-small size regime as the gaps of Ge\textsubscript{1-x}Sn\textsubscript{x} QDs are well above those of their bulk counterparts (0.1-0.6 eV).\textsuperscript{111}

Figure 45. (a) PL spectra of the Ge\textsubscript{1-x}Sn\textsubscript{x} QDs with varying Sn content investigated at 15 K, (b) Experimental (PL peak) and theoretical transition energies as a function of % Sn in 2.1 nm and 2.7 nm QDs. Inset shows the size histogram of Ge\textsubscript{0.77}Sn\textsubscript{0.23} QDs sample, representative of QDs with different Sn compositions, obtained from TEM analysis without any postsynthetic size selection.

The PL peak position, both at 15 K and 295 K, as a function of Sn content is plotted in Figure 45(b) along with the theoretical energy gaps calculated using tuned HSE for 2.1 and 2.7 nm size.
GeSn QDs. It is evident that the experimentally obtained band-gaps are consistent with theoretically calculated values for 2.7 nm QDs even though the TEM data revealed an average size of 2.0±0.7 nm. This deviation can be attributed to size variation within an experimental sample, where the PL is dominated by the emission from the larger particles because of their better passivation resulting in reduced non-radiative recombination. The PL peaks were observed to blue shift by 14-19 meV when the excitation density was increased from 40 mWcm$^{-2}$ to 40 Wcm$^{-2}$ at 15 K. X. Wen et al.\textsuperscript{112} reported a blue shift of 20 and 120 meV in Si QDs of sizes 2.5 and 3.8 nm, respectively when the excitation density was increased by three orders of magnitude at room temperature. They reported that the larger shift in 3.8 nm-QDs is due to quantum confinement effect. However, the smaller shift in 2.5 nm-QDs, where quantum confinement should be even stronger, was attributed to the dominance of surface states in luminescence.

As shown in Figure 45(b) PL measurements of the QD samples were also performed at room temperature (295 K). It is evident that the PL peak at room temperature for all the samples is blue shifted compared to that at low temperature. This temperature dependence of PL peak position can be ascribed to the interaction of two exciton states; dark and bright exciton. An exciton in which the electron and the hole spins are oriented parallel to each other is referred to as dark exciton which is not optically active and is characterized by long decay time.\textsuperscript{113} In contrast, spin state of electron is opposite to that of hole in a bright exciton which is optically active and has short lifetime. At low temperatures, excitons in the QDs occupy the lower-energy dark states and PL emission originates from these states. As the temperature increases, thermal activation of bright exciton (higher-energy states) takes place and consequently PL emission blue-shifts to higher energy. These two exciton states are separated by a bright-dark splitting energy, $\Delta_{\text{db}}$, because of
the electron-hole exchange interaction. $\Delta_{db}$ can be several meV to tens of meV depending on the material system as well as on the size of QDs.\textsuperscript{114}

In order to reveal the dynamics involving different relaxation and recombination processes of non-equilibrium carriers, TRPL spectroscopy was employed. PL transients measured at 15 K are shown in Figure 46. All samples exhibit biexponential PL decays with slow and fast decaying components, where the fast decays are most likely associated with surface nonradiative recombination and slow decays are due to radiative recombination in the bulk of the QDs. In QDs containing surface defects, carrier trapping is usually significantly faster than radiative recombination which leads to this two-component PL decay.\textsuperscript{115}

![Figure 46. PL transients of the Ge$_{1-x}$Sn$_x$ QD samples of different composition at 15 K.](image)

A biexponential decay function $A_{\text{fast}}e^{-t/\tau_{\text{fast}}} + A_{\text{slow}}e^{-t/\tau_{\text{slow}}}$ was used to fit the PL transients, where time constants $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ represent the fast and the slow decay components,
respectively. As shown in Figure 47(a), $\tau_{\text{slow}}$ ($\sim 24 \, \mu s$) is practically independent of the Sn content for up to 12% Sn, but decreases significantly to 3 $\mu s$ for 23% Sn. The fast decay components, $\tau_{\text{fast}}$, are shown in the inset of Figure 47(a).

![Figure 47](image)

**Figure 47.** Experimental PL decay times at (a) 15 K and (b) 295 K as a function of %Sn in Ge$_{1-x}$Sn$_x$ QDs. Fast decay components are shown in the insets of (a) and (b).

