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Optical Spectroscopy of Wide Bandgap Semiconductor Heterostructures and Group-IV Alloy Quantum Dots

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Optical Spectroscopy of Wide Bandgap Semiconductor Heterostructures and Group-IV Alloy Quantum Dots

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University.

by

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# Table of Contents

List of Figures.................................................................................................................................................v

List of Tables.....................................................................................................................................................viii

Abstract............................................................................................................................................................ix

1. **Introduction** ............................................................................................................................................... 1

2. **Localization in InGaN MQWs and BeMgZnO** ....................................................................................... 4
   2.1. InGaN Material system ......................................................................................................................... 4
   2.2. Localization ........................................................................................................................................... 6
       2.2.1. Temperature dependent carrier distributions .............................................................................. 6
       2.2.2. Considerations of Localization effect .......................................................................................... 9
   2.3. Representation of PL Behavior by Mathematical Models ................................................................. 11
   2.4. Relevant Recent Work on Localization in InGaN MQWs ............................................................... 17
   2.5. Results and Discussion ......................................................................................................................... 27
       2.5.1. QW thickness variation ................................................................................................................. 30
           2.5.1.1. Dependence on QW thickness ............................................................................................ 31
           2.5.1.2. Excitation Power dependence ............................................................................................. 36
       2.5.2. Varying number of MQW periods ............................................................................................. 38
           2.5.2.1. Dependence on number of wells ......................................................................................... 39
           2.5.2.2. Excitation Power dependence ............................................................................................. 40
   2.6. Localization in BeMgZnO ..................................................................................................................... 42
3. Optical Properties of Group-IV Alloy Quantum Dots ............................................. 47
   3.1. Background ......................................................................................................... 47
   3.2. Previous work ..................................................................................................... 48
   3.3. Results and Discussion ...................................................................................... 50
4. Conclusion and Future Work .................................................................................. 58

References .................................................................................................................. 62

Vita .............................................................................................................................. 65
List of Figures

Figure 2.1: Plot of bandgap vs. lattice constant for InGaN material systems. Notice that an alloy of GaN and InN spans the 2-3 eV range, corresponding to visible light. .............................................. 5

Figure 2.2: Plot of charge distribution with temperature. Charges are (Left panel) (a) at random locations at low temperature, (b) “localized” at global minima with addition of thermal energy and, (c) redistributed out of wells at high temperature. Correspondingly, (Right Panel) at (a) linewidth is significant but (b) decreases, then (c) increases due to thermal broadening at high temperature. ........................................................................................................ 8

Figure 2.3: PL peak energy as a function of temperature for LED samples (a) 1.8 nm, (b) 2.4 nm, (c) 3 nm, and (d) 3.6nm. The red lines are fits using the modified Varshni functional form (Li et al. Chinese Phys. B. 2017) ........................................................................................................ 19

Figure 2.4: Temperature dependent linewidth for the thinnest well sample (a) to thickest (d). Values at their largest magnitude are (a) 65.0 meV, (b) 75.4 meV, (c) 79.9 meV, and (d) 98.0 meV. (Li et al. Chinese Phys. B. 2017) ........................................................................................................ 19

Figure 2.5: Temperature dependent PL peak position with identically grown QWs but with quantum barrier width increasing from 6.6nm in sample B1, to 14.4nm in B2, and 25.3nm in B3. (Liang, Chinese Phys. B, 2014) ........................................................................................................ 22

Figure 2.6: Integrated PL for (a) resonant (405nm), and (b) non-resonant (325nm) excitation of the LED structures. In (b) an anomalous mid-temperature increase in PL intensity is measured. (Lu, Scientific Reports, 2014) ........................................................................................................ 24

Figure 2.7: Dependence of PL peak position and linewidth with temperature in an InGaN QD structure. (Zhao, Chinese Phys. Lett. 2014) ........................................................................................................ 25

Figure 2.8: Integrated PL intensity per temperature of a highly phase-separated InGaN MQW LED. (Wang, J. App. Phys., 2013) ........................................................................................................ 26

Figure 2.9: Cross-sectional HRTEM image of the highly phase-separated InGaN MQW. (Wang, J. App. Phys., 2013) ........................................................................................................ 26

Figure 2.10: A simplified conduction band schematic of the InGaN MQW LED structure ...... 28

Figure 2.11: Plot of PL spectra for 2.2nm QW sample LED2 at 300K, 5.16 W/cm² pump power. ........................................................................................................ 30
Figure 2.12: (a) Temperature dependent spectra of 1.5nm QW sample LED1, (b) 2.2nm QW LED2, and (c) 3.15nm QW sample LED3. The solid lines are the fitted modified Vina formula.

Figure 2.13: (a) Localization per pump power for each QW thickness. PL from each sample translated in energy where energy at 15K is zero (b) Low-power (0.052-5.16 W/cm²) peak energy per temperature for each QW thickness. (c) Medium-power (2.06-5.16 W/cm²) peak energy per temperature for each QW thickness. (d) High-power (206-516 W/cm²) peak energy per temperature for each QW thickness.

Figure 2.14: Temperature dependent spectra of (a) 6x2.2nm MQW sample LED2, (b) 9x2.2 nm MQW sample LED4, and (c) 15x3.15 nm MQW sample LED5. The solid line is a fit using the modified Vina formula.

Figure 2.15: Peak energies from each sample assembled per power. (a) Localization per pump power for each sample. (b) Peak energy for each sample at 0.0516 W/cm² (c) 5.16 W/cm², and (d) 50.16 W/cm².

Figure 2.16: Low temperature PL of BeMgZnO samples. Sample BMZ1 is Be_{0.04}Mg_{0.17}Zn_{0.79}O, sample BMZ2 is Be_{0.11}Mg_{0.15}Zn_{0.74}O and sample BMZ3 is Be_{0.10}Mg_{0.25}Zn_{0.65}O.

Figure 2.17: Temperature dependence of PL peak position for (a) BMZ1 Be_{0.04}Mg_{0.17}Zn_{0.79}O and (b) BMZ2 Be_{0.11}Mg_{0.15}Zn_{0.83}O grown on GaN.

Figure 2.18: Decay dependence on emission energy at 15K, and integrated PL for a) sample BMZ1: Be_{0.04}Mg_{0.17}Zn_{0.79}O; b) sample BMZ2: Be_{0.11}Mg_{0.15}Zn_{0.74}O; and c) sample BMZ3: Be_{0.10}Mg_{0.25}Zn_{0.65}O. The spectral sampling step is 1nm. The localization parameters are determined from the fit with Equation (7).

Figure 3.1: PL decay times measured 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) (Hafiz, J. Phys. Chem. Lett., 2016).

Figure 3.2: Normalized dropcast photoluminescence spectra of Ge_{1−x}Sn_{x} alloy NCs varying Sn compositions: (1) x = 0.015 (1.60 eV), (2) x = 0.019 (1.51 eV), (3) x = 0.027 (1.42 eV), (4) x = 0.034 (1.38 eV), and (5) x = 0.042 (1.34 eV), and (6) x = 0.056 (1.31 eV).

Figure 3.3: Diffuse reflectance spectra (converted to absorbance using the Kubelka–Munk (KM) remission function) of Ge_{1−x}Sn_{x} alloy NCs as a function of Sn composition: (1) x = 0.015 (1.60 eV), (2) x = 0.019 (1.51 eV), (3) x = 0.027 (1.42 eV), (4) x = 0.034 (1.38 eV), and (5) x = 0.042 (1.34 eV), and (6) x = 0.056 (1.31 eV).
Figure 3.4: Room temperature and low temperature steady-state PL for (a) 3.5%Sn QD sample, and (b) 3.8%Sn QD sample. .............................................................................................................................................52

Figure 3.5: Low temperature and Room temperature PL decays of GeSn QD samples (2) and (6) .................................................................................................................................................53

Figure 3.6: Schematic diagram of the radiative recombination pathways in Ge$_{1-x}$Sn$_x$ alloy QDs (Hafiz, J. Phys. Chem. Lett., 2016) .............................................................................................................................................54

Figure 3.7: Oscillator strengths of optical transitions for a series of D = 1.4 nm Ge$_{1-x}$Sn$_x$ alloy QDs of varying Sn concentrations. Red arrows indicate the dark–bright exciton splitting in each QD. Zero of the energy axis is placed at the lowest unoccupied HSE single-particle state. (Demchenko et al. J of Phys Chem C. 2017) ..........................................................................................................................55

Figure 3.8: (a) Normalized steady state room temperature PL for Si$_{-0.05}$Ge$_{0.90}$Sn$_{-0.05}$ nanoparticles in solution state and dropcast forms. Note that once deposited into dropcast form, PL emission is redshifted by ~0.25 eV, (b) decays of solution and dropcast forms showing that initially the dropcast sample decays more quickly but then both have a similar long decay, and (c) low temperature and room temperature decay for dropcast sample showing that low temperature and room temperature share the same order of magnitude in their decays............. 56

Figure 4.1: CdSe/CdS core–shell nanocrystals. (a), Device structure used for photoconductivity measurements. (b), Energy level offsets in CdSe cores and CdS shells allow facile transport of photogenerated electrons between the nanocrystals, whereas holes stay confined to CdSe cores. The combination of highly mobile electrons and trapped holes provides high internal photoconductive gain in the CdSe/CdS nanocrystal solids. (Lee et al. Nat. Nano. 2011) .............................................................................................................................................60

Figure 4.2: Schematic of a FET with the channel assembled from inorganically capped semiconductor nanocrystals. (Lee et al., Nat. Nanotech. 2011) .............................................................................................................................................60
List of Tables

Table 1: Comparison of the Elemental Composition (SEM/EDS), Primary Particle Size and Crystallite Sizes, Band-Gaps Obtained from Kubelka–Munk Function, and Photoluminescence for 3.2–4.4 nm Ge$_{1-x}$Sn$_x$ NC..........................................................49
Abstract

OPTICAL SPECTROSCOPY OF WIDE BANDGAP SEMICONDUCTOR HETEROSTRUCTURES AND GROUP-IV ALLOY QUANTUM DOTS

By Tanner Nakagawara, M.S.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University.

Virginia Commonwealth University, 2017.

Major Director: Ümit Özgür, Ph.D.
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Efficient and robust blue InGaN multiple quantum well (MQW) light emitters have become ubiquitous; however, they still have unattained theoretical potential. It is widely accepted that “localization” of carriers due to indium fluctuations theoretically enhance their efficiency by moderating defect-associated nonradiative recombination. To help develop a complete understanding of localization effects on carrier dynamics, this thesis explores degree of localization in InGaN MQWs and its dependence on well thickness and number of wells, through temperature and power dependent photoluminescence measurements. Additionally, silicon-compatible, nontoxic, colloidally synthesizable 2-5 nm Ge_{1-x}Sn_x alloy quantum-dots (QDs) are explored for potential visible to near-IR optoelectronic applications. While bulk Ge is an indirect gap material, QD confinement allows enhanced direct transitions, and alloying with Sn improves transition oscillator strengths. Temperature dependent steady-state and time-resolved photoluminescence reveal relaxation pathways involving bright/dark excitons and surface states in Ge_{1-x}Sn_x QDs, showing their great potential for future use.
1. Introduction

Blue indium gallium nitride (InGaN) multiple quantum wells (MQWs) and 2-5 nm silicon compatible germanium tin alloy (Ge$_{1-x}$Sn$_x$) quantum dots (QDs) are very important in visible and near-infrared (IR) light emitters and detectors. InGaN MQW light-emitting diodes (LEDs) already have efficiencies superior to fluorescent or halogen lamps; however, potential to improve efficiency remains. Fluctuations in indium concentration in InGaN MQWs are theorized to cause carriers to localize at microscopic potential wells, thereby escaping high defect density associated nonradiative centers and increasing the efficiency. [1]–[5] Although this enhancement by “localization” is widely accepted there is still no consensus regarding the whole dynamics of the phenomenon. Therefore, to help develop a better understanding of its effects on carrier dynamics, localization is explored through temperature and excitation power dependent photoluminescence (PL), where effects of QW thickness and number of QW periods on PL behavior are explored. It is shown that a complete model remains unknown, but trends are identified, including suppression of the localization effect from a measured maximum of 16.0 meV to 5 meV, with an increase in four orders of magnitude in excitation density, and an increase in measured localization with the addition of QW layers, from 11 meV in 6 periods, to 16 meV in 15 periods.

With respect to Ge$_{1-x}$Sn$_x$ QDs, which are colloidally synthesized and nontoxic, quantum confinement allows high efficiency optical transitions up to ~ 2eV, as compared to bulk Ge$_{1-x}$Sn$_x$ alloy which becomes direct at greater than x=6%-10%, depending on strain. Through steady-state and time-resolved photoluminescence (TRPL) at 15K and 295K, it is shown that with up to ~24% Sn, energy gaps decrease to 1.72 eV, but QDs show enhanced oscillator strengths compared to pure Ge or Si QDs. Charge carriers exhibit slow decays on the order of 1-10 μs at 15K and 10-20 ns at 295K, which is theorized to be a result of a spin-forbidden dark exciton and carrier surface
trapping at low temperature which, with additional thermal energy, transitions to a spin-allowed bright exciton and carrier de-trapping at 295K. In addition to increased oscillator strength with the alloying of Sn, probabilities of optical transition also increase due to a reduction in bright-dark exciton splitting and blending of excitonic states. As a next-step to improve the potential of this QD system for optoelectronic applications, small (~5%) incorporation of Si into Si$_x$Ge$_{1-x-y}$Sn$_y$ QDs is explored, which results in fast (10-20 ns) decays and increased energy gaps, gaining access to a wider range of energies in the visible, while still maintaining strong oscillator strengths.

To explore and discuss the large topics of localization in semiconductor heterostructures, and group IV QDs, this thesis is broken into several parts. The first chapter is a discussion of localization, beginning with a conceptual explanation of the temperature dependent carrier distributions and how those distributions theoretically play out in temperature dependent PL behavior. Once that conceptual groundwork is established, the mathematical techniques in quantifying the localization behavior in PL are described, first with modeling overall bandgap shrinkage with increasing temperature, and then how the effect of localization is incorporated. After that, a review of current research in the realm of InGaN MQW LEDs is explored, featuring examples and analysis of relevant works, informing the work presented here. At this point, since the theoretical and practical behaviors of InGaN MQW LEDs have been described, a walkthrough of newly collected data is conducted, further illustrating the concept of localization, and contributing to the discussion of the physics and mechanisms of the process. Additionally, an exploration of localization in the relatively new wide-bandgap quaternary material system (Be,Mg)ZnO is conducted. After exploring these new results and their discussion, the analysis of localization in wide-bandgap heterostructures is concluded.
Subsequently, in the second chapter this thesis transitions to consideration of group-IV alloy QDs. First, the overall motivations of utilizing the group-IV QD material system are described, as well as the challenges that are faced in investigating it. Next, recent work is described and explored, featuring QDs consisting of germanium and tin. This transitions to recent experimental results and a discussion of how the physics of these results can be explained, including the most recent attempts at, and results of, incorporation of a small amount of additional silicon into the QDs. The discussion of QDs is then concluded with a look to the future where the possibility of construction of optoelectronic devices featuring group-IV alloy QDs is explored.
2. Localization in InGaN MQWs and BeMgZnO

2.1. InGaN Material system

Before the advent of the successful blue Indium-Gallium-Nitride (InGaN) light emitting diode (LED), it was originally theorized that it would be a practical impossibility for any material utilizing Gallium-Nitride (GaN) to be an effective light emitter due to its characteristically high density of defects from non-lattice-matched substrates. While industry and research labs have successfully engineered very high efficiency, very bright blue LEDs over the past decades, some ambiguity concerning the specific physical mechanisms of the performance, and furthermore the dynamics at high injection, still persist. While it’s true that even though these questions persist the LED industry has still reached maturity. Therefore perhaps it is the case that these concerns are of little importance but quite on the contrary, these questions remain at the foundation of this burgeoning industry and must be doggedly pursued until a consistent, agreed-upon description of the physics can be made. These questions are extremely important and this paper will strive to explore and shed additional light on the nature and mechanisms involved in InGaN LED blue-light generation.

In terms of physical characteristics, Indium Gallium Nitride (InGaN) is a ternary group III-nitride direct bandgap semiconductor consisting of a mixture of Indium Nitride (InN) and Gallium Nitride (GaN) which typically possesses a hexagonal wurtzite crystal structure. The bandgap of InN is around .65 eV where the bandgap of GaN is around 3.39 eV at room temperature. Their hexagonal lattice parameters range from \( a = 3.545 \, \text{Å} \) and \( c = 5.703 \, \text{Å} \) in InN (larger size, narrower bandgap) to \( a = 3.186 \, \text{Å} \) and \( c = 5.186 \, \text{Å} \) in GaN (smaller size, wider bandgap). Therefore, in the
InGaN material system it’s possible to create an LED with a bandgap between these endpoints (see Figure 2.1), although for concentrations of InN approaching 15-20 percent, fabrication can be extremely difficult. At 30 percent, there would be greater than a 10 percent difference in lattice constants between the InGaN alloy and the potential substrate or “host” lattice of GaN, which then can cause phase separation and significant clustering of In. Still, with a concentration from 0 to 30 percent InN, a bandgap range of 3.4 eV to 2.4 eV, it’s possible to make LEDs emitting UV (about 365 nm) to green (about 510 nm). A change in emission energy from 2.83 eV to 2.86 eV, an increase of 30 meV, would correspond to a concentration of InN decreasing from 14.1% to 13.3%. While it can be shown that clustering of InN isn’t always bad, the often associated significant increase in defect density is disadvantageous.

Figure 2.1: Plot of bandgap vs. lattice constant for InGaN material systems. Notice that an alloy of GaN and InN spans the 2-3 eV range, corresponding to visible light.
2.2. Localization

In 1993 it was found by Shuji Nakamura that with the incorporation of Indium and the two flow MOCVD in addition to the use of the double-heterostructure, InGaN blue LED design could have high enough radiative efficiency to become a viable light source, despite its still large density of defects. It is now understood that a large contributing factor to this radiative efficiency can be attributed to microscopic potential minima in the electronic band structure at small-scale areas of increased indium concentrations. For the most part, in the active region of an InGaN LED, indium is alloyed evenly throughout the structure. The physical difference in size of the indium atom compared to the gallium atom though makes it thermodynamically favorable for the indium to form clusters. As a result, even though the structure is grown for the indium to be alloyed evenly, there is a tendency for minute clusters to form during growth. Since indium nitride is a semiconducting alloy with a low bandgap, in these locations where small clusters do exist, the bandgap will be slightly lower and charge carriers, in the case of this thesis photo-generated electron-hole pairs excitons, can linger and possibly avoid nonradiative recombination. This efficiency enhancement where charges become localized at potential minima is what is described as “Localization.”

2.2.1. Temperature dependent carrier distributions

In an LED under photoexcitation at low excitation densities, so as to avoid complicating-factors like band-filling or bandgap renormalization, carriers are sparsely generated randomly across the excited area of the device, as is depicted in image of left-side panel of Figure 2.2, part (a) corresponding to the lowest temperature. While at extremely low temperatures, around 15 K, the generated carriers quickly “fall” towards the directly-nearest local band minima, which could
be a defect or local area of increased indium concentration. At this point, since the carriers are generated randomly and have very little thermal energy, they may recombine very near the overall average bandgap of the LED active area without any efficiency enhancing effect from nearby areas of lower potential. Therefore, the energy of any radiative recombination should be fairly high in terms of the PL peak with temperature. Furthermore, the linewidth of light given off through radiative recombination should be relatively broad as depicted in the right-side panel of Figure 2.2 at low temperature point (a), since carriers are recombining at a range of energies; from locations with very high indium concentration to locations with lower indium content, having lower than average and higher than average energy, respectively.

Subsequently, as temperature increases, thermal energy becomes large enough to permit carriers to redistribute from their original local band minima and jump into adjacent minima. Since it is a statistical process, if there are deep minima within ten’s to perhaps up to hundreds of nanometers from wherever the charge carriers are generated, overall the charges will migrate into the larger scale global minima, the process of which is depicted in the left-side panel of Figure 2.2, part (b). In effect at this point the carriers have then become “localized” into these global minima. When the carriers redistribute to the global minima, their recombination energy overall is lowered because the carriers have collected at a global bandgap minimum, and thus the energy of the emitted light also lowers accordingly. This causes a small but readily measurable red-shifting of the bandgap from very-low temperature up to moderately-low temperature. At this point carriers have gone from being generated in a randomly-distributed fashion across the structure to becoming localized in global potential wells after gaining thermal energy. The overall
spread of energies at which the carriers recombine therefore should be reduced, and therefore the emission linewidth should also decrease accordingly as is depicted in the right-side panel of Figure 2.2, temperature point (b).

As temperature is increased further, while still using low excitation to avoid complicating factors, the carriers gain sufficient thermal energy to escape the localization centers overall and again redistribute out of these global minima. This effectively blue-shifts the bandgap from its lower value, as is depicted at an immediately higher temperature from the left-side panel of Figure 2.2, point (b). The carriers would continue to have higher overall energy with increasing temperature if it wasn’t for the overall corresponding red-shifting of bandgap with increasing temperature, as often modeled by the Varshni Equation (discussed in section 2.3), and depicted in Figure 2.2, part (c). This redshift $\rightarrow$ blueshift $\rightarrow$ redshift of the energy of the peak emission with temperature increasing from low to high gives the characteristic “S-behavior” that is known as a
result of the localization effect of charge carriers in the structure as depicted in the upper panel of the right-side of Figure 2.2, parts (a) through (c).

2.2.2. Considerations of Localization effect

While the concept of localization is an interesting phenomenon to consider, it is theorized to be the key of how and why high-defect-density InGaN is able to operate with high efficiency. Ideally, when charge carriers move towards these local and global minima, these excitons are able to persist long enough to combine radiatively, and therefore are not immediately channeled into non-radiative centers. Therefore, they effectively are able to bypass defects, trap states, and overall non-radiative recombination pathways. To function at room temperature, localization centers must be of deep enough potential energy that even with the addition of thermal energy at that temperature a large proportion of excitons still remain localized. Though while the general concept depicted and end result are very well understood, the details of the intermediate dynamics are still not consistently agreed upon.

Additionally, what was described earlier is the most idealized account possible. Realistically this is not necessarily always the case though, as depending on the nature and depth of localization centers, as well as the temperature when localization is at its maximum, thermal broadening may become progressively large enough that it prevents a clear drop in emission linewidth or emission energy. Furthermore, as temperature increases and charge carriers are able to travel across the lattice, they still do encounter an increasing amount of non-radiative recombination sites, but it’s also still possible in some samples for the charges to experience emission-enhancing thermal activation. In this case there is an interplay between increases in the rate of interaction between carriers, which can recombine at a greater rate and cause increased
emission, or can cause greater interaction with non-radiative centers and decreased emission, (which becomes dominant at high temperature), or an increase in efficiency through localization. If anything, different localization behaviors in PL are possible from sample to sample and structure to structure. High In content LEDs can have an entirely different temperature dependence than low In content LEDs, and for the same In content the distribution of localization centers can still be different from variations in growth conditions, for example. As will be shown, there is an entire range in the observability of the localization effect. What is observed practically can be very close to the idealized case but because of variations in factors such as the presence or absence of impurities, growth conditions, or in the nature of any possible fluctuations in the QW potential, depending on how many or indeed if all or additional fluctuations in QW characteristics are present, non-ideal behavior can be observed. In practice, there are always competing effects and it can be very difficult to extricate a single mechanism from observations.