Our calculations suggest that in colloidal GeSn QDs possible interplay between surface state localized carriers and dark-bright exciton splitting is responsible for the observed optical response. TD-HSE calculations indicate that dark excitons should have a lifetime of $\sim 1-10 \, \mu s$ at 0% Sn ideal QDs, followed by a roughly an order of magnitude drop for 5% Sn and a constant lifetimes for other Sn concentrations. However, the PL peak shifts with temperature suggest a significant contribution of surface traps. Therefore, at low temperatures, long biexponential decay suggests that carriers could be localized at the surface, with small overlap between the wavefunctions.\textsuperscript{116,117} The slow surface recombination of localized carriers could explain the fact that until concentrations of Sn reach 23%, there is almost no change in PL lifetime. Calculations also suggest that alloying with Sn smears the separation between dark and bright excitons in SnGe alloy QDs, introducing excitons with increasing optical oscillator strength with increasing Sn content. This
would lead to averaged slow decrease in PL lifetimes of excitonic transitions, revealed at high Sn concentrations.

PL decay times were found to be much faster at room temperature. As shown in Figure 47(b), \( \tau_{\text{slow}} \) is around 10 ns for QDs with Sn content up to 12% and 28 ns for the QD sample with 23% Sn. This dramatic decrease of three orders of magnitude in decay times with increasing temperature is a likely result of the thermal activation of dipole-allowed bright exciton transitions, while the PL decay at 15 K is dominated by slow recombination of spin-forbidden triplet dark excitons and surface traps. From theoretical calculations, the recombination of carriers localized on deep surface traps is found to be independent of temperature. In experiment it is probably somewhat dependent on temperature, but not as dramatic as dark-bright excitons recombination. Therefore, room temperature PL is likely dominated by the bright exciton recombination in the core of the QD. This dark-bright exciton splitting induced several orders of magnitude change in PL decay times with increasing temperature has also been observed in other colloidal semiconductor QDs such as PbSe, CdSe, Ge QDs.\(^{115,118,119}\) Our calculations suggest that room temperature lifetimes for radiative transitions, which are dominated by bright excitons, should have almost no dependence on %Sn (only very weakly decreasing with %Sn), and should be around 10-20 ns. Fast component is also likely due to surface state radiative recombination where the overlap between the surface state and the core carrier wavefunction significantly increases due to the increased thermal vibrations. Therefore, the observed dramatic increase of room temperature PL decay times can be attributed to the simultaneous effect of thermal activation of dipole-allowed bright excitons and carrier detrapping from surface states.

Tunability of energy gap and carrier dynamics in colloidally synthesized 2.0±0.7 nm sized Ge\(_{1-x}\)Sn\(_x\) QDs (x = 0.05 – 0.23) were discussed. Optical gap at 15 K, as deduced from steady-state
PL measurements, can be varied from 1.88 eV to 1.61 eV by changing Sn content from 5% to 23%. Taking the size and compositional variation of these QDs into account, experimental energy gap values are fairly consistent with theoretically calculated ones. PL decay times were found to be 3 – 27 μs at 15 K due to the slow recombination of dipole-forbidden dark excitons and effect of surface states. However, at room temperature, they decreased to 9 – 28 ns and this dramatic change was attributed to the effect of dipole-allowed bright exciton and carrier detrapping from surface states.

4.2. Optical investigation of BeMgZnO quaternary alloys

Carrier localization is a common phenomenon in semiconductor alloys. A simple schematic of carrier localization is shown in Figure 48. It mainly originates due to alloy compositional fluctuation. Depending on the temperature and excitation density, carrier can reside either in shallow localized states or in deep localized states.