Although there are many different approaches to examining this phenomenon and data isn’t always the clearest, it will be shown that with increasing QW thickness overall the measured degree of localization is increased, but in increasing PL pumping intensity, the localization effect is reduced as localization centers become saturated and therefore ineffective in allowing carriers to bypass non-radiative recombination sites. This saturation effect is understood to contribute to the causes of one of the current obstacles in high-efficiency LED lighting and white light generation, being the known efficiency-droop at high-injection in high-power LEDs. First though, it is important to understand how numerical analysis of this behavior might be conducted before drawing conclusions from new research.
2.3. Representation of PL Behavior by Mathematical Models

In striving to understand a system in general, an important step going beyond the initial conceptualization of what some of the processes might be, is to attempt to construct a mathematical model that can accurately represent the phenomenon. Being able to represent complex systems in terms of variables, derivatives, and distributions for example, can provide additional insight that would have been difficult to obtain otherwise. One example of a successful model that is based firmly on its underlying physics is the band-structure theory of semiconductors. Through this model important characteristics like the Fermi Level and doping concentrations are calculated and a myriad of breakthroughs in semiconductor science have been found, where a vast many of them have been revolutionary for society.

Another model that isn’t quite as complex but has been in use since the late 1960s is the Varshni equation, or the Varshni empirical formula [6]. This models the common narrowing of semiconductor bandgap with an increase in temperature that is the result of thermal lattice expansion and increased electron scattering through interactions with an increase in phonon populations and energies, without any effect of localization. At very low temperatures, the bandgap of a semiconductor typically shows negative-quadratic dependency with temperature increase and then transitions to a linear decrease in bandgap as temperature continues to increases above 100 to 200K. While the physics of the temperature dependence of electronic properties can be very complex, Varshni utilized an empirical approach, where the model attempts to reproduce the overall behavior, but isn’t necessarily meant to directly represent the physical processes that are occurring. The functional form of the Varshni empirical formula is:

\[
E(T) = E(0) - \frac{\alpha T^2}{(T + \beta)}
\]  

(1)
where $E(T)$ is the represented value of the bandgap that varies with temperature $T$, $E(0)$ is the bandgap at theoretical zero temperature, and then $\alpha$ and $\beta$ are described as Varshni’s fitting parameters [6]. The goal for this functional form has been to incorporate a quadratic behavior at low temperatures, and a linear dependence at higher temperatures. The variable $\alpha$ is the limiting coefficient, or slope, of the bandgap with high temperature, and $\beta$ is a fitting parameter which can be loosely related to the Debye temperature. The Debye temperature is a material specific parameter, physically related to the how phonons are excited and transmit in a crystal, and the speed of sound in the crystal. Although these fitting parameters have units of eV/K for $\alpha$ and Kelvin for $\beta$, they don’t actually represent any physical properties directly. They can be used to compare changes from one similar semiconductor sample to another though, but alone they don’t actually directly indicate any physical mechanisms. As high-bandgap and compound material systems like GaN have been explored, compared to elemental Si or Ge for example, the fitting parameters could give negative values, where numerical fits still follow observations, but are non-physical. While this can be true, the empirical Varshni functional form is a good characterization starting point, where in general it is often the case that the simplest approach is best. Furthermore, since it has been used so widely for so long, it makes comparison to other samples from different experiments that much less difficult. This is why even now, when the shortcomings of the model are understood, it is still often used to model the temperature dependent bandgap.

The next step logically would be to develop a model based on theorized physical mechanisms in the material. One such model was developed by Vina et al. [7] and appears as follows:
\[ E(T) = E(0) \frac{2\alpha}{\exp\left(\Theta/T\right) - 1} \]  

(2)

This functional form is still semi-empirical but attempts to recognize the modification of the bandgap due to the electron-phonon interaction at thermal equilibrium, giving it a semi-phenomenological basis [8]. The interaction is developed from the Bose-Einstein approximation for the lattice vibration energy (related to the harmonic oscillator) \( \langle E \rangle = \left( \frac{1}{2} + \langle n \rangle \right) \hbar \omega \), where \( \langle n \rangle \) is the average phonon occupation number, \( \hbar \) is the reduced Plank constant, and \( \omega \) is frequency [8]. Again, in equation (2) as in equation (1), \( E(0) \) is the bandgap at theoretical zero temperature, but this time \( \alpha \) is related to the strength of the electron-average phonon interaction, and \( \Theta \) corresponds to a mean temperature value of both the longitudinal acoustic and optical phonons participating in the interaction [8]. \( \Theta \) is called the average phonon temperature and if \( k_B \) is the Boltzmann constant, it is related by \( \Theta * k_B = \text{average phonon energy} \). The units of \( \alpha \) are in eV, and \( \Theta \) as well as \( T \) are in Kelvin.

This model more closely represents the physical mechanisms happening in the material with changes in temperature, and can also provide good fits to data for bandgap narrowing with increased temperature. This model still isn’t perfect though, since it is still semi-empirical and because it is also reliant on the assumption that the system is at thermal equilibrium, which while under excitation, isn’t strictly true. In the case of very low excitation though this assumption can be considered accurate, and at higher excitation it could still be utilized, but the limitations of the model must be kept in mind. Also, at very low temperature, this model shows a flattening-out behavior, which is also not shown in observations. Still, as will be shown next, because of the way
localization is determined by fitting in this application, very low temperature fitting is excluded, so this model can still work quite well.

Between the Varshni and Vina functional forms, it is possible to model the overall shrinkage of bandgap with temperature, where perhaps the Vina formalism has a stronger footing in material physics, but what is of main concern here is how the localization-effect in a sample can be characterized. One such model that does this utilizes the idea of the presence of a generic distribution of bandtail states that extend into the bandgap as a result of nonspecific impurities. If we assume the distribution of the Density Of States (DOS) can be described by a Gaussian, and the occupation statistics are nondegenerate and close to the Boltzmann one (that is, if carriers are spread across the distribution and aren’t almost entirely only below the fermi level), then between a Gaussian distribution of DOS for electrons and holes, the bandgap emission will actually be from between the states extending into the bandgap. Since this model is purposely open to whatever source that might cause a distribution of states and is not specific to a single mechanism, as long the impurity states follow Gaussian distributions, we can be confident that this model can be applied here[1], [9], [10]. Therefore, emission will be red-shifted by a value of:

$$\frac{\sigma^2}{kT} = \left(\frac{\sigma_1^2 + \sigma_2^2}{kT}\right)$$

where $\sigma_1$ and $\sigma_2$ are the dispersions of the Gaussian distributions of the valence and conduction bands, respectively, $k$ again is the Boltzmann constant, and $T$ is the temperature in Kelvin [1], [9], [10]. At moderate to low temperature, the band tail states would be the most occupied, giving a reduction in the effective width of the bandgap. At high temperature, the carriers do not occupy the bandtail states as thoroughly and their effect is reduced. Also in this description, the overall
shift in spectra at a given temperature can be represented by the magnitude of $\sigma$ (in eV or meV) in the left-hand side of equation (3).

Care must be taken to not extend this model into very low temperatures though (minimum 50 to 100 K, depending on behavior) because it is only strictly accurate in the non-degenerate case. In the case where carriers are degenerate, in the theoretical picture, the bandtail states would be completely occupied and the effective bandgap would be drastically lowered. In an extreme picture, at very low temperature the occupied infinitesimal tails of the theoretical Gaussians distributions could possibly exist so far into the gap that potentially the model would suggest that the gap goes to zero, which is obviously not seen in the real behavior. Furthermore, by looking at the equation, it can be seen that at as $T \rightarrow 0$ the value of both sides of equation and the value of $\sigma$ in equation (3) goes to infinity, and again therefore the bandgap would go to zero, which again is not physical. Therefore, if some care is exercised in the determination of the low-end of the temperature of the range in consideration, then this model can still offer a good representation of the temperature dependent bandtail occupation and therefore the overall depth of the impurity related bandtail distribution.

Combining the previously discussed factors, in terms of functional forms to model the temperature dependent PL peak position with bandgap shrinkage and bandtail occupation, an equation can be made that appears as:

$$E_{\text{peak}} = E(T) - \sigma^2 / kT$$

(4)

where $E(T)$ is the regular temperature depended bandgap, without any localization effect [10]. This leads to the full functional forms that can be used to model the temperature dependent
bandgap shrinkage while also characterizing the temperature dependent effects of generic-impurity related bandtail states, which can appear as in the modified Varshni formula:

\[
E(T) = E(0) - \frac{\alpha T^2}{(T+\beta)} - \frac{\sigma^2}{kT}
\]  

(5)

and the modified Vina formula which will be utilized in this thesis:

\[
E(T) = E(0) - \frac{2\alpha}{\exp\left(\frac{\Theta}{T}\right) - 1} - \frac{\sigma^2}{kT}
\]  

(6)

Overall, these formalisms can be used to model the temperature dependent PL behavior of InGaN MQW LEDs, where parameters can be extracted from fits to data, including a value possibly related to the Debye temperature in a sample, an estimated strength of the electron-average phonon interaction, an estimated mean temperature of phonons participating in the interaction, and a valuation of the measured degree of localization. Consideration must be taken in applying these formula though because there are cases where they can still give important information, but physically they strictly don’t apply, such as at low temperature or away from thermal equilibrium.

A problem that immediately springs to mind is if these formalisms can still be applied under higher-power excitation. Although this concern is valid, either way it is still better to utilize this formalism than not since it’s still a good way to quantify the temperature dependent PL behavior. In reality there are many competing effects overall in the MQW structures and the PL behavior doesn’t always follow easily discernable patterns, so whichever model is utilized, the derived values must not necessarily be taken at face value but should only be used in comparing related samples/structures. As was mentioned earlier, the modified Vina equation is still semi-
empirical so, while the functional form attempts to take physical processes into consideration, it still doesn’t perfectly represent the physics in the MQW device. So with the knowledge in mind that this model doesn’t perfectly represent physical phenomena, but still is helpful to characterize behavior, that means the model doesn’t need to be limited to only a narrow range of applications. Specifically, when modeling PL from a MQW under high-power excitation we can still extract important qualities that relate to how the PL evolves, particularly the measured degree of localization. In other words, whether or not a MQW is under high-power excitation, if the evolution of PL shows strong or weak “S-behavior,” which is evidence of carrier localization, it’s still important to evaluate and find a numerical description of the measured degree of localization.

Therefore, while keeping the potential pitfalls in mind, this thesis will move forward in confidence utilizing the modified Vina functional form incorporating the bandtail model characterized by “σ” to extract information from PL evolution with temperature.

2.4. Relevant Recent Work on Localization in InGaN MQWs

This theoretical understanding is put in practice researching InGaN LEDs through multiple avenues. The ultimate goal of research into InGaN LEDs is to create greater efficiency. One relevant avenue is the explorations of changes in structures including thickness of wells and barriers [11]–[13]. With many different possible variations in design, studies featuring variation in excitation power[14], [15] and energy, [16] while keeping similar structures has also been recently explored. Moreover, studies in utilizing wholly different qualitative approaches to quantum confinement such as growing embedded QDs [17]–[19] are being pursued. Beyond these important topics, the field of study into InGaN is highly diverse, with some research approaching the topic from completely different perspectives. Some of these approaches do not directly relate to the research presented here though, such as those regarding treatments during the growth process.
or exploration of the effects of differing substrate orientation, so will not be discussed. However, they are still vital to an informed discussion on this topic.

InGaN PL behavior is highly dependent on quantum confinement and material quality which is determined largely by the thicknesses of the layers of the structure. One highly relevant study of structure and localization is by Li et al. (2017) [11] in which well widths were varied. This is interesting because it demonstrates a clear dependence of measured localization on well width. Additionally, linewidth is also incorporated into the analysis which also shows a strong sign of localization.

In this study, Li et al. actually approached it with the objective to investigate the effect of well width on carrier localization and IQE. There were 4 samples with well widths of 1.8 nm, 2.4 nm, 3 nm, and 3.6 nm. All of these samples were of 3 MQW periods with barriers of GaN where the barrier thickness was not specified. The content of In was not specified but emission was in the ~420 nm range. They found that integrated PL intensity was the lowest for the 1.8 nm QW structure which then increased to the next thicker 2.4 nm sample, and was most intense for the 3 nm sample, then of moderate intensity for the thickest sample. It’s interesting to note that the thickest well sample, though still having the same design and number of MQW layers, shows decreased intensity emission. They attribute this though to probable decrease in crystal quality with the larger QW layers, although they also found that the measured degree of localization was in fact the greatest in this thickest well which should enhance emission. This is in contradiction to the general theory that enhanced localization also enhances efficiency. Overall though, the PL peak positions of all the samples followed the characteristic “S-behavior” as seen in Figure 2.3, and the degree of localization increased monotonically with increasing well width, which they
modeled using the Varshni formula. The degrees of localization were fitted to be 11.4 meV, 11.9 meV, 15.6 meV, and 16.5 meV for samples of 1.8 nm, 2.4 nm, 3 nm, and 3.6 nm, respectively.

Li et al also found that in the temperature evolution of linewidth for each sample, while not in direct contradiction to theory but perhaps confusingly, the thinnest well structure showed something more akin to a “W” instead of a “V” shape evolution, as in Figure 2.4. This was theorized to be from carriers first hopping into global minima as the temperature increases from the initial value, where the linewidth should decrease, then carriers are able to immediately begin to delocalize and linewidth subsequently increases. Then, at moderate temperature, even the deeply localized carriers also begin to redistribute to higher energy, where the linewidth would then decrease since the carriers are recombining at a narrower high-energy range, before linewidth increased again with higher-temperature thermal broadening.

Overall, they did show that increasing well width can consistently increase the degree of localization, but there are also possible inconsistencies. The clear difference in evolution of the emission linewidth for the thinnest well is inconsistent, and what the relationship is in the thickest

19
well sample that had the largest degree of localization but also a much lower PL intensity than its absorbing volume would suggest. This shows that while localization can increase efficiency, the effect may not be a strong enough to overcome extreme cases of low crystal quality. This type of research is important in further understanding the interactions between well width and the effects of localization.

In a similarly relevant paper a slightly more complicated picture is required to explain the behavior, where there are theorized to be two different localization effects related to QW thickness, by Liu et al. [12]. They observe that likely composition-related deep localization states dominate the light emission in thinner MQWs, while in thicker MQWs shallow localization states induced by the fluctuations of InGaN well thickness dominate the luminescence efficiency.

In their study, 3 samples of increasing QW thickness of 2.6 nm, 3 nm, and 3.4 nm respectively, were measured. All samples had 5 period MQW structure and wells consisting of 18.2 to 20.0% In, corresponding to ~500nm green emission, and 8 nm thick GaN barriers, and they were measured by temperature dependent PL. In their findings all three samples showed full “S-behavior,” where in order of decreasing thickness the degree of localization was found to be 8.0 meV, 17.6 meV, and 18.1 meV. Also, in the thickest well the temperature of blueshift after initial low temperature redshift was lower than the other two. This signifies that carriers began delocalizing in this sample at lower temperature, and therefore only a small amount of thermal energy was required for carriers to delocalize, so the localization centers in the thick QW sample must be of shallower energy. Furthermore, an additional observation was that in the order of decreasing QW width, and increasing measured localization, an increasing intensity of emission was measured from the samples.
The increasing emission from decreasing QW thickness, with increased localization, was theorized to be the result of a reduced quantum confined stark effect (QCSE) and more defects existing in the thicker InGaN well layers. The intensity of emission from the thickest QW sample was so low that it was suggested that if the In content was as high as 20%, the critical thickness of an InGaN/GaN single QW would be about 3.5 nm, and in the case of a 5 period MQW the material quality should be even worse, hence very poor material quality. The physical source of the different localization states was theorized that in the thinner QWs, during barrier growth, there would be less strain energy and so be more prone spinodal decomposition. In other words, in the thin QW layers there is a stronger tendency toward phase separation during GaN growth to form more concentrated, deeper localization centers, but in the thicker QW sample the higher accumulation of strain energy across the thicker QW suppresses the thermodynamic mechanism of decomposition. Also, since localization is still present in the thick well sample, but to a much lesser degree, thickness fluctuations were considered as the source of those states.

Therefore they had results opposite of the previous study, where increased thickness had led to increased localization. Here it was found that thinner wells had more, deeper, states and so a stronger localization effect. Results such as this must be considered while research continues.

Another relevant study of InGaN LEDs, rather than focusing only on the light-emitting QW layers, is to focus on the effect of the barrier layers that serve to separate the QWs within the MQW structure [13]. A thorough understanding and evaluation of QW barrier layers is important to be able to create the best conditions for optimization of light-emitting QW layers. In the study by Liang et al. [13], they demonstrated this approach by growing 3 samples with the InGaN QW layers with an identical 3.5 nm thickness with 25% In concentration (corresponding to ~510 nm green emission), but then varying the growth times, and therefore thicknesses, of the GaN barrier
layers from 6.6 nm, to 14.4 nm, and 25.3 nm. Their samples were of 10 MQW periods, and found that with increasing barrier thickness the temperature at which the transition from blueshifting back to redshifting energy of PL emission occurred was greater, as shown in Figure 2.5. Although PL peak position did follow “S-behavior,” this study didn’t quantify the degree of localization, but looked at the temperature, and therefore the thermal energy at which PL features occurred. They found that although the QW layers were all grown the same, the linewidth and temperature of blueshift-to-redshift transition increased with increasing barrier thickness. They attribute this change not directly to QW cross-talk effects or loss of material quality, but to the fact that in the process of growing a thicker GaN barrier layer, the InGaN QW layers are subjected to longer times at the higher growth temperature required for high quality GaN. This high-temperature exposure can be regarded as thermal annealing and the thicker barrier represents a longer annealing time. It has been shown [20] that In-rich dot-like structures form with annealing at over 725 °C, while here the GaN growth temperature was 850 °C, so some annealing effect is expected. Therefore, larger In dot-like structures can form, creating deeper localization centers in which carriers require
greater thermal energy to redistribute out of. This indicates the complex interplay between the factors involved with the fabrication and operation of InGaN MQW LEDs.

Another vital investigation with respect potential efficiency gains is through consideration of excitation power and energy. This is still an ongoing field of research because at high power there are multiple competing factors, such as auger recombination, electron overflow, and saturation of localization centers, that all effect efficiency where it is unclear what dominates in different InGaN MQW samples in different excitation conditions, be it high temperature electrical injection, or room temperature photoexcitation.

Some relevant results from a study by Haiyan et al [14] found evidence of light emission from deep localization states from quasi-quantum dots, in addition to light emission from the surrounding InGaN well matrix. These results were found in 8 MQW period, 3 nm thick InGaN layers at 15% In and 14 nm thick GaN barriers from .0005 mW to 50 mW. Their excitation area was not specified. At low temperature a dominant emission at 2.66 eV is attributed to the main QW emission. At ~30K a secondary lower energy emission at 2.42 eV was measured and attributed to deep quantum dot states within the wells. As power was increased to above ~3 mW the secondary emission diminished then was no longer observable, which was attributed to a saturation of the quantum dot states, while the larger density of available states in the rest of the QW InGaN matrix continued to be increasingly occupied and increasingly emitting with additional power.

Further evidence supporting the notion of suppression of the localization effect at high power is found by Wang et al. [15]. They found at low excitation density there was strong S behavior and a W shaped evolution of line width. With increased power though, “S behavior” was suppressed, to an inverted U shape, and line width transitions to only monotonically increasing. The loss of both “S behavior” and linewidth features indicate the suppression of the relevant
mechanisms. These results were found in 8 MQW, 3 nm thick InGaN QWs at 15% In and 14 nm thick barriers with excitation power from 0.05 mW to 20 mW, though they did not define their excitation area. They also measured with increasing power, corresponding to a reduction in “S behavior,” a monotonic decrease in the measured degree of localization per excitation power from a high of ~23 meV to ~13 meV, as modeled using the Varshni formula. They drew the conclusion that at high excitation power the band filling effect dominates and injected carriers escape more easily from localized states.

Beyond studying the differences in excitation power, the effects of excitation energy can also be important to probe properties of carrier dynamics. By changing the excitation energy it is possible to explore the carrier interactions between the layers of the MQWs. In Lu et al. [16] They used MQWs with five periods with 2 nm thick wells separated by 12 nm thick GaN barriers. The barriers were lightly silicon doped (n-doping = 3x10^{17} cm^{-3}). Excitation was conducted with a 325-nm laser and a 405-nm laser at two fixed excitation powers of 30 mW and 1 mW. They found that with non-resonant excitation, the carriers generated in the barrier layers would drift due to the built in electric field into the quantum well regions. At moderate temperatures this would actually

![Figure 2.6](image_url)

Figure 2.6: Integrated PL for (a) resonant (405nm), and (b) non-resonant (325nm) excitation of the LED structures. In (b) an anomalous mid-temperature increase in PL intensity is measured. (Lu, Scientific Reports, 2014)
enhance the intensity of PL emissions, as seen in Figure 2.6 part (b), by occupying non radiative channels. They argue that with the occupation of non-radiative channels by the additional barrier-sourced carriers, measurements of intrinsic IQE in the QW layers is better reflected. Their ultimate conclusion was that non-resonant excitation was in fact more appropriate for the study of carrier transport dynamics than resonant excitation. However, while compelling, this thesis’ author believes it is important to probe directly the PL evolution of the QW layers. Non-resonant excitation can give additional information about dynamics as a supplemental tool, but resonant excitation gives a more direct measurements of the QW layers themselves, which are critical to understanding the light emitting layers of an LED.

Localization centers in InGaN QW layers are typically a product of microscopic concentrations of In, which basically have the character of embedded quantum dots. Therefore research directly into the behavior of purpose grown embedded quantum dots can be insightful. Research by a group at Xiamen University [17], [18] grew quantum confining InGaN dots-like structures in the space where a MQW structure would go in a typical InGaN MQW LED. The dots were actually a thickness of about 2.5 nm with a diameter of 20-60 nm, so perhaps would be more accurately called quantum disks. Nonetheless, they found evidence of largely increased localization. In the first (2014) paper, with temperature dependent PL peak position, which

![Figure 2.7: Dependence of PL peak position and linewidth with temperature in an InGaN QD structure. (Zhao, Chinese Phys. Lett. 2014)](image-url)
typically would follow an S shape, only went through the red shift to blue shift process where room temperature thermal energy was insufficient for high temperature red shifting, but the total energy range for their peak emission was still as large as almost 40 meV as shown in Figure 2.7. Because of the limitations of the Varshni formalism they did not have a measurement of degree of localization $\sigma$, but the indication of the requirement of a very high temperature to induce redshift shows a very large potential localization effect.