![Schematic of carrier localization](image)

*Figure 48. Schematic of carrier localization*
To investigate the effects of localization in BeMgZnO quaternary alloys grown on GaN and the effect of Mg/Be ratio on localization and optical performance of the quaternary thin films, SSPL and TRPL were performed. Figure 49 shows the cross-sectional schematics of the O-polar and Zn-polar BeMgZnO samples investigated. BeMgZnO thin films were grown by plasma assisted molecular beam epitaxy (P-MBE) with an RF oxygen plasma source and Knudsen cells for Zn, Be, and Mg. BeMgZnO thin films were grown on epitaxial carbon compensated high resistivity GaN(0001)/Al₂O₃(0001) templates. Pyrolytic boron nitride (PBN) crucibles were used for Zn and Mg sources and a BeO crucible for the Be source. The polarity of the grown layer was controlled by varying VI/II ratio during low temperature ZnO growth. First, a ~15 nm-thick low temperature ZnO buffer layer was grown at 300 °C followed by annealing at 730 °C to achieve an atomically flat surface. Then, a 120 nm thick high temperature ZnO layer was grown at 680 °C. BeMgZnO films were deposited at ~1.3 x 10⁻⁵ Torr oxygen pressure with thicknesses 130 nm and 100 nm for Zn-polar and O-polar films. The average growth rate of Zn-polar samples was 170 nm/h and that of O-polar was 75 nm/h.

<table>
<thead>
<tr>
<th>BeMgZnO (0001) / (000\overline{1})</th>
<th>130 / 100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT ZnO (0001) / (000\overline{1})</td>
<td>120 nm</td>
</tr>
<tr>
<td>Buffer ZnO (0001) / (000\overline{1})</td>
<td>15 nm</td>
</tr>
<tr>
<td>High resistivity GaN (0001)</td>
<td>2.5 (\mu)m</td>
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<tr>
<td>Buffer AlN (0001)</td>
<td>350 nm</td>
</tr>
<tr>
<td>Sapphire (0001)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 49. The schematic diagram of Zn-polar (0001) and O-polar (000\overline{1}) BeMgZnO samples grown on GaN templates.
PL and TRPL measurements were performed using frequency-tripled Ti:Sapphire laser excitation (4.68 eV) with 150 fs pulse width and 80 MHz repetition rate. PL was analyzed by a liquid nitrogen cooled charge couple device (CCD) camera connected to a 30 cm focal length monochromator. TRPL was analyzed by a spectrometer attached to a 30 ps resolution Hamamatsu streak camera. The photoexcited carrier densities were estimated as 8×10^{15} \text{ cm}^{-3} and 8×10^{17} \text{ cm}^{-3} for PL and TRPL measurements, respectively. The compositions of quaternary Be_{x}Mg_{y}Zn_{1-x-y}O alloys studied here were deduced by comparing the measured c lattice parameters (from X-ray diffraction) and bandgaps (from absorption edge) with previously determined values for the full range of compositions.\textsuperscript{121,122} The lattice parameters, low temperature PL peak positions and Mg/Be ratios are shown in Table 4.

Low temperature (LT) and room temperature (RT) SSPL spectra of BeMgZnO samples grown on GaN are shown in Figure 50. From LT spectra, sample A and Z with the highest Mg/Be ratio, r_{Mg/Be}, and lowest PL energy peak position, E_{PL}, exhibits the highest PL intensity. Sample B has \sim 0.1 \text{ eV} higher E_{PL} than that of sample B1. The PL intensity at LT, I_{LT}, is inversely proportional to r_{Mg/Be}. Sample B3, despite its higher PL peak position is featured by higher I_{LT} than that of sample B2 due to mutual compensation effects between Be and Mg (higher r_{Mg/Be} than that of sample B2). On the other hand, at RT sample B3 with r_{Mg/Be}=2.5 shows highest PL intensity, I_{RT}. The reason will be discussed later in the text. Additionally, subbandgap BL2 GaN transitions are clearly observed. Demchenko et al.\textsuperscript{123} attributed BL2 transitions to a hydrogen-carbon defect complex, either C_{N}O_{N}H_{i} or C_{N}H_{i}. Weak band-to-band GaN luminescence is absorbed in the ZnO layer and masked with BeMgZnO luminescent shoulder. The Zn-polar sample Z has stronger LT PL intensity and similar bandgap in comparison to sample B1 most likely due to better crystal quality of the quaternary layer provided by lower film thickness (100 nm for Z and 130 nm for B1,
B2, B3) which may provide better crystal quality of the quaternary layer. The absorption depth at 265nm excitation is ~50nm for our samples.