A study utilizing a different approach, which used InGaN MQWs with highly “phase separated” wells that approximated quantum dots, researchers found “S behavior,” but an increasing intensity of emission with temperature up to 100K [19] as in Figure 2.8. The phase separation was characterized by high resolution transmission electron microscopy (HRTEM) where the phases are clearly visible on the 1~10 nm scale as seen in Figure 2.9, but no direct measurement of degree of concentration difference or physical size was provided. The increase in emission intensity is attributed to the QD-like character of the In-rich regions, where within the dot structures localization depth is greater. Therefore with increasing temperature and higher

![Figure 2.8: Integrated PL intensity per temperature of a highly phase-separated InGaN MQW LED. (Wang, J. App. Phys., 2013)](image)

![Figure 2.9: Cross-sectional HRTEM image of the highly phase-separated InGaN MQW. (Wang, J. App. Phys., 2013)](image)
carrier mobility, a larger and larger amount of carriers transfer to the localization centers and undergoes increasing radiative recombination, until increasing temperature dependent non radiative recombination becomes dominant. These contributions are important to understanding the underlying physics of InGaN light emitters. There is a spectrum of samples ranging from an “ideal” sample with an even distribution and defect free, to structures with separated and concentrated locations of In. By purposely studying samples with highly concentrated In, they open an avenue for research into efficiency gains by incorporating quantum dots into synthesis. It also informs research such as my own, by giving data on an alternate types of samples, since real world samples are often of moderate quality and possess fluctuations.

2.5. Results and Discussion

In this thesis work a number of InGaN LED structures were measured and analyzed. All of the samples had an emission ranging from 2.5 to 3 eV, corresponding to approximately 495-410 nm. Between samples the QW width and number of wells were varied to investigate their effect on localization.

The primary measurement technique was to collect photoluminescence (PL) spectra to find the PL peak emission at temperatures from 15 K to room temperature, at steady-state excitation power levels from 0.0516 W/cm² to 515.92 W/cm². The purpose of varying the excitation power level is not only to examine the way each structure responds to different level of pump fluence, but also to be able to compare the response of one structure to the response of another. The excitation source was a mode-locked Ti:Sapphire laser, which was frequency doubled to 385 nm and had a pulse width of approximately 150 fs at 80 MHz repetition rate. Spectra were collected with a liquid nitrogen cooled charged coupled device (CCD) camera connected to a 30 cm focal
length monochromator. Multi Gaussian peak fitting was applied to the spectra for a consistent technique to find the peak energy of emission because of variations in the spectral intensity due to Fabry-Perot fringes which appear from reflections off substrate interfaces. A fit of the plotted peak position per temperature using the modified semi-empirical formalism developed by Vina et al. [7] was performed, incorporating the bandtail model of distributed states existing near the bandedge.

The LED structures themselves were synthesized through low pressure metal organic chemical vapor deposition (MOCVD) onto C-plane sapphire substrates. To quickly review, first a thin low-temperature GaN buffer layer was deposited which was then annealed to allow nucleation islands to coalesce. After that, a high temperature GaN layer, followed by a thin porous SiN treatment to block the further extension of defects, and then another high temperature GaN layer was grown. Then, there was a Si-doped n-GaN layer followed by the InGaN MQW active region. This consisted of a ~60nm underlying In$_{0.01}$Ga$_{0.99}$N layer, followed by a step-graded injector (SGI) structure [21] to reduce electron overflow in the case of electrical injection, and then the MQW region itself, where 6 to 15 In$_{-0.15}$Ga$_{0.85}$ QW-and-barrier periods were grown. Most

Figure 2.10: A simplified conduction band schematic of the InGaN MQW LED structure
of the samples had barriers of GaN, but some had up to ~6% In incorporation. The MQW region was followed by a Mg-doped p-GaN capping layer. The thicknesses were determined through calculation from growth rate and XRD, and the general structure is depicted in Figure 2.10.

Contrary to what was described in the ideal theoretical situation in section 2.2.1, it was found that the evolution of PL peak position, though not unheard of, spectra show no clear evidence of transition to lower energy from local into global potential minima in the low temperature range, as shown in Figure 2.12. This can be accounted for depending on the practical characteristics of the depth and distribution of localization states in the samples. If the structure has a majority of localization centers consisting of close, deep potential then most carriers are generated already located closely to a global minima. Then, in this case as temperature increases, there are not many places where the charges can transition to that will give a significant redshift in spectra. As temperature continues to increase though, the carriers begin to have sufficient thermal energy to start transferring up and out of the localization centers to recombine at higher energies.

This is also shown through analysis of the linewidth of the corresponding spectra. In this entire study the linewidth increases monotonically with temperature in all of the samples, while theory would say that it should first decrease. This signifies that in these samples, the charges are generated such that they already are close to localization centers at very low temperature, and that the only place for them to subsequently redistribute to, is to an increasing range of energies where linewidth only increases. At high temperature though, thermal broadening of the emission should become the dominant effect in increasing the linewidth.
2.5.1. QW thickness variation

The first set of samples and data that are to be considered are comparing the effect of varying the thickness of the QW layers, while keeping the number of QW-barrier periods to 6 from sample to sample, as well as indium content in the 14%-15% range. The samples are designated LED1, LED2, and LED3, with QW width increasing from 1.5 nm to 2.2 nm, then 3 nm per period, respectively. The barriers remain at 3nm thickness. A representative spectra from sample LED2 is presented in Figure 2.11 which does show some asymmetry. It is theorized that this is evidence of exceptionally deep localization centers and possibly structural variations like fluctuations of well width, which would make for lower energy longer wavelength PL from those areas. Despite the asymmetry, the cumulative-fit peak position was still taken as the characteristic value for the peak energy of that spectra, and the resultant localization measurement was taken to reflect the evolution for sample LED2. The goal of the fitting process was not to extract possible individual recombination pathways at this time, though this is interesting, but to accurately determine the real

Figure 2.11: Plot of PL spectra for 2.2nm QW sample LED2 at 300K, 5.16 W/cm² pump power.
peak of the spectra through the Fabry-Perot fringes. Exploration of possible sources of spectral asymmetry could be very insightful, but as can be seen in Figure 2.11 the asymmetry is not exceedingly great. Considering the two different Gaussian peaks, utilizing Vegard’s Law with a bowing parameter of 1.43 eV, if the center value of each peak might be taken as the result of changes in In concentration, then the peak centered at 2.864 eV would correspond to an InN concentration of ~13.2%, and the peak centered at 2.818 eV would correspond to an InN concentration of ~14.4%. This shows that an energy difference of 46 meV at this wavelength corresponds to a change of about 1.2% in In content. An exception to the small asymmetry though, is the PL gathered from the 15 MQW period, LED5 sample, which shows strong asymmetry and will be examined further in this thesis, but in that case the asymmetry can again be attributed to an increase in the amount and depth of localization centers and structural fluctuations, but to a much greater extent as the greater number of additional QW layers were grown. Overall, the end result of measured degree of localization for structures of differing QW width versus excitation pump fluence is presented in Figure 2.13, plot (a). As was seen across the review of research and described in the section regarding mathematical modeling though, care must be taken when considering the data because the context of the measurements and results is important.

2.5.1.1. Dependence on QW thickness

In sample LED1 (thinnest 1.5 nm QW structure), at low power, 0.0516 W/cm², with increasing temperature, as can be seen in Figure 2.12: (a) Temperature dependent spectra of 1.5nm QW sample LED1, (b) 2.2nm QW LED2, and (c) 3.15nm QW sample LED3 plot (a), carriers combine and emit at increasing relative energies from the low temperature point, so localization centers are already occupied at low temperature, and with the addition of thermal energy charges immediately move up and out of localization centers. Looking to Figure 2.13 (b)-(d), spectra have
been translated in energy to have the PL peak position at 15K correspond to zero meV, so that changes and patterns in emission energy with temperature can be compared sample-to-sample. The other structures, compared to LED1, don’t show energy increase as strongly. Therefore when considering low power in Figure 2.13 plot (b), the thinnest QW exhibits the largest degree of localization measured, the value of which is plotted in Figure 2.13 (a) at ~10.5 meV. In Figure 2.13 plot (c) at medium power of 2.1 W/cm², compared to plot (b), the localization effect is already beginning to be reduced and is measured to a much lesser degree of ~8.25 meV for the same structure. The relative amount of energy-increase per temperature appears less before bandgap shrinkage becomes dominant. With the highest power excitation and still considering LED1, at 206 W/cm², in Figure 2.13 plot (d), carriers appear to entirely saturate the localization states where the measured degree, still for the 1.5nm structure, is 0 meV because PL evolution entirely follows the pattern for general bandgap shrinkage with increasing temperature. It is extremely clear that between 5 and 500 W/cm², the temperature redistribution and possible localization of carriers has very little apparent effect on PL, and then by extension, any potential efficiency gains through the localization effect would be lost as well. Also, an interesting observation is that there is the greatest range in PL peak energies for the thinnest well, from between the other samples. This is just like the increased energy spacing between quantum states in an especially thin QW and makes sense to be seen in this sample.
In the medium thickness structure (Sample LED2, 2.2 nm QWs) in Figure 2.12 plot (b), at lowest power (see also Figure 2.13 plot (a)), the PL evolution also shows localization behavior, at \( \sim 9.5 \text{meV} \), but not quite as strongly as in the thinnest well at low power. The same density of carriers at low power apparently does not garner as strong a localization effect in the slightly wider (2.2nm) QW as it does in the thinner. This could signify that a thicker QW has a larger DOS of localization centers, so the low-power excitation has a reduced effect in the larger QW. Continuing to consider medium power pump fluence (\( \sim 5.16 \text{ W/cm}^2 \)) again but continuing with sample LED2,
the magnitude of energy blueshift before redshifting at higher temperature is increased from the low-power magnitude of blueshift, and correspondingly the localization effect is at its largest for this sample at ~12 meV. Again, contrary to theory that the lowest possible pump power is best to observe “S-behavior”, this can be evidence that some density of carriers is needed to show the maximal degree of localization for a given structure. Depending on the size and depth of the localization centers, less (more) carriers show greater range in emission energy than in thinner

![Figure 2.13](image.png)

**Figure 2.13:** (a) Localization per pump power for each QW thickness. PL from each sample translated in energy where energy at 15K is zero. (b) Low-power (0.052-5.16 W/cm$^2$) peak energy per temperature for each QW thickness. (c) Medium-power (2.06-5.16 W/cm$^2$) peak energy per temperature for each QW thickness. (d) High-power (206-516 W/cm$^2$) peak energy per temperature for each QW thickness.
(thicker) QW layers. At heavy excitation power (516 W/cm²), the amount of blueshift for LED2 is its smallest amount, as well as the measured degree of localization is the least, at ~7.25 meV. This can be additional evidence that localization centers have possibly become saturated at increased pump fluence and the localization of carriers has become less effective.

In sample LED3 (3 nm QWs) at low power, there is very little change in energy of PL with temperature until greater than 250K (see Figure 2.13 (b)), but there is still evidence of localization, though it is very small (see Figure 2.13 (a)). This makes sense in that there may not be a high enough density of carriers to show a change from being accumulated in localization centers, to showing significant redistribution and delocalization at higher temperature. At medium pump fluence though, there now appears to be a significant amount of carriers so that the localization effect is clearly visible, and in this power range for the thickest QW structure, the largest degree of localization of this sample set is measured at ~13.5 meV, before decreasing with heavy excitation power. Under heavy excitation power, there is only a small blueshift with temperature signifying carriers increasingly escaping up and out of the localization centers, but even as high as room temperature there has not been any redshifting of the PL peak. This could show that thermal energies greater than that at room temperature are required to impart enough energy to carriers to allow them to escape from localization centers. Additionally, while there is not a lot of absolute change in the PL peak position, which gives a low value for the Vina model fit-derived measurable degree of localization, this could also be an indication of a larger underlying localization effect still in the structure since even up to room temperature, temperature bandgap shrinkage is still not a dominant effect.
Also, in comparison to the thinnest QW structure, in this structure with the wider QW, the smallest range of PL peak energies are shown, just like the reduction in energy spacing between quantum states in an especially wide QW.

### 2.5.1.2. Excitation Power dependence

Overall is seems that excitation power in the 5 to 20 W/cm$^2$ (in the case of our physical setup, 0.5 to 2 mW laser power) range best illustrates the effect of well thickness and its effect on localization, which is that the greatest degree of localization is observed in sample LED3, which possessed 3 nm wide QWs. Of course though, at thicknesses larger than this, quantum confinement and material quality will likely start to be lost, so any efficiency enhancement by localization through thicker QW growth wouldn’t be practical. An analogy representing the QWs and charge carrier density could be a bumpy field in a strong rain, where puddles as well as exposed grass both can be seen, as could be said also for a mostly flat field (representing smaller magnitude potential variations in a thin QW and smaller DOS for localization centers) and for a very bumpy field (representing a larger magnitude of potential variations in a thick QW and a larger DOS for localization centers). An additional observation is that while under medium pump fluence, the temperature and therefore the thermal energy, where the changeover from initial blueshift to subsequent redshift occurs, with increasing QW thickness up to 3nm, happens at increasing temperature as seen in Figure 2.13 plot (b). This is not apparent with higher or lower pump fluence, and clearly signifies that increasing thermal energy is needed for carriers to redistribute out of localization centers in increasingly thick QWs.

At low power the effect of thickness of the QW on the energy of recombination appears to be greater than what can be observed from the temperature dependent redistribution of carriers,
where relatively strong localization is observed in sample LED1 (1.5nm wells), but not in sample LED3 (3nm wells). This could show that there is just not a high enough density of carriers to show significant localization behavior in the thicker well sample LED3, similar to a light sprinkle of rain on a flat or bumpy field. There simply may not be puddles to observe. In sample LED1, localization is more measureable since the depth of centers and localization DOS could be small, so only a small density of carriers are needed to accumulate and then delocalize from the centers and show the localization effect. Overall though, recombination is also very likely to occur outside of a center and show a higher energy overall. In the thicker sample LED2, there is less evidence of localization since the depth and DOS of the centers could be much greater, so a larger density of carriers are needed to show the localization effect, until centers perhaps become saturated at high pump fluence. In sample LED3 a larger density of carriers is needed to show localization, unless the centers are so deep that the temperature required to provide enough thermal energy for redistribution causes the bandgap narrowing to become large enough that it then becomes the dominant effect with increasing temperature, instead of carrier redistribution.

At high power the localization effect is totally washed out in sample LED1 – the temperature required for carriers to redistribute out of centers seems to already be met at 15K. In sample LED3 though, where the temperature required for redshift is possibly as high as room temperature, it still only maybe saturated. Though, the measureable degree of localization is not as strong. Like a bumpy field in a torrential rain, although the depths and DOS of the localization centers might be greater, still mostly just water is visible and what redistribution there is, it is masked.
2.5.2. Varying number of MQW periods

In the next phase of data collection, the previous “medium thickness” sample LED2, 6x2.2 nm MQW LED structure, becomes the “smallest” structure sample because measurements were then compared between the 6 period, 2.2nm thick MQW (sample LED2), a 9 MQW with 2.2 nm thick QWs designated as sample LED4, and then also a 15 MQW with 3.15 nm QWs designated as sample LED5. Although in sample LED5 the thickness of the QWs deviates to ~143% thickness from the other two, the design is similar, and the absolute value of the change in thickness is less than 1 nm, which can be important but is still not an enormous change in this setting. As will be seen in regards to QDs though, 1 nm can be an important change. Furthermore, when looking at the effect of increasing the number of periods in a MWQ LED, either way this sample still gives an additional point of comparison.

Overall the measured degree of localization from the samples is higher (up to 16 meV). Of course sample LED2 is still associated with its same data, but while it was in the middle of the range of measured localization in the previous sample set, here it gives relatively lower energy degrees of localization per pump power compared to the more numerous MQW samples. Also in comparison to the previous sample set, where samples LED2 and LED3 were on the extreme ends of measured localization in showing highest and lowest degrees from 0 meV to 13.5 meV respectively, sample LED2 was in the middle of the range and showed a more consistent degree of localization around 8-11 meV throughout. Carrying that over to this study, where samples LED4 and LED5 have similar QW thicknesses, they also do not show as extreme of localization behavior. One overall main finding in this set that will be shown, is that again with increasing pump fluence, the localization effect is suppressed and the redistribution of carriers becomes less
observable. Also, it is found that increasing the number of periods from 6 to 15 increases the observed degree of localization to a maximum of 16 meV at low pump fluence.

2.5.2.1. Dependence on number of wells.

Looking at the 6 period sample LED2 in Figure 2.14 plot (a), at 15 K there is a greater range of emission energies than there are, at low temperature, for the 9 period sample LED4 in Figure 2.14 plot (b), and the 15 period sample LED5 Figure 2.14 plot (c). This is excluding the...
highest pump power in sample LED5, which will be addressed shortly. This can be evidence of an overall smaller capacity for localization centers in the 6 well sample LED2 than in the 9 well sample LED4 or 15 well sample LED3. This is shown because as a larger pump fluence is used, similarly to the previous sample set at low temperature, localization centers can immediately begin in a near-saturated state so carriers recombine and radiate at higher overall energy. Whereas in samples LED4 and LED5, the increase in carrier density doesn’t have as significant an effect on sample LED4, and an even smaller effect in sample LED5. An exception is sample LED5 at the highest power excitation, where possibly a threshold appears to be abruptly met and the largest pump fluence requires carriers to occupy and recombine significantly from higher energy states compared to lower power levels in the same sample. A possible explanation of the threshold is that since there are many more periods, the quality or distribution and depth of localization center in the QW may change across the multiple periods. Perhaps the first period of the 15 QWs is similar to the conditions in the 6 QW sample, and a threshold for saturation is met in that well to show similar, mostly energetically flat with minimal blueshift emission, but there is different behavior for the later wells where the increased carrier density isn’t as significant.

2.5.2.2. Excitation Power dependence

The data shows that, in support of the findings in the previous section where QW thickness was addressed, also within these samples increased pump power shows a reduced degree of localization in the samples. At the lowest power excitation the greatest range of energies is shown which can be evidence of a reduced DOS of localization centers, that with an increase in carrier density the states become filled and a greater range in emission energy can be observed. Conversely with the highest power excitation the range of energies is least where initially, the centers in the sample are saturated and any redistribution of carriers with temperature is masked.
This can be clearly seen in Figure 2.15. Through greater ranges of energy, larger “S behavior” is apparent. Because of larger S behavior, larger localization values are measured. With increasing power as was seen previously, the range of energies is reduced and correspondingly, the degree of observed localization also reduces. Another interesting behavior worth noting is that even with the largest excitation density, that pump fluence level was not sufficient to provide saturation in these samples. This makes sense in that all of these samples have a total active region that is larger than in LED1, where the clearest saturation of localization centers was observed.
2.6. Localization in BeMgZnO

An additional material system that we have found to show strong localization, but is a quaternary compound and possesses a very wide bandgap that is tunable up to 5 eV, is (Be,Mg)ZnO. The quaternary Be$_x$Mg$_y$Zn$_{1-x-y}$O, is attractive for UV optoelectronic applications, intersubband transition devices, and heterostructure field effect transistors (FETs) [22], [23].

Due to the large differences in the covalent radii of Mg (1.41 Å)[24] and Be (0.96 Å)[24], compared to Zn (1.22 Å)[24], the Be and Mg actually have a compensating effect and mutually aid in the incorporation of the other, while increasing the bandgap beyond that of the ternaries MgZnO and BeZnO. Additionally, this compensation prevents strain-induced phase separation and reduction of material quality, while the strain that does exist drives compositional variations within epitaxial films, which in turn cause large potential fluctuations. Therefore, as in InGaN MQW, localization may suppress nonradiative recombination and lead to high-efficiency optoelectronic devices.

To investigate this system further, O-polar BeMgZnO quaternary alloys were grown on GaN through plasma assisted molecular beam epitaxy (MBE), as per Toporkov et al. and Ullah et al. [22], [23]. PL was collected to characterize three BeMgZnO samples, where again as in the InGaN study, the excitation source was a Ti:Sapphire laser but frequency tripled to 266 nm (4.68 eV), with 150 fs pulse width and 80 MHz repetition rate. Also, PL was collected and analyzed with use of a liquid nitrogen cooled CCD connected to a 30 cm monochromator, and time resolved photoluminescence (TRPL) decays were measured with a 30 ps resolution streak scope.
Steady state PL at 15K are presented in Figure 2.16. Sample BMZ1 had the highest Mg/Be ratio, lowest PL peak energy, and highest intensity. Sample BMZ2 had ~0.1 eV higher PL peak energy than sample BMZ1 and showed the lowest intensity with the lowest Mg/Be ratio. Sample BMZ3 had the highest energy PL peak and higher intensity than sample BMZ2, likely from the higher Mg/Be ratio and therefore higher mutual compensation than in sample BMZ2. Additionally, sub-bandgap BL2 GaN transition was attributed to a possible hydrogen-carbon defect complex [25], and a band-to-band GaN luminescence is absorbed and emitted in the ZnO layer and appears in the BeMgZnO shoulder.

![Figure 2.16: Low temperature PL of BeMgZnO samples. Sample BMZ1 is Be$_{0.04}$Mg$_{0.17}$Zn$_{0.79}$O, sample BMZ2 is Be$_{0.11}$Mg$_{0.15}$Zn$_{0.74}$O and sample BMZ3 is Be$_{0.10}$Mg$_{0.25}$Zn$_{0.65}$O](image)

It was theorized that with increased Mg/Be ratio, because of the mutual compensation of lattice strain and energy of formation in ZnO, the layer should therefore only support smaller depths of localization, and with reduced Mg/Be ratio deeper localization. Therefore, the two
samples with the highest and lowest Mg/Be ratios (sample BMZ1 and sample BMZ2) were selected and the temperature dependence of PL peak positions were collected and presented in Figure 2.17

As depicted in the figure, “S-behavior” is observed in sample BMZ1, but is not in sample BMZ2. This was surprising based on the expectation that the material with the smallest ratio would also show the least compensation, largest degree of localization, and should have the largest “S-behavior.” In sample BMZ1, a degree of localization of 22 meV was found. In sample BMZ2 no “S-behavior” was observed, thus when the fitting function was applied, it gave that $\sigma$ equaled zero. Since the experimental results were contrary to our expectations, further investigation was conducted.

To better understand the dynamics of carriers in the material, low-temperature TRPL measurements were also conducted, where single exponential decays were applied. The single exponential decay is modeled by [22]:

Figure 2.17: Temperature dependence of PL peak position for (a) BMZ1 $Be_{0.04}Mg_{0.17}Zn_{0.79}O$ and (b) BMZ2 $Be_{0.11}Mg_{0.15}Zn_{0.83}O$ grown on GaN
\[
\tau(E) = \frac{\tau_0}{1 + \exp\left(\frac{E - E_0}{\Delta_0}\right)}
\]  

(7)

where \( \tau_0 \) is defined as the exciton recombination time in the absence of energy transfer, \( \Delta_0 \) is the degree of localization in the bandtail state, and \( E_0 \) is the characteristic energy where the recombination rate equals the delocalization rate [22]. This equation assumes that if carriers have

**Figure 2.18:** Decay dependence on emission energy at 15K, and integrated PL for a) sample BMZ1: Be0.04Mg0.17Zn0.79O; b) sample BMZ2: Be0.11Mg0.15Zn0.74O; and c) sample BMZ3: Be0.10Mg0.25Zn0.65O. The spectral sampling step is 1nm. The localization parameters are determined from the fit with Equation (7).
energy greater than the characteristic energy \((E > E_0)\) then a localized carrier will delocalize and undergo nonradiative recombination, and if below that energy \((E < E_0)\) a carrier remains localized and recombines radiatively [22]. The findings are presented in Figure 2.18. The fitted value of localization for sample BMZ1 was 0.098 eV, and for sample BMZ2 was 0.268 eV.

These results are important because they lead us to believe that “S-behavior” is in fact present in sample BMZ2 but on such a scale that it was not measurable using only peak position. While determining localization through measurement of “S-behavior” is more direct, if the degree of localization is exceedingly large, then it is possible that above room-temperatures would be needed. Since this is not practical, in this case alternate indirect methods are needed. Also, it is important to note that it does appear that sample BMZ2 has a very large degree of localization, and so might be able to benefit from efficiency gains as a result of localization, as long as material quality can be maintained.

Overall, this material system has great potential for applications requiring wide bandgap as well as bandgap tunability, from solar-blind detectors to HFETs. Further study is needed to investigate the possibly very large degree of localization, where this quaternary could experience large efficiency gains once fabrication is refined, as was the case for GaN in the late 1990s. Despite the amount of time the localization phenomena has been known, there are still new and novel places where its application can be extremely valuable.
3. Optical Properties of Group-IV Alloy Quantum Dots

3.1. Background

Germanium (Ge) itself is a relatively nontoxic group IV metal in the same periodic group as Silicon (Si). In bulk Ge, as well as in bulk Si, at the minimum of their bandgap they have an indirect transition. If germanium can be engineered by alloying with other materials, useful properties can be found, which if possible would be a practical advantage in itself since the technology would be compatible with current silicon processing techniques. Experimental efforts in the last decade has focused on engineering the bandgap of Ge from indirect to direct, which could potentially lead to new, more efficient devices. This could be done by alloying it with a similar material that is either direct bandgap itself, or is perhaps a good conductor such as Tin (Sn). It has been shown that by alloying Ge with Sn, the lattice constants can be made to change which in turn does modify the bandgap in potentially useful ways.[26]–[28] With the incorporation of Sn to make a bulk Ge$_{1-x}$Sn$_{x}$ alloy, the energy gap transitions to quasi-direct at 6-10%, depending on strain, which shows increased efficiency, but also, alloying will decrease the bandgap further from the low-bandgap value that pure germanium already has. [26]–[28] At these low gap values thermal effects and quenching are an issue. Therefore it is advantageous to use quantum confinement intrinsic to QDs to increase performance. There is a compensating effect for the narrowing of the bandgap from alloying because of the enhancement of energy gaps that is a result of confinement. [29] Additionally, at size scales smaller than the exciton Bohr radius, the electron and hole wavefunctions begin to overlap, and so therefore, with incorporation of Sn or not, at QD size energy gaps are direct and efficiency is immediately be increased. Also, through first-principles simulations it can be shown that in the GeSn QD system, by alloying Ge with Sn, the
oscillator strengths could be enhanced and the QDs can be made to be more efficient light emitters. An additional advantage to this material system is that QDs can be synthesized simply through colloidal chemistry, which is easily scalable and cost effective, as described by Hafiz et al. [29] in addition to others [30]–[33].

While GeSn has many potential advantages, there are some challenges to making a successful optoelectronic system. One of these challenges to maximizing efficiency in the QD system is the competition between minimizing particle size and maximizing Sn incorporation. This competition occurs because Sn is a larger atom, so it strains the lattice around it causing the lattice constants to expand. This effect has an extremely large influence on bandgap, or energy-gap as the case of NPs. Furthermore, because of the finite size of the organic ligands used for passivation of the surface, at the very small (less-than ~2 nm) size QDs, the ligands can become crowded and not able to passivate all of the free surface states. Also, at larger 5-10 nm sizes, although the particles should be fully passivated, there is a loss of emission in that case too. [34] This has been attributed to a loss of quantum confinement effects and a subsequent lowering of the energy gap to the point where apparent remaining defects and thermal variations caused complete quenching of any radiative recombination.

3.2. Previous work

Previous to the samples measured in this research, this research team studied ultra-small QDs in the 1.8-2.2 nm size range, to investigate the full capability of quantum confinement. In the 1.8-2.2 nm range each QD only consists of a couple hundred atoms and the effect of quantum confinement is strong. It was determined that these particles possessed the diamond cubic structure that is expected from larger GeSn NPs and thin-films, as well as a homogeneous distribution of
Ge and Sn. With a Sn concentration of $x = 0.018$ to 0.236, the energy gaps range from 2.05 to 1.72 eV, correspondingly.

Through temperature dependent TRPL it was found that there was 3 orders of magnitude difference in decay times at 15K to room temperature. After analysis, this drastic difference in decay time was attributed to dark and bright exciton states, and the involvement of surface traps with core states of the QDs. At low temperature as depicted in Figure 3.1 (a), decays were on the order of 10-20 μs, then at room temperature as in Figure 3.1 (b) were on the order of 10-20 ns, as modeled with the biexponential decay function $A_{\text{fast}} e^{-t/\tau_{\text{fast}}} + A_{\text{slow}} e^{-t/\tau_{\text{slow}}}$ where $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ represent the fast and slow decay components, respectively.

One alteration to this approach in the current research was the switching out of the passivating capping ligand from oleylamine (OLA) to hexadecylamine (HDA), with the hypothesis that it could provide better size uniformity by preventing growth of larger alloys. It was also desirable to attempt to push into the near-IR range, by attempting to grow particles in the 3-6 nm size, which would potential have greater electronic applications.
3.3. Results and Discussion

Where other types of characterization exist to evaluate these NPs, like transmission electron microscopy (TEM), this thesis focuses on optical characterization. Measurements were performed on 3-6 nm NPs of GeSn. Using the same technique as with the InGaN MQW LEDs, for characterization the excitation source was a Ti:Sapphire laser which was frequency doubled to 385 nm and had a pulse width of approximately 150 fs at 80 MHz repetition rate. Measurements of the steady state spectra were collected with a liquid nitrogen cooled CCD connected to a 30 cm focal length monochromator, and additionally in this experiment a streak-scope with 30 ps resolution was used to collect PL decay information. As was shown, at low temperature the optical decays can be on the order of μ-seconds. Therefore in addition to the laser and detector, a pulse picker system is utilized to direct the mode-locked laser pulses to either the sample, or into a beam block.
The previous research using smaller particles did show some tunability [35] in lattice parameters and in absorption, but the particle size dispersity was very large. For example the previous research synthesized particles of 1.85±0.47nm to 2.28±0.48, for Sn concentration from 1.8%-23.6%. In this current sample set though, it was grown with much smaller relative size dispersity, such as 5.0±0.4 nm. More importantly, with the new samples we have achieved PL emission, which was not possible for the same size QDs previously.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sn Composition (SEM/EDS) x</th>
<th>Particle Size (nm)</th>
<th>Crystallite Size (PXRD) (nm)</th>
<th>Bandgap (eV) Kubelka–Munk</th>
<th>PL Peak Position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.015</td>
<td>3.2 ± 0.2nm</td>
<td>1.9 ± 0.2</td>
<td>1.70</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>0.019</td>
<td>3.3 ± 0.2 nm</td>
<td>2.1 ± 0.2</td>
<td>1.53</td>
<td>1.53</td>
</tr>
<tr>
<td>3</td>
<td>0.027</td>
<td>3.4 ± 0.3 nm</td>
<td>2.2 ± 0.2</td>
<td>1.42</td>
<td>1.42</td>
</tr>
<tr>
<td>4</td>
<td>0.034</td>
<td>3.6 ± 0.3 nm</td>
<td>2.4 ± 0.2</td>
<td>1.31</td>
<td>1.38</td>
</tr>
<tr>
<td>5</td>
<td>0.042</td>
<td>3.8 ± 0.3 nm</td>
<td>2.8 ± 0.2</td>
<td>1.26</td>
<td>1.34</td>
</tr>
<tr>
<td>6</td>
<td>0.056</td>
<td>4.4 ± 0.4nm</td>
<td>2.8 ± 0.2</td>
<td>1.16</td>
<td>1.31</td>
</tr>
<tr>
<td>7</td>
<td>0.064</td>
<td>4.5 ± 0.4 nm</td>
<td>2.9 ± 0.2</td>
<td>1.02</td>
<td>n/a</td>
</tr>
<tr>
<td>8</td>
<td>0.079</td>
<td>4.6 ± 0.4 nm</td>
<td>3.0 ± 0.3</td>
<td>0.94</td>
<td>n/a</td>
</tr>
<tr>
<td>9</td>
<td>0.091</td>
<td>4.9 ± 0.4 nm</td>
<td>3.3 ± 0.2</td>
<td>0.84</td>
<td>n/a</td>
</tr>
<tr>
<td>10</td>
<td>0.112</td>
<td>5.0 ± 0.4 nm</td>
<td>3.5 ± 0.3</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>11</td>
<td>0.154</td>
<td>5.3 ± 0.5 nm</td>
<td>3.6 ± 0.3</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>12</td>
<td>0.206</td>
<td>5.7 ± 0.5 nm</td>
<td>3.8 ± 0.2</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

When measured utilizing steady state PL, it was confirmed that with increasing Sn the energy gap is shown to be able to be tuned from long visual wavelengths (775 nm, 1.60 eV) to near-IR (945 nm, 1.31 eV). With Sn incorporation up to 5.6%, energy gaps into the near-IR range were able to be achieved as shown in the PL and absorbance spectra of Figure 3.2 and Figure 3.3. At Sn concentrations exceeding 5.6% though, PL emission was not observed. By using diffuse
reflectance spectroscopy though, which can then be processed into absorbance using the Kubelka–Munk (KM) remission function to obtain bandedge absorption onset, bandgaps can effectively continue to be measured into very high Sn content as shown in Table 1. This potential for a wide range of tunability is an advantage since it increases the overall utility of this material system and opens possibilities for wider ranging applications.

Similarly to the previous work [29], it was found that at room temperature, the PL decay of the GeSn NPs was on the order of 10-20 ns. Also, when cooled to 15K the PL decay became much slower, on the order of 1-10 μs. Although at low temperature there was much slower decays, in addition to the drastically less frequent laser pulses to accommodate the long decay times, the intensity at low temperature was still significant. In steady state spectra, using the same excitation power for two GeSn samples similar to sample (4), in Figure 3.4 (a) and (b) it can be seen that the low temperature PL has an intensity of approximately an order of magnitude greater than that of room temperature PL, and is consistent from sample to sample. This intensity difference is attributed to large amounts of nonradiative channels becoming accessible at room temperature.

Figure 3.4: Room temperature and low temperature steady-state PL for (a) 3.5%Sn QD sample, and (b) 3.8%Sn QD sample.
This timescale difference in decays is theorized to be because at low temperature charges become trapped in low energy surface states where they eventually recombine, possibly with separated opposite charge HOMO and LUMO states at the core. This physical separation of charges can lead to long lifetimes. Also, because of quantum transition selection-rules, charges located together at the core of the QD are spin-forbidden to recombine. At low temperature decay lifetimes are exceedingly long, so this describes the slower dark-exciton state. With the addition of thermal energy though, charges at the surface can experience de-trapping and are able to

\[
\tau_{fast} = 1.09 \pm 0.09 \mu s \\
\tau_{slow} = 7.81 \pm 0.42 \mu s \\
\frac{A_{fast}}{A_{slow}} = 1.64
\]

\[
\tau_{fast} = 1.62 \pm 0.05 \mu s \\
\tau_{slow} = 8.50 \pm 0.20 \mu s \\
\frac{A_{fast}}{A_{slow}} = 1.78
\]

\[
\tau_{fast} = 8.0 \pm 0.2 \text{ ns} \\
\tau_{slow} = 80.2 \pm 1.3 \text{ ns}, \\
\frac{A_{fast}}{A_{slow}} = 2.44
\]

\[
\tau_{fast} = 11.5 \pm 0.6 \text{ ns} \\
\tau_{slow} = 111.11 \pm 2.7 \text{ ns} \\
\frac{A_{fast}}{A_{slow}} = 1.41
\]

Figure 3.5: Low temperature and Room temperature PL decays of GeSn QD samples (2) and (6)
transition to allowed fast decays in the QD core. This information is presented in Figure 3.5. Also, with the addition of thermal energy, the charges are more readily able to flip their quantum spins, additionally transitioning to fast, spin-allowed bright-exciton states [36]. This system of transitions is depicted in Figure 3.6. Simulations by a collaborator were conducted to further investigate the dynamics of the transitions within the quantum dots.

![Figure 3.6: Schematic diagram of the radiative recombination pathways in Ge-:Sn alloy QDs (Hafiz, J. Phys. Chem. Lett., 2016)](image)

One such simulation technique was to utilize time-dependent hybrid functional calculations, utilizing the Heyd–Scuseria–Ernzerhof hybrid functional (TD-HSE). This allowed the calculation of optical absorption and the dark-bright excitonic states of the QDs [36]. Using this technique it is possible to simulate the oscillator strengths of optical transitions around the energy gap, while taking into account the electron-hole interactions. With increasing Sn concentration, the energy splitting between the lowest energy dark exciton (recombination transition of very low magnitude oscillator strength) and the first significant strong transition (recombination transition of large magnitude oscillator strength) decreases. Also it was found that with the addition of Sn, the overall strength of the other transitions increase too. This shows that mathematically, with the addition of Sn, the dark-bright exciton states become blurred, where the splitting becomes smaller, as well as the magnitude of the difference in oscillator strengths become
less. The most important point though is that overall, optical transitions become stronger and therefore brighter with the addition of Sn. These changes in transition oscillator strength are represented in Figure 3.7, with a decreased splitting between the dark and bright transitions, and an overall increase in transition probably. Overall, research is underway to increase our understanding of surface states and size dependence of dark exciton bright exciton splitting.

The next step in this project is to explore the incorporation of Si into the NPs also. Although bulk Si is indirect, and has a lower bandgap than the energy gaps found in the QDs featured here, when also reduced to QD sizes the energy gap of Si correspondingly also increases. In preliminary experiments, with a small (~5%) incorporation of Si, it was found that while the SiGeSn was still in the solution phase, before deposition for solid-state analysis, the energy of PL

![Figure 3.7: Oscillator strengths of optical transitions for a series of D = 1.4 nm Ge1–xSnx alloy QDs of varying Sn concentrations. Red arrows indicate the dark–bright exciton splitting in each QD. Zero of the energy axis is placed at the lowest unoccupied HSE single-particle state. (Demchenko et al. J of Phys Chem C. 2017)](image-url)
was actually blueshifted by ~0.25 eV from the emission found when deposited in a solid-state form, as shown in Figure 3.8 (a). This is theorized to be a result of increased passivation while still in the solution phase, so more emission is seen from the smaller NPs which have higher confinement, but again this is preliminary research and will be investigated further. This is also

\[
\text{RT Si}_{0.05}\text{Ge}_{0.90}\text{Sn}_{0.05}
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![Graph showing normalized steady state room temperature PL for Si$_{0.05}$Ge$_{0.90}$Sn$_{0.05}$ nanoparticles in solution state and dropcast forms.](a)

![Graph showing decays of solution and dropcast forms.](b)

![Graph showing low temperature and room temperature decay for dropcast sample.](c)

**Figure 3.8:** (a) Normalized steady state room temperature PL for Si$_{0.05}$Ge$_{0.90}$Sn$_{0.05}$ nanoparticles in solution state and dropcast forms. Note that once deposited into dropcast form, PL emission is redshifted by ~0.25 eV, (b) decays of solution and dropcast forms showing that initially the dropcast sample decays more quickly but then both have a similar long decay, and (c) low temperature and room temperature decay for dropcast sample showing that low temperature and room temperature share the same order of magnitude in their decays.
supported by Figure 3.8 (b), because if there is higher passivation, then the lifetimes should be overall be very similar, but a rapid initial decay is suppressed. Also it was found that in room temperature TRPL, as in the case without Si, decays occur at the <10 ns time scale, but with the addition of Si a faster decay was actually found in the less-than 1 ns time scale. However, at 15K it was found that decays still were also on the order of less-than 1 ns. In fact the amplitudes of the fast bi-exponential decay constants were greater at low temperature, as in Figure 3.8 (c). So, although the time constants were very similar, the decay actually occurred in a shorter span of time. This is significantly different than the behavior of NPs only consisting of Ge and Sn.

In terms of underlying physics, it is theorized that since Si is smaller than all of the other constituent elements, it actually has a compensating effect in the strain in the Ge lattice due to Sn. This should potentially decrease the effect of Sn, but the end result is that (since the bandgap in Si is larger than in Ge or Sn) the energy gap further enhances the energy gain from quantum confinement and compensates for the reduction from the addition of Sn, and while it should reduce the transition strengths in the particle, this potential reduction in performance from Si is also compensated for by the enhancement of the Sn, where Sn has a greater effect with the addition of Si. Therefore, with the potential addition of Si, a wider range of energies in the visible become accessible, while maintaining strong oscillator strengths. Furthermore, additional studies are continuing to investigate the SiGeSn QD material system.
4. Conclusion and Future Work

As MQW thickness and number of MQW periods in an LED is increased, the localization effect has been measured to grow. Under high carrier density though, localization is reduced and in some cases completely obscured. Different factors can change the degree of localization measured in a material. Including suppression of the localization effect from a maximum of 16 meV down to 5 meV in a 15x3.15 nm MQW sample, or from a maximum of 10.5 meV to 0 meV in a 6x1.5 nm MQW, over an increase in four orders of magnitude in excitation density. Also, with the addition of QW layers an increase in measured localization is able to be observed, with an increase from 11 meV to 16 meV, from a MQW sample with 6 periods to a MQW with 15 periods.

Localization is believed to have been key to the discovery of effective blue LED light generation, and therefore LED white light generation also. Despite the enormous strides made in the decades since the discovery, there is still now a theoretically unmet potential in LED light generation. Through the continued study of localization it may be possible to still overcome the hurdles that face modern LED lighting.

The study of localization still poses many challenges. Results from studies with similar conditions can still produce inconsistent, possibly arbitrary results. To better understand what is truly happening, researchers would need to be able to somehow track the movement of individual carriers through the layers of a MQW, through different temperatures and be able to directly observe carrier dynamics at an atomic level. Baring that possibility, continued careful and attentive study, ideally on large, selectively iterated differences, with multiple growth techniques and different excitation modes as well as structural types is likely required to continue to improve efficacies.
Localization can also be found in other materials besides InGaN, such as in (Be,Mg)ZnO. In this quaternary compound, localization could possibly be so great that carriers are still localized at room temperature. This material system could be an ideal candidate for very wide bandgap applications, and could show that if there is a large degree of localization, then even materials with high strain and possibly low quality can still potentially be effective.

In the study of localization in MQWs and in the study of nanoparticles, both share an emphasis on the results of quantum effects. For GeSn and SiGeSn nanoparticles which can be difficult to produce, while still in the research phase still show great promise. They require passivation, the uniform incorporation of Sn, and narrow size dispersity. GeSn nanoparticles still have a very good outlook, primarily because they have the potential to be synthesized using fast and cost effective colloidal chemistry, as well as being typically nontoxic and silicon compatible. As I have shown, this material system has already been proven in the current primary research phase, so far fulfilling that promise. Looking to future, it may become possible to apply these nanoparticles in devices manufactured through use of metal chalcogenide complexes to embed them in thin film matrices, where their advantages can be leveraged for great technological advances.

While nanoparticles passivated by organic ligands are stable and emissive, they don’t work well in practical device applications because of their inability to conduct carriers from particle to particle. If the ligands are able to be exchanged with metal chalcogenide complexes (MCCs) though, the nanoparticles can be deposited into thin-films to form a semiconducting matrix[37]–[39]. Already some research groups have seen success in applying this theory to produce functioning devices [37], [39]. Through this technology, nanoparticles have the potential to truly revolutionize device synthesis. One example is the possibility of all-solution device fabrication,
which would be very appealing for large area creation of devices where, for example, it could be possible to combine electron-conducting nanowires with hole-conducting host structures to produce solution-based materials with distributed networks for p-n junctions. Specific devices that have already been made in the primary research phase include photoconductors and field effect transistors, as presented in Figure 4.1 and Figure 4.2 [39]. These devices are fabricated by first QD and MCC synthesis, followed by chemical ligand exchange of the original long organic passivating agents on the QDs with the much smaller, conductive inorganic MCCs. Then, the newly passivated and colloidally stable QDs are simply spin coated onto a suitable substrate and annealed at low temperature for a relatively brief ~30 minutes. Metal contact electrodes can be patterned and applied for the creation of a FET structure, or if a conducting glass/indium-tin-oxide substrate was used, the QD thin-film can be sandwiched between the substrate and electrodes to

![Diagram](image1.png)

**Figure 4.1:** CdSe/CdS core–shell nanocrystals. (a), Device structure used for photoconductivity measurements. (b), Energy level offsets in CdSe cores and CdS shells allow facile transport of photogenerated electrons between the nanocrystals, whereas holes stay confined stay confined to CdSe cores. The combination of highly mobile electrons and trapped holes provides high internal photoconductive gain in the CdSe/CdS nanocrystal solids. (Lee et al. Nat. Nano. 2011)

![Diagram](image2.png)

**Figure 4.2:** Schematic of a FET with the channel assembled from inorganically capped semiconductor nanocrystals. (Lee et al., Nat. Nanotech. 2011)
create a photoconductor device [37]–[39]. The only obstacle is that their implementation needs refinement to maximize performance and minimize cost.

As stated, the potential of this is technology is nothing short of revolutionary. In addition to FETs, large area all-solution based roll-to-roll applications such as for manufacture of thin-film solar cells [39] are possible.

Between the ongoing research in localization within wide bandgap semiconductors and forthcoming, groundbreaking research in QDs, not only does the future appear very efficient and sensitive, it is also looking very bright.
References


Vita

Tanner Nakagawara was born on October 26, 1984, in the city of Seattle, Washington, and is a US citizen. He graduated from Shorecrest High School, Shoreline, Washington in 2003. He received his Bachelor of Science in physics and astronomy from The University of Washington, Seattle, Washington in 2009. With the completion of this thesis, in the fall of 2017 he received his Master of Science in electrical engineering from Virginia Commonwealth University.