![Graph showing PL intensity vs energy for different samples](image)

**Figure 50.** Low temperature and room temperature PL spectra of O-polar BeMgZnO samples grown on GaN. Sample B1 is Be$_{0.04}$Mg$_{0.17}$Zn$_{0.79}$O, sample B2 is Be$_{0.11}$Mg$_{0.15}$Zn$_{0.74}$O, sample B3 is Be$_{0.10}$Mg$_{0.25}$Zn$_{0.65}$O and sample Z is Be$_{0.03}$Mg$_{0.18}$Zn$_{0.79}$O.

To evaluate the carrier dynamics in BeMgZnO layers, TRPL measurements were performed at 15 K. The PL transients were fitted using single exponential decays for samples B1, B2, B3 and double exponentials for sample Z. Figure 51 shows PL decay dependence on the emission energy. The time-integrated spectra exhibit two peaks that correspond to buffer ZnO (3.39eV) and BeMgZnO (3.62 – 3.90 eV) with dramatically different decay time values. All decay times for BeMgZnO layers monotonically decrease with increasing emission energy. Such behavior is characteristic for localized excitons. It is important to note that the measured buffer ZnO decay times are not representative as they are very close to the system response time.

The observed decay times can be expressed as
\[ \tau(E) = \frac{\tau_0}{1 + \exp\left(\frac{E - E_0}{\Delta_0}\right)} \] (23)

where \( \tau_0 \) is the exciton recombination time in the absence of the energy transfer, \( \Delta_0 \) is the degree of the localization depth in the bandtail state, and \( E_0 \) is the characteristic energy where recombination rate equals the delocalization rate. It is assumed that above the characteristic energy \((E > E_0)\) localized excitons will transfer out of localized states and eventually undergo nonradiative recombination; below the characteristic energy \((E < E_0)\) localized excitons do not have sufficient energy and undergo radiative recombination. Longer decay times of Zn-polar sample Z were used for the fitting.
Figure 51. PL decay time dependence on the emission energy at 15 K and time integrated PL for a) sample B1: Be_{0.04}Mg_{0.17}Zn_{0.79}O; b) sample B2: Be_{0.11}Mg_{0.15}Zn_{0.74}O; c) sample B3: Be_{0.10}Mg_{0.25}Zn_{0.65}O; d) sample Z: Be_{0.03}Mg_{0.18}Zn_{0.79}O. The spectral sampling width is 1nm. The localization parameters are determined from the fit with Equation (23).

Table 4 summarized the localization parameters obtained by fitting experimental decay times with Equation (23). Sample Z with the smallest E_{PL} and the highest r_{Mg/Be} shows the smallest localization depth, Δ₀. Sample B2 with the lowest r_{Mg/Be} shows the highest Δ₀. On the other hand,
sample B3 that has the highest PL peak energy and intermediate Mg/Be ratio shows significantly smaller $\Delta_0$ in comparison with sample B2. Despite the increase in PL peak position, the higher $r_{\text{Mg/Be}}$ supports smaller localization depth by allowing Be and Mg to mutually compensate each other’s effects on the lattice of ZnO by reducing formation energy and strain. Sample B2 has almost twice longer decay time, $\tau_0$ in comparison to other two samples, which possibly originates from high degree of localization or potential fluctuations. All O-polar samples show single exponential decays and Zn-polar samples shows double exponential decay with faster decay time related to nonradiative recombination. The slower decay time of sample Z that is related to radiative processes is significantly longer suggesting enhanced optical quality in comparison to that of O-polar samples. No TRPL investigation was reported for BeMgZnO or BeZnO. Thus, only values for MgZnO and CdZnO are presented for comparison. Chernikov et al.\textsuperscript{124} reported longer decay time ($\tau_0 = 1 \text{ ns}$) and smaller localization depth ($\Delta_0 = 0.06 \text{ eV}$) and a characteristic energy of $E_0 = 3.90 \text{ eV}$ for Mg$_{0.21}$Zn$_{0.79}$O with low temperature bandgap of 3.75 eV.

Table 4. Composition, Mg to Be content ratio ($r_{\text{Mg/Be}}$), out-of-plane lattice parameter ($c$), PL peak position ($E_{\text{PL}}$), characteristic energy ($E_0$), the exciton recombination time in the absence of the energy transfer ($\tau_0$), PL transients ($\tau$), degree of localization depth determined from the fit with Equation (23) to the spectral dependence of the decay time ($\Delta_0$), and $\Delta E_t$ is the observed temporal redshift of the PL peak position.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$r_{\text{Mg/Be}}$</th>
<th>$c$, Å</th>
<th>$E_{\text{PL}}$, eV</th>
<th>$E_0$, eV</th>
<th>$\tau_0$, ns</th>
<th>$\tau$, ns</th>
<th>$\Delta_0$, meV</th>
<th>$\Delta E_t$, meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1 Be$<em>{0.04}$Mg$</em>{0.17}$Zn$_{0.79}$O</td>
<td>4.3</td>
<td>5.143</td>
<td>3.62</td>
<td>3.76</td>
<td>0.44</td>
<td>0.294</td>
<td>98</td>
<td>8</td>
</tr>
<tr>
<td>B2 Be$<em>{0.11}$Mg$</em>{0.13}$Zn$_{0.76}$O</td>
<td>1.4</td>
<td>5.124</td>
<td>3.69</td>
<td>3.54</td>
<td>0.83</td>
<td>0.300</td>
<td>268</td>
<td>55</td>
</tr>
<tr>
<td>B3 Be$<em>{0.10}$Mg$</em>{0.22}$Zn$_{0.68}$O</td>
<td>2.5</td>
<td>5.117</td>
<td>3.93</td>
<td>3.96</td>
<td>0.45</td>
<td>0.294</td>
<td>173</td>
<td>42</td>
</tr>
<tr>
<td>Z Be$<em>{0.03}$Mg$</em>{0.16}$Zn$_{0.79}$O</td>
<td>6</td>
<td>5.64</td>
<td>3.75</td>
<td>0.48</td>
<td>0.485 ($\tau_1$) 0.169 ($\tau_2$)</td>
<td>46</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>[124] Mg$<em>{0.27}$Zn$</em>{0.73}$O</td>
<td>N/A</td>
<td>-</td>
<td>3.75</td>
<td>3.90</td>
<td>1</td>
<td>60</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[125] ZnO/Mg$<em>{0.27}$Zn$</em>{0.73}$O MQW</td>
<td>N/A</td>
<td>-</td>
<td>3.44</td>
<td>3.64</td>
<td>0.19</td>
<td>13.6</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[126] Zn$<em>{0.91}$Cd$</em>{0.09}$O (Zn$<em>{0.84}$Cd$</em>{0.16}$O)</td>
<td>N/A</td>
<td>-</td>
<td>2.65 (3.00)</td>
<td>2.96 (2.76)</td>
<td>0.065 (0.023)</td>
<td>70 (55)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
The temporal dependence of the PL peak position for BeMgZnO samples grown on GaN is shown in Figure 52. As evident from Figure 51, decay rates at high emission energies are higher. This results in the redshift of the PL spectra with time. The observed redshifts $\Delta E_t$ are 10 meV, 8 meV, 55 meV, and 42 meV for samples Z, B1, B2, and B3, respectively, under the same excitation density. Samples with higher $\Delta_0$ also show higher $\Delta E_t$.

Figure 52. Temporal dependence of PL peak position of O-polar BeMgZnO samples grown on GaN at 15 K. Delay time equal to zero corresponds to the moment of pulse excitation. Note, vertical scales are different.
There are two potential possibilities explaining large shift in the peak position. The first one is potential fluctuations that originate from an inhomogeneous distribution of charged defects.\textsuperscript{127} The diagonal tunnel transitions with reduced energy take longer time to recombine than direct fast transitions and, therefore, redshift is expected as time progresses. Another possibility is band filling of the localized states that would result in carriers occupying higher energy non-localized states; with time, localized states will become available and remaining de-localized carriers would fall-in to the localized states which would result in observed temporal redshift in the PL spectra. Both of these processes may exist simultaneously.

Figure 53 shows that both the dependence of degree of localization depth $\Delta_0$ and the temporal redshift of the PL peak $\Delta E_t$ are decreasing with increasing Mg/Be content ratio. Such dependence may be explained by mutual compensation of ZnO lattice distortion and minimization of formation energy due to incorporation of Mg and Be.\textsuperscript{128–130} Lower Mg/Be ratio would result in stronger internal strain and thus strain-driven potential fluctuations and localizations. Localized carriers have higher probability to recombine radiatively in the localized state, unless there are non-radiative centers in close proximity to the potential minima. However, if the localization is driven by strong internal strain which also generate high density of defects acting as nonradiative recombination channels, localizations centers may be located near non-radiative center and confine carriers for non-radiative transitions.
Figure 53. The dependence of the degree of localization depth $\Delta_0$ (top) and the temporal redshift of the PL peak $\Delta E_t$ (bottom) on $r_{\text{Mg/Be}}$ content ratio.

TRPL measurements revealed an increase in the degree of localization depth and temporal redshift with the increase in $r_{\text{Mg/Be}}$ content ratio in BeMgZnO samples grown on GaN which are attributed to mutual compensation effects of Be and Mg to reduce formation energy and strain. The localization depths (temporal redshift) are 46 meV (10 meV), 98 meV (8 meV), 173 meV (42 meV), and 268 meV (55 meV) for Be$_{0.03}$Mg$_{0.18}$Zn$_{0.79}$O, Be$_{0.04}$Mg$_{0.17}$Zn$_{0.79}$O, Be$_{0.10}$Mg$_{0.25}$Zn$_{0.65}$O and Be$_{0.11}$Mg$_{0.15}$Zn$_{0.74}$O, respectively. PL transients indicate that emission at low temperature is dominated by recombination of localized excitons, which exhibit decay times as long as $\tau_1 = 0.485$ ns at PL peak position. The inverse proportionality of low temperature PL intensity and $r_{\text{Mg/Be}}$ content ratio was observed. However, at room temperature this proportionality was broken. With reducing $r_{\text{Mg/Be}}$ the compensation effects between Mg and Be weakens, which increases both number of defects as well as strain induced localization $\Delta_0$. For room temperature performance higher degree of localization is necessary. Since localization depth and defect density are somewhat coupled, there exists optimum $r_{\text{Mg/Be}}$ content ratio. At room temperature, the optimum $r_{\text{Mg/Be}}$ ratio is around 2.5.
Chapter 5. Conclusions and outlook

Optical investigations have been carried out on InGaN heterostructures, for improved performance in photonic and phononic applications, as well as on Ge$_{1-x}$Sn$_x$ QDs and BeMgZnO thin films, as potential candidates for optoelectronics. A set of experimental techniques such as SSPL, TRPL, NSOM, TRDT were used to evaluate and optimize the active region quality of light emitting devices and acoustic cavities based on polar InGaN heterostructures, to explore the nature of defects and defect related luminescence in semipolar InGaN heterostructures, and to investigate recombination dynamics in colloidal Ge$_{1-x}$Sn$_x$ QDs and BeMgZnO thin films. Silvaco Atlas software was used to simulate the electronic energy bands, carrier concentration and radiative efficiency in InGaN based LED structures and these results were found to be consistent with what was observed experimentally and they also helped establish a better understanding of the device physics.

In order to improve the quantum efficiency of InGaN LEDs, optimization of electron injector (EI) layer was explored as well as the effectiveness of δ p-doped MQWs barrier. EI layer thickness plays an important role in quantum efficiency of LED structures through reduction of electron overflow. Increasing the two-layer staircase electron injector (SEI) thickness from 4+4 nm to 20+20 nm in single 3 nm DH LEDs substantially reduced the electron overflow and increased EQE both at low and high injection without degrading material quality. In addition, the optimum SEI design was found to depend on the active region structure employed. However, graded electron injectors (GEI) instead of SEI should be more effective in reducing electron overflow because the conditions imposed on heterojunction discontinuities (in the case of SEI) are eliminated entirely as GEI automatically cools electrons when they gain sufficient kinetic energy to emit LO phonons.
Moreover, electrons in the graded injector are continuously accelerated in the direction normal to the heterointerface due to the electric field. Therefore, LED structures incorporating GEI should be investigated for further reduction in electron overflow and consequently, efficiency droop. In an effort to improve the carrier symmetry and reduce the electron overflow further, δ-doping of barriers with Mg was found to significantly improve the quantum efficiency of multi-well LEDs. With Mg δ-doping of the first barrier on the n-GaN side, the relative peak EQE was increased by 20% compared with the reference structure due to enhanced hole injection and the reduction of carrier-injection asymmetry as supported by numerical simulations. Moreover, employment of AlN/GaN periodic MLs was found to efficiently enhance indium incorporation efficiency in the InGaN MQWs by promoting the strain relaxations and this approach could be a potential candidate to alleviate the efficiency limitations for long wavelength light emitters. In addition, carrier diffusion lengths in p- and n-type GaN were measured using simple spectroscopic techniques and the measured value was used to calculate electron escape rate in InGaN LEDs.

The polar c-plane orientation forms the mainstay of nitride based optoelectronics. However, significant improvement of electron-hole wavefunction overlap in semipolar InGaN heterostructures, due to the presence of reduced polarization fields compared to their c-plane counterpart, makes them promising candidates for light emitting devices provided that they can be manufactured with good crystal quality. The spatial variations of extended defects, stacking faults and threading dislocations, and their effects on the optical quality for semi-polar [(1̅01) and (11̅22)] InGaN light emitting diodes (LEDs) were investigated by near-field scanning optical microscopy at 85 K. The near-field PL from the c+ wings in (1̅101) heterostructures was found to be relatively strong and uniform across the sample but the emission from the c- wings was substantially weaker due to the presence of high density of threading dislocations and basal plane
stacking faults. In case of (11\2\2) heterostructures, striated regions had weaker PL intensities compared to other regions and the meeting fronts of different facets were characterized by higher Indium content due to the varying internal field.

To investigate their potential for terahertz sources, zone-folded longitudinal acoustic phonon (ZFLAP) oscillations have been studied in InGaN MQWs with different In content separated by InGaN barriers containing 3% In. The amplitude of ZFLAP oscillations was observed to increase with increasing piezoelectric field (i.e. In content) in the InGaN QWs as well as with increasing excitation (pump) power density. Oscillation frequency, independent of excitation power density, was confirmed to reduce with increasing MQW period. Further enhancement of oscillations and increased decay times can be achieved by forming an acoustic cavity, which incorporates a phonon generating active region (InGaN MQW), placed between suitably designed two acoustic mirrors (AlN/GaN superlattice). Design of such a nanocavity has been proposed which would lead to the realization of terahertz generating devices based on InGaN heterostructures.

Ultrafast carrier dynamics and radiative efficiency were investigated in other material systems that are promising for optoelectronic applications such as colloidal Ge\(_{1-x}\)Sn\(_x\) QDs and epitaxial BeMgZnO quaternary. Tunability of transition energies and carrier dynamics in colloidal synthesized 2 nm sized Ge\(_{1-x}\)Sn\(_x\) QDs (x = 0.05 – 0.23) has been achieved. Optical gap at 15 K can be varied from 1.88 eV to 1.61 eV by changing Sn content from 5% to 23%. PL decay times were found to be 3 – 27 μs at 15 K due to surface traps and the slow recombination of spin-forbidden dark excitons. However, at room temperature, they decreased to 9 – 28 ns and this dramatic change was attributed to the effect of spin-allowed bright excitons. Further investigations are required in order to achieve faster radiative recombination rates and possibly direct gap transition in Ge\(_{1-x}\)Sn\(_x\) QDs by incorporating more Sn. Better surface passivation should be
employed to reduce the effect of surface recombination. Carrier dynamics and optical properties were studied also in BeMgZnO/ZnO thin films grown on GaN, another material system that has the potential for applications in UV and intersubband optoelectronics owing to its wide bandgap and large conduction band offsets. The degree of localization depth was found to increase with the decrease in r_{Mg/Be} content ratio which is attributed to mutual compensation effects of Be and Mg to reduce formation energy and strain. The localization depth increased from 46 meV for Be_{0.03}Mg_{0.18}Zn_{0.79}O to 268 meV for Be_{0.11}Mg_{0.15}Zn_{0.74}O. Based on the observed correlation between localization depth and defect density, an optimum r_{Mg/Be} content ratio of around 2.5 has been estimated for high quality BeMgZnO layers.
References

5. (n.d.).


Curriculum Vitae

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Peer reviewed journal papers:

2. R. Esteves, S. Hafiz, D. Demchenko, Ü. Özgür, and I. Arachchige, “Ultra-small Ge$_{1-x}$Sn$_x$ quantum dots with visible photoluminescence”, Submitted to Chemical Communications


Peer reviewed conference papers:


