Characterization of Novel Semiconductor Alloys for Band Gap Engineering

By

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Abstract

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The novel semiconductor alloys, In$_{1-x}$Al$_x$N, GaN$_{1-x}$As$_x$, and ZnSe$_{1-x}$O$_x$, are promising materials for low-cost and high-efficiency solar cells and efficient solid-state lighting. The band gap of all of the alloys can be controlled through the visible electromagnetic energy spectrum by varying x.

In-rich InAlN tends to be degenerately n-type due to the high electron affinity of InN and the conduction band and light hole band are non-parabolic due to the narrow band gap and the interaction of the conduction band and valence bands. The absorption spectra can be blue shifted due to the Burstein-Moss Shift.

GaNAs and ZnSeO are highly mismatched alloys, where the alloying involves elements that are very dissimilar in terms of electronegativity and size. The band anticrossing model, which treats the interaction of a localized defect level with the extended states of the conduction and valence bands, quantitatively describes the properties of highly mismatched alloys.

The band gap bowing parameter, which quantifies the band gap dependence on composition, of InAlN is determined while accounting for the effects of degenerate electron concentrations and non-parabolic bands on the absorption spectra. The composition is independently determined by two complimentary methods.

The band gap and temperature dependence of the band gap of ZnSe$_{1-x}$O$_x$ are determined by optical spectroscopy and can be understood in terms of the band anticrossing model. The exciton kinetics is quantified through time-resolved photoluminescence and is found to cause a low temperature enhancement of the photoluminescence.

The band gaps of GaNAs are determined for the full composition range for both crystalline and amorphous phases. The composition dependence of the band gap can be quantified by the band anticrossing model across the full composition range through a linear interpolation of the conduction band and valence band anticrossing models.
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1 Band Gap Engineering

Since the discovery of the transistor at Bell Labs in 1947, semiconductor devices have become an increasingly important for modern life. Transistors, diodes and integrated circuits are the foundation of modern electronics and computers, which are now ubiquitous. Continuous improvement in the control of the properties of semiconductors has lead to smaller and more powerful computers and more diverse applications, including light emitting diodes and photovoltaic cells. The ability to control all of the properties of a semiconductor is critical for device optimization.

1.1 Introduction to Band Gap Engineering

The study of semiconductors alloys has been motivated, in part, by the need to tune the properties of semiconductors to optimize their performance for specific applications. Band gap engineering is the controlled alloying of semiconductors to tune the band gap of the material. The band gap ($E_g$) is important for optoelectronic applications, as it defines the energy of the transition involved in the absorption and emission of light; the band gap defines the emission color of light in a light emitting diode (LED) or solid state laser and the onset of absorption for a photovoltaic device. Because of the importance of the band gap in device design, it is critically important to quantify and understand how and why the band gap changes with composition for a new semiconductor alloy to be useful.

![Figure 1.1 Band gaps for common III-V compound semiconductors and their alloys plotted against their lattice constants.](image)

Figure 1.1 Band gaps for common III-V compound semiconductors and their alloys plotted against their lattice constants.

The band gaps of common III-V cubic semiconductors and their alloys are shown in figure 1.1 and are plotted in relation to their lattice parameter [1]. The highest direct band gap energy for these materials is about 2eV. A direct band gap is more efficient than an indirect band gap at emitting and absorbing light, because direct band gap transitions are two body processes (involving electrons and holes) where as a phonon (a third body) is needed to achieve these transitions in an indirect semiconductor.
The band gap and lattice parameter of common cubic II-VI semiconductors and their alloys are shown in figure 1.2 [2] and of III-N wurzite semiconductors and their alloys in figure 1.3 [3, 4]. All of the band gaps for these materials are direct. The band gap change with alloying shown in figures 1.1, 1.2 and 1.3 are linear or have a constant curvature, unless there is a change in the Brillouin zone direction of the lowest energy conduction band. When the Brillouin zone direction of the lowest conduction band changes, there is a kink in the band gap dependence on lattice parameter. The fact that the band gap change is not the same in all alloys raises the obvious question of why certain materials behave the way they do and how this behavior can be predicted.
Figure 1.3 Band gaps for III-N compound semiconductors and their alloys plotted against their lattice constants.

The most basic approach to predict the effect of alloying on the properties of semiconductors is to assume a linear change with composition. This approach works well for the change in lattice parameter of semiconductor alloys where it is termed Vegard’s law [5]. In a similar vein the Virtual Crystal Approximation (VCA) treats the random crystal potential that the valence electrons experience as a uniform periodic potential [6, 7]. The crystal potential of the two pure compound semiconductors are linearly interpolated to determine the new potential at each composition. For the band gap, this approach predicts very little deviation from a linear change with composition [6, 7].

An empirical quadratic “bowing” parameter has been used to fit the band gap dependence since semiconductor alloys were first studied in the 1930s [6]. For an alloyed semiconductor, \( A_xB_{1-x} \), the band gap dependence is given by

\[
E_{g}^{A_xB_{1-x}}(x) = (x) \cdot E_{g}^{A} + (1 - x) \cdot E_{g}^{B} - (x) \cdot (1 - x) \cdot b
\]

(1.1)

where \( E_{g}^{A} \) and \( E_{g}^{B} \) are the band gaps of the end point materials and \( b \) is the bowing parameter. It has been proposed that in addition to the *intrinsic* bowing, \( b_{i} \), predicted by the VCA an additional *extrinsic* bowing parameter, \( b_{e} \), can be added to account for disorder broadening [8]. Additionally, it has been predicted that the bowing parameter will depend on the relative electronegativity of the alloying element [8].

This work examines the optoelectronic properties of three novel semiconductor alloy systems with band gaps that cover all or part of the visible energy spectrum. New material development in this area is critical for advancement in several optoelectronic applications, including high efficiency photovoltaics and light emitting diodes.
1.2 Selected Applications of Band Gap Engineering

1.2.1 High Efficiency Photovoltaics

There has been increasing interest in non-fossil fuel energy sources due to the effects of burning fossil fuels on global warming due to the emission of CO$_2$ into the atmosphere and the geopolitical implications of securing and importing oil. The conversion of sunlight into useable energy is the only renewable energy source in abundance to meet society’s full and growing energy needs [9]. Enough energy strikes the earth from the sun in one hour to meet the energy needs of the entire world for an entire year, but the conversion processes are still too expensive when compared to the marginal costs of traditional power generation [9]. Assuming the cost of competing technologies stays constant, the efficiency of these devices must be increased and/or the cost of production must be decreased in order to make photovoltaics cost effective.

The photovoltaic conversion efficiency depends directly on the band gap of the semiconductor absorber. The most basic solar cell consists of a single semiconductor with a p-n junction to separate the electron-hole pair created by the absorption of a photon with energy greater than the band gap.

Higher efficiencies can be achieved by using more than one absorber material, each with a different band gap. This approach reduces the thermalization losses from high-energy photons and non-absorption losses from low energy photons. The typical approach is to create a stack of solar cells, with the lowest band gap material on the bottom and with each progressively larger band gap material on top, which is illustrated in figure 1.4. A p-n junction must be formed in each material to separate charge and a transparent tunnel junction must connect each p-n junction. The absorber thicknesses must be tuned to match the current produced by each junction. The semiconductor materials are typically lattice matched in order to achieve the best material quality and device performance, although recent advancements in metamorphic thin film growth have yielded the record for solar cell efficiency without lattice matching [10].

![Figure 1.4 Schematic diagram of a triple-junction solar cell. The sunlight is traveling from left to right and is shown as the AM1.5 normalized irradiance.](image-url)
Table 1.1 lists the absorber band gaps and ideal system efficiencies under 1000x illumination for devices up to 10 junctions [11]. The maximum possible efficiency increases from 32.4% to 44.3% when an additional junction is added and plateaus at about 61%. There are many ways to calculate maximum efficiency and care should be taken to only compare numbers that are derived from the same approach.

### 1.2.2 High Efficiency White Light Emitting Diodes

White light emitting diodes (LEDs) are a lighting option that is more energy efficient than incandescent light bulbs. A light emitting diode emits light from a narrow range of energy that is close to the band gap energy. There are two approaches to produce white light. The first is to use an ultra-violet or blue LED and down-convert the emitted light with a phosphor that has broad white emission. This is the current approach for commercial white LEDs, but both the emitting materials and the down conversion process limit efficiency.

The second approach is to have a separate emitter for red, green and blue light that together make white light. This approach should yield a more efficient device, as it does not rely on two energy conversion processes in series, but three parallel ones. The band gaps of the three emitting materials must be engineered to produce the desired temperature of light. An additional advantage of this approach is that tuning the relative intensity of the three light sources can change the color and “feel” of the light. Both approaches require careful control of the semiconductor band gaps.

### 1.3 Opportunities in Novel Semiconductor Alloys: InAlN, ZnSeO and GaNAs

The band gaps of the InAlN alloy system span the widest range of any semiconductor alloy system, from InN with $E_g = 0.64\text{eV}$ to AlN with $E_g = 6.2\text{eV}$, which spans the full solar spectrum. The wide band gap tunability makes the alloy system an interesting candidate for a single material system multi-junction solar cell [12].
quality alloys have only been achieved in the past several years and many of the properties of the intermediate alloys are still unknown. This work quantifies the band gap bowing parameter of InAlN in chapter 3.

Adding oxygen to ZnSe (E_g = 2.68eV) results in a 130meV decrease in the band gap with 1 atomic percent of oxygen. This allows for control of the direct band gap into the visible energy spectrum with efficient emission, making ZnSe_{1-x}O_x an interesting candidate for light emitting diodes and solid-state lasers. This work studies the effect of oxygen on the band structure and the temperature dependence of the band gap of ZnSeO in chapter 4 and the effect of oxygen on the photo-excited exciton recombination kinetics in chapter 5.

The band gaps of the GaNAs alloy system also cover a wide energy range, from 3.4eV for GaN to 1eV for GaAs_{0.92}N_{0.08}, which spans the full visible energy spectrum and makes GaNAs an interesting candidate for single alloy system multi-junction solar cells. Stable amorphous GaNAs alloys have been grown on glass substrates with band gaps from 2.2eV to 1eV, which could provide a route to low-cost and high-efficiency solar cells [13]. This work quantifies the band gap dependence on composition for GaNAs through the band anticrossing model in chapter 6.
2 Materials Properties and Background: In$_{1-x}$Al$_x$N, GaN$_{1-x}$As$_x$, ZnSe$_{1-x}$O$_x$

This dissertation reports on the properties of novel semiconductor alloys that provide a new means to tailor semiconductors for optoelectronic applications. The background theory necessary to understand the characterization of these materials is presented in this chapter.

2.1 Introduction to InN and In-rich In$_{1-x}$Al$_x$N

2.1.1 History of InN

Initial attempts to grow InN relied on radio-frequency sputtering [14], which resulted in polycrystalline films with a high defect and impurity density and electron concentrations greater than $10^{20}$ cm$^{-3}$ with electron mobilities up to 250 cm$^2$/(V s) [15]. The band gap of these materials was determined to be about 1.9eV from absorption spectroscopy [16, 17]. These films did not exhibit photoluminescence (PL) unlike the other III-N semiconductors that showed strong PL despite high defect concentrations [18]. Beginning in 1989 molecular beam epitaxy (MBE) was used to grow single crystal InN on sapphire substrates [19-22]. Eventually, crystal growth improved enough to produce films with electron concentrations below $10^{18}$ cm$^{-3}$.

During this time of improved InN thin film quality and decreasing electron concentration, the band gap determined from absorption spectroscopy was revised down from 1.9eV to 1.5eV, 1.1eV [23], 0.9eV [20] and has finally settle on 0.64eV [24]. The 0.64eV band gap has been measured and confirmed by absorption spectroscopy, photoluminescence spectroscopy, photo-modulated reflectance spectroscopy and is now the accepted value [4]. Below is a brief introduction to the band structure and optical properties of InN relevant to this work.

2.1.2 Band Structure of InN

The conduction band and valence bands of most semiconductors can be treated as parabolas where the curvature is inversely proportional to effective mass of the electrons and holes, respectively. The small (0.64eV) band gap of InN and In-rich alloys results in non-parabolic conduction band and light hole band dispersions from a $k\cdot p$ interaction (where $k$ is the wavevector and $p$ is the momentum operator) between the conduction and valence bands [25, 26]. A similar effect has been found in InAs and InSb [25, 27]. The non-parabolicity of the conduction band is a result of the interaction and admixing of the conduction band, which has $s$-type symmetry, with the valence bands, which have $p$-type symmetry [25]. The $k\cdot p$ interaction becomes stronger at higher $k$.

The $k\cdot p$ interaction can be understood in terms of Kane’s model [25], neglecting the spin orbit band and crystal field splitting, both of which are very small in InN, and remote bands, which are more than 4eV away, and assuming an isotropic band at small $k$. The dispersion of the conduction band is given by:

$$E_C(k) = -\frac{E_g}{2} + \frac{\hbar^2 k^2}{2m_o} + \frac{1}{2}\sqrt{E_g^2 + 4k^2P^2}$$  \hspace{1cm} (2.1)
where $E_g$ is the band gap, $m_e$ is the electron rest mass, $k$ is the magnitude of the wavevector and $P$ is:

$$P = \frac{-i\hbar}{m_o} \langle S|p|Z \rangle$$ \hspace{1cm} (2.2)

which is the momentum matrix element for the transition between the valence and conduction bands. The energies are referenced to the conduction band edge (CBE). Equation (2.2) can be further simplified in terms of the effective mass at the band edge, give by [28]:

$$P = \sqrt{\frac{\hbar^2 E_g}{2m_o}}$$ \hspace{1cm} (2.3)

Combining equations (2.1) and (2.3) results in the simplified version of the non-parabolic dispersion relationship of the conduction band [26]:

$$E_c(k) = -\frac{E_g}{2} + \frac{\hbar^2 k^2}{2m_o} + \sqrt{\frac{E_g^2}{4} + E_g \frac{\hbar^2 k^2}{2m_o}}. \hspace{1cm} (2.4)$$

The light hole valence band similarly interacts with the conduction band, which results in a nonparabolic band with a dispersion given by

$$E_{lh}(k) = -\frac{E_g}{2} + \frac{\hbar^2 k^2}{2m_o} - \sqrt{\frac{E_g^2}{4} + E_g \frac{\hbar^2 k^2}{2m_o}}. \hspace{1cm} (2.5)$$

The two important parameters for determining the dispersion relation for the conduction band are the band gap, $E_g$, and the band edge electron effective mass, $m_e$. The former has been determined to be 0.64eV but the latter is still under some debate. The values for the electron effective mass in the literature vary from 0.07$m_o$ to 0.033 $m_o$ [4]. Figure 2.1 shows the dispersion relation for a parabolic and non-parabolic conduction band with a band gap of 0.64eV and effective mass of 0.07$m_o$ [4]. Only the heavy hole valence band is shown for clarity, which has an effective mass of ~0.65.

Clearly from the figure, the variation from parabolicity increases with $k$ and $E$.

The conduction band dispersion relation of In-rich alloys can be calculated by changing the band gap and effective mass with composition. The band gap dependence on composition is given by a bowing parameter and the effective mass can be assumed to linearly vary with alloying. The bowing parameter of In$_{1-x}$Ga$_x$N is 1.4eV [29], whereas the bowing parameter of In$_{1-x}$Al$_x$N has been a point of controversy that will be addressed in chapter 3. Reported values range from 2.9 to 6.2eV [3, 30-36] and the author has reported a value of $4.7 \pm 0.4$ eV [37].
2.1.3 Optical Properties of InN and In-rich Alloys

The measured absorption spectrum of InN as a function of electron concentration is shown in figure 2.2. For the lowest electron concentration sample, with \( n = 1.7 \times 10^{18} \text{ cm}^{-3} \), the onset of absorption is close to the band gap of 0.64 eV. As the electron concentration increases, the onset of absorption blue shifts by over 1 eV. This shift in the absorption edge is called the Burstein-Moss Shift and is illustrated in figure 2.3 [38]. At high electron concentrations, InN is degenerately doped, so the Fermi level, \( E_F \), resides in the conduction band. Conduction band states below \( E_F \) are full and are not available for a transition from the valence band, so absorption is not possible. The optical absorption edge is determined by the position of \( E_F \) instead of \( E_g \). This phenomenon explains the historical downward shift in the band gap of InN as crystal growth improved, decreasing the electron concentration.
Figure 2.2 Measured absorption spectrum of InN with four different electron concentrations.

Figure 2.3 The band structure of degenerately doped InN, illustrating the Burstein-Moss Shift. Optical transitions are not possible to conduction band states below the Fermi level.

The Burstein-Moss Shift can be calculated for a given electron concentration from the non-parabolic dispersion relationship of the conduction band [38]. The calculated values of the optical absorption edge for a parabolic and non-parabolic conduction band along with experimentally determined values are shown in figure 2.4. The optical absorption edge shifts from 0.7eV to 2eV when the electron concentration increases.
from $3 \times 10^{17} \text{ cm}^{-3}$ to over $10^{20} \text{ cm}^{-3}$. This huge shift in absorption edge is quantitatively explained by the Burstein-Moss Shift through the full energy and electron concentration range [38]. The measured values are well explained by the calculation including the non-parabolic conduction band. Similar effects have been observed in In-rich $\text{In}_{1-x}\text{Ga}_x\text{N}$ [39] and $\text{In}_{1-x}\text{Al}_x\text{N}$ [40]. Interested readers can find additional information in literature reviews of $\text{InN}$ and In-rich alloys [4, 17, 41].

![Figure 2.4](image)

**Figure 2.4** Experimental determination of the optical absorption edge of $\text{InN}$ for various electron concentrations along with the calculated dependence for a parabolic and non-parabolic conduction bands. [4]

### 2.2 Introduction to Highly Mismatched Alloys

Highly mismatched alloys (HMAs) are a class of materials in which the anion of a compound semiconductor is replaced by an isoelectronic impurity that is highly dissimilar in terms of size and electronegativity. Figure 2.5 shows a modified version of the relevant portion of the periodic table for compound semiconductors that indicates the size and electronegativity of the elements. The substitution of a more electronegative anion, such as nitrogen replacing arsenic in $\text{GaAs}$, results in a local defect potential [42]. The impurity is isovalent, so it appears charge neutral except over very short ranges. This is in direct contrast to hydrogenic impurities that are not isoelectronic and form delocalized states. The localized nature of the isoelectronic impurities means that they behave like deep level defects even though their binding energy can be very small. The localized impurities will be broad in k-space, due to the Heisenberg uncertainty principle, and will interact with bands in multiple Brillouin zone directions. As the concentration of the isoelectronic impurity goes from doping levels to alloying levels, the defect levels interact with the host matrix to change the alloy’s properties.

The most striking effect of alloying with a highly dissimilar element is the very large downward shift in the band gap seen in both II-VI and III-V compound semiconductor HMAs [43-49]. Figure 2.6 shows the experimentally determined band
gaps for GaAs$_{1-x}$N$_x$ up to $x = 0.04$ [50-52]. The band gap decreases by more than 180meV for GaAs with only a single percent of alloying with GaN. The VCA would predict a linearly increasing band gap with alloying. A bowing parameter quadratic fit results in $b = 18.4$eV, which implies the conversion of the alloy to a semimetal at certain compositions. Figure 2.6 also shows the band gap change for the analogous II-VI material, ZnSe$_{1-x}$O$_x$ with up to $x = 0.065$ [43, 45, 53]. Again the VCA approximation predicts an increase in the band gap, but the band gap decreases by over 130meV with only a single percent of alloying with ZnO. Here a bowing parameter of $b = 8.4$eV fits the data.

![Periodic Table Portion](image)

**Figure 2.5** A modified portion of the periodic table relevant to semiconductors in this work, including the Pauling scale of electronegativity and atomic radius.

A number of theoretical approaches have been proposed to explain the large decrease in band gap of HMAs. An early approach was through a dielectric two-band method using an experimental pseudopotential and the virtual crystal approximation that resulted in a bowing parameter that depended on how dissimilar the constituent semiconductors are [8]. Another approach utilized *ab initio* molecular dynamics and concluded that the band gap decrease was due to symmetry induced effects [54]. A third approach concluded that the effect was due to an impurity band from nitrogen impurity pairs that have an energy level in the band gap [55]. None of these approaches were able to predict the behavior of new alloys and explain all of the properties of this new class of materials.
2.2.1 Conduction Band Anti-crossing Model

The band structure of HMAs has also been explained in terms of a two band anti-crossing model (BAC) [56, 57]. The model explains the properties of HMAs, including the composition and pressure dependence of the band gap, the presence of a new high energy transition and a nitrogen-induced enhancement of the electron effective mass. The BAC model treats the interaction of the localized defect states and the extended states of the conduction band in analogy to perturbation theory for a two-level system. This interaction leads to a splitting of the matrix band into two characteristic non-parabolic bands that are typically labeled $E_+$ and $E_-$ for the high and low energy bands respectively. The resulting bands have mixed localized and delocalized character from the interaction of the two types of states.

The alloying of an HMA can be treated as an anti-crossing interaction if it is assumed that the defect states are randomly distributed over the lattice, replace the anion sites, and are weakly coupled to the host lattice. First for the case of the substitution of a more electronegative anion into the lattice results in an energy level close to the conduction band. The eigenvalue problem for the perturbed system can be written as [56]:

$$
\begin{vmatrix}
E_M(k) - E(k) & V_{MD} \\
V_{MD} & E_D - E(k)
\end{vmatrix} = 0
$$

(2.6)

where $E_M(k)$ is the dispersion relation for the unperturbed host conduction band, $E_D$ is the defect energy level, $E(k)$ is the dispersion relation of the perturbed system that are all relative to the valence band edge (VBE). $V_{MD} = \langle k | V | D \rangle$ is the matrix element describing the coupling between the localized defect states, $D$, and the extended host...
matrix conduction band states. The matrix element, $V_{MD}$, can be simplified to $C_{MN}^{1/2}$ assuming that the defect states are randomly distributed and their concentration is low enough so there is no appreciable defect state wavefunction overlap. $C_{MN}$ is an empirically determined coupling constant between the extended matrix states and the localized defect states and $x$ is the mole fraction of the defect. The solution to equation (2.6) is then

$$E_{\pm}(k,x) = \frac{1}{2} \left\{ E_M(k) + E_D \pm \sqrt{[E_M(k) - E_D]^2 + 4C_{MD}^2 \cdot x^2} \right\} \quad \text{(2.7)}$$

so the original system of a parabolic band and a localized defect level results in a splitting into two highly non-parabolic bands, $E_{\pm}(k)$, that depend on the composition, $x$ [56]. $E(k)$ becomes the new conduction band dispersion relation of the alloy and defines the band gap. Figure 2.7 shows two examples of this band anticrossing interaction. Figure 2.7a is the case where the defect level is resonant with the conduction band, as in GaAs$_{1-x}$N$_x$ or ZnSe$_{1-x}$O$_x$. Figure 2.7b is the case where the defect level is in the band gap, as in GaP$_{1-x}$N$_x$ or ZnTe$_{1-x}$O$_x$. When the defect level is in the conduction band, $E_-$ will be dominated by the delocalized character of the conduction band and $E_+$ will be dominated by the localized character of the defect level. When the defect level is in the band gap, the opposite is true.

![Figure 2.7 Band structure calculation from the band anticrossing model for the defect level in (a) the conduction band and (b) the band gap.](image)

As the alloying is increased, the separation between $E_-$ and $E_+$ increases and the band gap decreases. Figure 2.8 shows the BAC fit for the band gap dependence on composition for GaAs$_{1-x}$N$_x$ with $C_{MN} = 2.70$eV and $E_N = 1.65$eV [56] and ZnSe$_{1-x}$O$_x$ with $C_{MO} = 1.95$eV and $E_O = 2.90$eV [45, 53]. These fits show very good agreement with the experimental data and provide a physical explanation for how alloying with a highly dissimilar anion changes the band structure of the HMA.

This basic perturbation theory approach was given a more solid theoretical foundation when the same solution was found using a many-impurity Anderson model.
that is widely used to quantify the effects of an interaction between a defect level and band states [58]. From this treatment, Wu et al found that there is an intrinsic broadening in the resulting bands from the broadening in the defect level energy. Figure 2.9 shows the broadened bands from figure 2.7a. Interested readers can find more detail on the conduction band anti-crossing model in the works of W. Shan, W. Walukiewicz and J. Wu et al [47, 56, 57, 59-62].

Figure 2.8 Experimentally determined band gaps along with the band anticrossing model fit for GaAs$_{1-x}$N$_x$ and ZnSe$_{1-x}$O$_x$. 
2.2.2 Valence Band Anti-crossing Model

The complimentary case to the nitrogen defect in GaAs is the arsenic defect in GaN. The more metallic and larger arsenic atom replaces the highly electronegative nitrogen anion. It has been reported that the doping of GaN with arsenic results in a new emission band at about 2.65eV [63] and the arsenic defect level has been theoretically predicted to lie 0.4eV above the valence band [64]. Figure 2.10 shows the experimentally determined band gap for GaN$_{1-x}$As$_x$ (GaN-rich), along with the bowing parameter determined for GaAs$_{1-x}$N$_x$ (GaAs-rich) and the virtual crystal approximation [65]. As GaAs is alloyed with GaN there is a discontinuous decrease in the band gap as it shifts from 3.4eV to about 2.6eV, where the arsenic defect level resides. The band gap continues to decrease with increasing arsenic concentration. Neither the bowing parameter nor the VCA fit the experimental data.
Figure 2.10 Experimentally determined band gaps for GaN$_{1-x}$As$_x$ along with the predicted band gaps from the VCA and the bowing parameter fit for GaAs-rich GaN$_{1-x}$As$_x$ [65].

The full treatment of this system considers the perturbation of the valence band due to the presence of the metallic defects through $k \cdot p$ formalism. The approach is the same as the conduction band anti-crossing model, except that a 6 x 6 matrix element is needed to describe the valence bands and the $p$-type defect level. The metallic defects are $p$-type states with $T_2$ symmetry, which are represented by a 6 x 6 matrix [66]. The valence band Hamiltonian is constructed on the basis of the six time-reversal symmetry invariant wavefunctions:

\begin{align}
\left| \frac{3}{2}, \frac{3}{2} \right\rangle &= \frac{1}{\sqrt{2}} \left| (X + iY) \uparrow \right\rangle \\
\left| \frac{3}{2}, \frac{1}{2} \right\rangle &= \frac{i}{\sqrt{2}} \left| (X + iY) \downarrow -2Z \uparrow \right\rangle \\
\left| \frac{3}{2}, -\frac{1}{2} \right\rangle &= \frac{1}{\sqrt{6}} \left| (X - iY) \uparrow +2Z \downarrow \right\rangle \\
\left| \frac{3}{2}, -\frac{3}{2} \right\rangle &= \frac{i}{\sqrt{2}} \left| (X - iY) \downarrow \right\rangle \\
\left| -\frac{1}{2}, \frac{1}{2} \right\rangle &= \frac{1}{\sqrt{3}} \left| (X + iY) \downarrow +Z \uparrow \right\rangle \\
\left| -\frac{1}{2}, -\frac{1}{2} \right\rangle &= \frac{i}{\sqrt{3}} \left| (-X + iY) \uparrow +Z \downarrow \right\rangle
\end{align}
Using the standard 6 x 6 Kohn-Luttinger matrix describing the Γ₇ and Γ₈ valence bands [67, 68]. The random distribution of impurities can be resolved through configurationally averaging within the coherent potential approximation [58]. The 6 x 6 valence band matrix is enhanced by the 6 x 6 defect matrix resulting in a 12 x 12 matrix is given by:

\[
H_v = \begin{bmatrix}
H & \alpha & \beta & 0 & \frac{i\alpha}{\sqrt{2}} & -i\sqrt{2}\beta & V(x) & 0 & 0 & 0 & 0 & 0 \\
\alpha^* & L & 0 & \beta & \frac{iD}{\sqrt{2}} & i\frac{\sqrt{3}}{2}\alpha & 0 & V(x) & 0 & 0 & 0 \\
\beta^* & 0 & L & -\alpha & -i\sqrt{2}\beta & 0 & 0 & V(x) & 0 & 0 & 0 \\
0 & \beta^* & -\alpha^* & H & -i\sqrt{2}\beta^* & \frac{i\alpha^*}{\sqrt{2}} & 0 & 0 & 0 & V(x) & 0 \\
V(x) & 0 & V(x) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & V(x) & 0 & 0 & 0 & 0 & E_d + i\Gamma_d & 0 & 0 & 0 & 0 \\
0 & 0 & V(x) & 0 & 0 & 0 & 0 & E_d + i\Gamma_d & 0 & 0 & 0 \\
0 & 0 & 0 & V(x) & 0 & 0 & 0 & 0 & E_d + i\Gamma_d & 0 & 0 \\
0 & 0 & 0 & 0 & V(x) & 0 & 0 & 0 & 0 & E_d + i\Gamma_d & 0 \\
0 & 0 & 0 & 0 & 0 & V(x) & 0 & 0 & 0 & 0 & E_d + i\Gamma_d
\end{bmatrix}
\]

(2.9)

where

\[
H = -\frac{\hbar^2}{2m_o} \left[ (k_x^2 + k_y^2)(\gamma_1 + \gamma_2) + k_z^2(\gamma_1 - 2\gamma_2) \right]
\]

(2.10a)

\[
L = -\frac{\hbar^2}{2m_o} \left[ (k_x^2 + k_y^2)(\gamma_1 - \gamma_2) + k_z^2(\gamma_1 + 2\gamma_2) \right]
\]

(2.10b)

\[
\alpha = \sqrt{3} \frac{\hbar^2}{m_o} \left[ k_z(k_x - ik_y)\gamma_3 \right]
\]

(2.10c)

\[
\beta = \frac{\sqrt{3}}{2} \frac{\hbar^2}{m_o} \left[ (k_x^2 - k_y^2)\gamma_2 - 2ik_xk_y\gamma_3 \right]
\]

(2.10d)

\[
D = L - H
\]

(2.10f)

\[
S = \frac{1}{2}(L + H) - \Delta_o
\]

(2.10g)

and β, γ₂ and γ₃ are the Luttinger parameters of the host semiconductor and Δₒ is the spin orbit splitting energy of the host semiconductor. Diagonalization of the matrix yields the dispersion relations for the Eᵣ and Eᵣ⁺ bands for each of the original valence bands. Again, V can be simplified to CᵥMDx¹/₂ as for the conduction band. CᵥMD is the empirically determined coupling parameter. An interested reader can find more detail in the work of K. Alberi and J. Wu et al [65, 66, 69-71].

Figure 2.11 shows the VBAC fitting for the band gap change of GaNₓAs₁₋ₓ with CᵥMAs = 1.60eV and EᵣAs = 0.62eV. The fit shows very good agreement with the experimental data and provides a physical explanation for the discontinuous band gap change in GaNₓAs₁₋ₓ.
2.2.3 Band Anti-Crossing Across the Full Compositional Range

The VBAC and CBAC models are only valid until the defect states begin to overlap, which is at about $x = 0.15$. In order to extend the models across the full composition range, a linear interpolation approach has been shown to fit the band gap dependence of ZnSe$_{1-x}$Te$_x$ and ZnSe$_{1-x}$S$_x$ across the full composition range [71]. In the case of ZnSe$_{1-x}$Te$_x$, the linear extrapolation would take the form:

$$E_g^{ZnSe_{1-x}Te_x}(x) = (1-x)E_g^{Se-rich}(x) + xE_g^{Te-rich}(x) \quad (2.11)$$

where $x$ is the mole fraction of ZnTe, $E_g^{Se-rich}$ is the band gap determined from VBAC model and $E_g^{Te-rich}$ is the band gap determined from the CBAC model. This approach essentially combines the band anti-crossing model that accounts for the effect of the localized impurity on its neighboring band and the VCA approach for the shift in the unperturbed band. Figure 2.12 shows the linear interpolation fit for ZnSe$_{1-x}$Te$_x$ [71].
Figure 2.12 Experimentally determined band gaps for ZnSe$_{1-x}$Te$_x$ along with a BAC derived fit across the full composition range [71].
3 Band Gap Bowing Parameter of In$_{1-x}$Al$_x$N

The direct band gaps of the In$_{1-x}$Al$_x$N alloy system span the widest range of any semiconductor alloy system, from 0.64 eV (InN) [72] to 6.2 eV (AlN) [73]. This makes these alloys candidates for a range of optoelectronic applications, including solar cells, detectors, sensors, transistors, laser diodes, and light emitting diodes. In order to effectively design InAlN devices, it is important to know the band gap bowing parameter, which describes the variation of the band gap with alloy composition. There is significant variation in the band gap bowing parameters reported in the literature. Since the discovery of the narrow band gap of InN [74, 75], the reported bowing parameters have ranged from 2.9 to 6.2 eV [3, 33, 36, 76-80].

The large discrepancy in the reported bowing parameters may be attributed to a number of factors, including poor sample quality, limited composition range [3, 36, 76, 77], and the methodology and techniques used to determine both the band gaps and the compositions of the samples. In particular, in determining the band gap of In-rich compositions, many studies [3, 33, 78] have neglected to account for the Burstein-Moss shift of the absorption edge and the nonparabolicity of the conduction band, which have been described in chapter 2. In addition, most studies use x-ray diffraction (XRD) to determine alloy composition [33, 76-78, 80], but it has been suggested that this may not always give accurate results. There are reports of a Vegard’s law bowing parameter in InAlN [79, 81], but also a report indicating that strain can explain the deviation from Vegard’s law for films that are close to lattice matched to GaN [82]. We combine compositional determination through Rutherford backscattering spectrometry (RBS) and XRD in order to provide the most accurate determination of composition and a comparison between the two approaches. There have also been several theoretical calculations of the bowing parameter. To our knowledge, only one has used the proper value of the band gap of InN; Liou et al. [79] found a bowing parameter of 3.46-3.67 eV.

High quality, single crystal growth of In-rich and intermediate compositions of the InAlN alloys has been achieved by collaborators at Cornell University, allowing for a reexamination of the band gap bowing parameter. The compositions of the films are determined by RBS and XRD. Crystal quality and homogeneity are examined by channeling-RBS and high resolution XRD. The band gaps of the InAlN alloys are determined by modeling the optical absorption spectroscopy. This allows for more accurate determination of the band gap than the simple and commonly used linear extrapolation of the square of the absorption coefficient, as will be discussed below.

3.1 Experimental Details

A set of In$_{1-x}$Al$_x$N samples, with x ranging from 0.017 to 0.60, were grown by molecular beam epitaxy (MBE) with 200 nm AlN buffer layers on c-plane sapphire substrates. The InAlN epilayers range in thickness from 180 to 280 nm and are all c-plane oriented. The details of growth can be found elsewhere [83]. The sample data are summarized in table 3.1.

The experimental optical absorption coefficients were calculated from the photon energy dependence of transmission, which was measured with a Perkin Elmer Lambda 950 NIR-VIS-UV spectrophotometer at room temperature. Prior to measurement, the backsides of the sapphire substrates were polished successively with 3 µm and 1 µm diamond grit, to minimize optical scattering. The polishing decreased the scattering by
an order of magnitude and greatly enhanced the quality of the transmission spectroscopy data. To account for any remaining scattering losses, which were assumed to be independent of photon energy, a constant baseline was subtracted from the data. In addition, reflection spectroscopy measurements were performed for the InAlN films. The reflection correction to the transmission data did not change the band gap determined from modeling when the baseline is subtracted.

Table 3.1 Summary of properties of the In$_{1-x}$Al$_x$N samples.

<table>
<thead>
<tr>
<th>$x$ (Fraction AlN) from RBS</th>
<th>$x$ (Fraction AlN) from XRD</th>
<th>Thickness (nm)</th>
<th>Channeling Ratio</th>
<th>XRD FWHM $2\theta$-ω (arcmin)</th>
<th>XRD FWHM $\omega$ (arcmin)</th>
<th>Electron Concentration (cm$^{-3}$)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.015</td>
<td>242</td>
<td>0.09</td>
<td>10.0</td>
<td>21.5</td>
<td>3x10$^{18}$</td>
<td>0.70</td>
</tr>
<tr>
<td>0.05</td>
<td>0.04</td>
<td>238</td>
<td>0.13</td>
<td>10.2</td>
<td>20.3</td>
<td>3x10$^{18}$</td>
<td>0.80</td>
</tr>
<tr>
<td>0.09</td>
<td>0.07</td>
<td>247</td>
<td>0.08</td>
<td>10.5</td>
<td>31.6</td>
<td>3x10$^{18}$</td>
<td>0.88</td>
</tr>
<tr>
<td>0.12</td>
<td>0.12</td>
<td>255</td>
<td>0.22</td>
<td>11.1</td>
<td>35.9</td>
<td>4x10$^{18}$</td>
<td>0.92</td>
</tr>
<tr>
<td>0.17</td>
<td>0.17</td>
<td>250</td>
<td>0.33</td>
<td>10.7</td>
<td>40.1</td>
<td>4x10$^{18}$</td>
<td>1.04</td>
</tr>
<tr>
<td>0.25</td>
<td>0.28</td>
<td>200</td>
<td>0.16</td>
<td>11.5</td>
<td>33.8</td>
<td>2x10$^{18}$</td>
<td>1.28</td>
</tr>
<tr>
<td>0.33</td>
<td>0.35</td>
<td>210</td>
<td>0.41</td>
<td>12.2</td>
<td>29.0</td>
<td>1x10$^{18}$</td>
<td>1.57</td>
</tr>
<tr>
<td>0.36</td>
<td>0.39</td>
<td>210</td>
<td>0.41</td>
<td>11.0</td>
<td>33.6</td>
<td>5x10$^{16}$</td>
<td>1.72</td>
</tr>
<tr>
<td>0.37</td>
<td>0.40</td>
<td>220</td>
<td>0.25</td>
<td>10.9</td>
<td>21.7</td>
<td>5x10$^{14}$</td>
<td>1.73</td>
</tr>
<tr>
<td>0.40</td>
<td>0.41</td>
<td>190</td>
<td>0.25</td>
<td>11.0</td>
<td>30.7</td>
<td>2x10$^{18}$</td>
<td>1.68</td>
</tr>
<tr>
<td>0.46</td>
<td>0.48</td>
<td>235</td>
<td>0.28</td>
<td>11.6</td>
<td>29.5</td>
<td>Insulating</td>
<td>2.02</td>
</tr>
<tr>
<td>0.60</td>
<td>0.63</td>
<td>270</td>
<td>0.68</td>
<td>14.4</td>
<td>49.8</td>
<td>Insulating</td>
<td>2.43</td>
</tr>
</tbody>
</table>

The film thickness and compositions ($x$) of In$_{1-x}$Al$_x$N were determined by RBS using a 2 MeV $^4$He$^+$ beam with a particle detector located at a backscattering angle of 165°. The data were analyzed using the RUMP software package [84]. Sample homogeneity, quality and composition were measured with an X'Pert Pro x-ray diffractometer, using $2\theta$-ω and ω (rocking curve) scans about the 0002 peak of InAlN. Film homogeneity was determined from the full width at half max (FWHM) values of the $2\theta$-ω 0002 InAlN peaks. Film quality was determined from the FWHM values of the ω-scans of the same peaks.

Electron concentrations were measured using the Hall effect with a 6000 gauss magnet and indium contacts in the van der Pauw configuration. The Mg doped samples showed no photoluminescence, which is consistent with results from InN and InGaN alloys [85, 86].

3.2 Modeling of Optical Absorption Spectroscopy

The modeling in this study was performed in collaboration with Dr. R. Jones, who developed the model for the study of irradiation and native defects in In-rich In$_{1-x}$Al$_x$N [40]. Typically, the band gap ($E_g$) of a direct gap semiconductor is found from the experimental optical absorption spectrum by making a linear extrapolation of the square of the absorption coefficient (or this value multiplied by the square of the photon energy) to the energy axis. However, this approach does not account for the Burstein-Moss shift. This becomes important in degenerate semiconductors, such as many of the InAlN samples in this study as well as in the literature. Further, the process of linear
extrapolation assumes a parabolic conduction band dispersion relation, which is not a good approximation for narrow gap semiconductors like the In-rich InAlN alloys.

The model quantifies the optical absorption following the $k\cdot p$ approach developed by Kane for narrow gap semiconductors [87] to consider the nonparabolicity of the band gap and uses the measured electron concentration to determine the position of the Fermi level for the Burstein-Moss shift. The model considers a non-parabolic conduction band and light hole band, but assumes a parabolic heavy hole band and spin orbit band. The values of the electron effective mass were linear interpolations between the values for InN (0.07 $m_0$ [88]) and AlN (0.32 $m_0$ [89]). The model was not sensitive to the chosen effective masses for the other bands, and 1.0 and 0.2 were used for the heavy hole and spin orbit effective masses, respectively.

The assumptions in Kane’s model break down when the higher energy bands begin to interact with the conduction band and light hole valence band. At this point (roughly when energies above the conduction band edge become comparable to the band gap energy), this treatment will become invalid. The energy range above the band gap used for fitting is significantly smaller than the band gap for all samples.

At high electron concentrations, electron-electron and electron-ion interactions have been calculated to cause a net decrease in the band gap [90-92]. However, there has not been consistent experimental evidence to support the accuracy of these calculations in the literature [93, 94]. Previous studies [40, 95] did not find evidence for a narrowing of the band gap in the photoluminescence spectra of InGaN and InAlN samples with increasing electron concentrations. Because of a relatively low electron concentration, these effects are neglected in the present study.

The energy dependence of the absorption coefficient, $\alpha_o(E)$, is given by

$$\alpha_o(E) = \frac{4\pi^2 e^2 \hbar}{m_e c n_r E} \sum_j M_j^2(E) \rho_j(E)$$

where $c$ is the speed of light, $m_e$ is the electron rest mass, $e$ is the electron charge, $n_r$ is the refractive index and $j$ is the index that defines which band is involved in the transition to the conduction band (light hole, heavy hole and spin orbit valence bands) [37]. Assuming full coupling between the valence and conduction bands the square of the optical matrix is constant with energy and given by:

$$M_j^2 = \frac{2m_0^* P^2}{3\hbar^2}$$

where $P$ is the momentum matrix given by:

$$P^2 = \frac{\hbar^2 E_g}{2m_0^*}$$

and $m_0^*$ is the band edge effective mass. The density of states is given by:

$$\rho_j = \frac{k_j^2}{2\pi^2 dE_c/dk_j - dE_j/dk_j}$$

where $k_j$ is the wavevector. The nonparabolic conduction band and light hole band are given by equation (2.4) [37].

The energy dependence of the absorption coefficient, $\alpha_o(E)$, is multiplied by the electron distribution in the conduction band, given by the Fermi distribution function. The electron concentration, $n$, is related to the Fermi level, $E_F$, by
\[ n = \frac{1}{3\pi^2} \int_{E_C/k_B T}^{\infty} \frac{e^{-\frac{E_k}{k_B T}}}{1 + e^{-\frac{E_k}{k_B T}}} z k_c(z)dz \]  

(3.5)

where \(E_C\) is the conduction band edge, \(k_B\) is the Boltzmann constant, and \(k_c(z)\) is found by solving equation (2.4) for \(k\) and changing variable to \(z = E/k_B T\). The electron concentration, \(n\), was measured by the Hall effect and the Fermi level is determined by solving equation (3.5) for \(E_F\). The absorption coefficient is convoluted with a Gaussian function to account for inhomogeneous broadening to do compositional variation [37].

The model results in an energy dependence to the absorption given by

\[ \alpha(E) = \frac{a}{\Delta \sqrt{\pi}} \int_{-\infty}^{E} \alpha_0(E') \left[ 1 + \exp \left( \frac{E' - E_F}{kT} \right) \right]^{-1} \exp \left[ -\left( \frac{E' - E}{\Delta} \right)^2 \right] dE' \]  

(3.6)

where \(\Delta\) is the Gaussian broadening parameter, and \(a\) is a unitless, multiplicative factor that was used to fit the data that factors in the effective mass and refractive index for the alloys. Equation (3.6) was fit to the observed spectra (solid lines in figure 3.4) to extract the band gap. The fitting parameters were \(E_g\), \(\Delta\) and \(a\). The \(\Delta\) values lie between 0.10 - 0.30 eV and the values for \(a\) were 0.8-1.4.

### 3.3 Experimental Results

#### 3.3.1 Determination of alloy composition and crystalline quality

Rutherford Backscattering Spectrometry (RBS) provides a direct analysis of sample composition and thickness. Figure 3.1 shows typical RBS data for the InAlN films along with the simulation and channeling data. Channeling-RBS in the <0001> direction reveals that the InAlN films are single crystals. The crystalline quality of the \(\text{In}_{1-x}\text{Al}_x\text{N}\) film degrades as \(x\) increases. Minimum channeling yields (c) for low \(x\) (< 0.10) are less than 0.05, similar to InN films grown on GaN buffer layers. As \(x\) increases above 0.30, c also increases to greater than 0.4. The only published papers on InAlN band gap bowing with RBS data are for samples with higher \(x\) than considered in this study [36, 81], ranging from 0.81 ≤ \(x\) ≤ 0.87 and c from 0.04-0.07 for the best samples. The samples with higher \(x\) were grown on GaN, in an attempt to achieve lattice matched InAlN epilayers. Those films are pseudomorphic, so it is expected that they would have lower channeling yields than non-lattice matches samples considered in this study.
Figure 3.1 RBS data for the In$_{0.54}$Al$_{0.46}$N film oriented in a random crystal direction, with the simulation and channeling data for the $<$0001$>$ direction. (Data courtesy of K. M. Yu)

Figure 3.2 shows three typical 2$\theta$-ω X-Ray Diffraction (XRD) scans for a range of In$_{1-x}$Al$_x$N compositions. All of the samples used in this study are single phase InAlN, determined from the presence of a single 0002 InAlN diffraction peak. The FWHM of this peak quantifies the compositional homogeneity and is listed for each sample in Table 3.1. The FWHM ranges from 10 to 14 arcmin, increasing with $x$, which is consistent with the increase in $c$ found by RBS. These values are also similar to those of the best samples in the literature and are lower than the values of samples in the literature in the middle composition ranges [33, 78].
Figure 3.2 Representative 2θ-ω scans about the 0002 peak of InAlN. Dashed lines indicate the expected position of the InN and AlN 0002 peaks and Al₂O₃ 0006 peak. Arrows mark the InAlN 0002 peak. The curves are vertically offset. The composition indicated is from XRD.

The sample composition is also determined using Vegard’s law from the 0002 peak of InAlN using the sapphire 0006 peak as a reference. The compositions determined from both RBS and XRD are listed in table 3.1 and are similar across the full composition range.

Rocking curve measurements were taken on the 0002 InAlN peaks as an additional quantification of sample quality. These measurements are an indication of the mosaicity of the samples, as slight tilts in the columnar growth will broaden the peak. Results are listed in table 1. The FWHM of these peaks varies between 22 and 50 arcmin, which is in the same range as recent results in the literature [33, 78]. Rocking curve scans for three representative samples are shown in figure 3.3.
Figure 3.3 Representative set of 0002 rocking curve measurements for three InAlN samples. Data are normalized and vertically offset for clarity. The FWHM are marked with an arrow.

3.3.2 Band Gap Determination

Figure 3.4 shows the experimental optical absorption data for all of the films in this study. The absorption edge blue shifts as \( x \) increases, as expected. The band gaps are determined by fitting the model to the data. Figure 3.5 shows the results of the model and the data for two representative samples. In In-rich films, the plot of \( \alpha^2 \) versus photon energy is nonlinear (e.g., figure 3.5a), due to the nonparabolic conduction band structure. Therefore, there would be substantial error in band gap determination by the linear extrapolation of \( \alpha^2 \) to the energy axis, since there is a range of possible linear fits. For higher values of \( x \) (e.g., \( x > 0.3 \)), the parabolic dispersion becomes a better approximation for the conduction band, and the electron concentrations used here (\( \leq 10^{18} \text{cm}^{-3} \)) do not create significant Burstein-Moss Shifts. For these samples, the band gap energies can be accurately found from linear extrapolation of \( \alpha^2 \) (e.g., figure 3.5b). With higher electron concentrations in this range of \( x \), the band gaps could be accurately estimated by linear extrapolation of \( \alpha^2 \) followed by adjustment for the Burstein-Moss Shift.
Figure 3.4 Optical absorption coefficients as a function of photon energy for all samples in this work.

Figure 3.5 Experimental and modeled optical absorption spectra for two InAlN films, a) In$_{0.88}$Al$_{0.12}$N and b) In$_{0.60}$Al$_{0.40}$N. The band gaps determined by the modeling are listed. Oscillations below the band edge of the In$_{0.60}$Al$_{0.40}$N data are from Fabry-Perot interference.

3.4 Discussion

In order to describe the compositional dependence of the band gap of the In$_{1-x}$Al$_x$N alloys, the standard bowing equation is used:

$$E_g^{\text{InAlN}}(x) = (1-x)E_g^{\text{InN}} + xE_g^{\text{AlN}} - bx(1-x)$$  \hspace{1cm} (3.7)

where the bowing parameter $b$ describes the deviation of the band gap from a linear composition dependence between the InN and AlN endpoints. Fitting this equation to the data, and assuming band gaps of 0.64 eV for InN [72] and 6.2 eV for AlN [73] gives $b = 4.7 \pm 0.4$ eV. The error bars are determined from the values of $b$ found from the
highest and lowest possible fits to the absorption data. Figure 3.7 shows the experimental data and the band gaps given by equation (3.2) with \( b = 4.7 \) eV.

![Figure 3.6 Band gap energies from this work (red circles) and the literature (grey shapes). The solid line was calculated using a bowing parameter of 4.7 eV. (Figure courtesy of Dr. R. Jones)](image)

The value of \( b \) is sensitive to the process and assumptions made here. If a band gap of 6.1 eV is assumed rather than 6.2 eV for AlN, as has been recently reported [73, 96], then \( b = 4.5 \pm 0.4 \) eV. If the compositions is determined by XRD with Vegard’s law, then \( b = 5.1 \pm 0.4 \) eV.

Figure 3.6 shows the data from this study with composition determined by RBS along with the band gaps determined by optical absorption [33, 78, 97-101], reflectivity [80, 102], ellipsometry [77], and photoluminescence excitation spectroscopy [36] in the literature. For the In-rich films, our values are lower than those of in other references [33, 97, 100]. This can be attributed, at least in part, to our consideration of the Burstein-Moss Shift and the nonparabolic conduction band. Sample quality may also be important. The photoluminescence energies reported by Naoi et al. [33] are close to our values, which may indicate band edge luminescence in their films with a Burstein-Moss Shift of the absorption edge. The data agree well with Goldhahn et al. [77] and Terashima et al. [78]; Goldhahn et al. also accounted for the Burstein-Moss shift and a nonparabolic conduction band. For large \( x \), our calculated band gaps are near the upper edge of the experimental data. In the mid-range compositions, our results differ significantly from Onuma et al. [80], Kubota et al. [99] and Yamaguchi et al. [101]. All of these papers report significant compositional fluctuations, and Kubota et al. further reported films that were “mixed crystalline.”

In conclusion, the optical absorption has been measured and modeled for a series of high quality InAlN samples to determine the band gap. The complications created by nonparabolcity, Burstein-Moss shift, and compositional broadening were accounted for in this treatment. The composition of the samples has been measured with Rutherford backscattering spectrometry and x-ray diffraction and the quality has been quantified.
by 2θ-ω and rocking curve XRD scans and by channeling-RBS. From these results, we report a band gap bowing parameter of 4.7 ± 0.4eV for the composition determined by RBS and 5.1 ± 0.4eV for the composition determined by XRD.
4 Temperature Dependence of the Band Gap of ZnSe$_{1-x}$O$_x$

The temperature dependence of the band gap of semiconductors is an important parameter for light emitting diodes (LEDs) and solid state lasers (SSLs). The color of light emission depends on the band gap, so a large temperature dependence of the band gap will lead to a large change in emission wavelength with temperature. LEDs and SSLs operate in a range of environmental conditions and produce heat during operation, so a small band gap temperature dependence is desirable for stable light emission color.

Alloying small amounts of ZnO with ZnSe has been shown to yield a decrease in the band gap through the visible spectrum, making it appealing for light emission applications [103]. A previous study found no effect of oxygen on the temperature dependence of the band gap in ZnSe$_{1-x}$O$_x$ for samples with low oxygen concentration (x=0.0023-0.0090) [104]. Here the results of a study of the optical properties of ZnSe$_{1-x}$O$_x$ with the oxygen molar fraction, x, ranging from 0 to 0.049 are presented. In contrast to the previous study of Polimeni et al., I find that oxygen incorporation has a clearly discernible effect on the temperature dependence of the band gap of ZnSe$_{1-x}$O$_x$ alloys that can be quantified by the BAC model.

4.1 Experimental Details

The ZnSe$_{1-x}$O$_x$ samples used in this study were grown by RF-plasma assisted molecular beam epitaxy (MBE) on GaAs (100) substrates at a substrate temperature of 300°C. A 100-200nm ZnSe buffer layer was used between the GaAs and ZnSe$_{1-x}$O$_x$. The oxygen composition was tuned by controlling the O$_2$ flow rate through the RF plasma. The ZnSe$_{1-x}$O$_x$ films are about 900nm thick. The composition was determined using Vegard’s law and the lattice parameters were determined from x-ray diffraction rocking curves of the 400 and 115 planes. The details of the growth and composition determination can be found elsewhere [43, 105]. The ZnSe$_{1-x}$O$_x$ samples in this study have x = 0.004, 0.013, 0.021 and 0.049. Table 4.1 is a data summary for the samples studied in this chapter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO Fraction from XRD</th>
<th>ZnO Fraction from BAC</th>
<th>Eg(0K) [eV]</th>
<th>$\beta$ [K]</th>
<th>$\gamma$ [meV/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe</td>
<td>0</td>
<td>-</td>
<td>2.80</td>
<td>556</td>
<td>1.20</td>
</tr>
<tr>
<td>ZSO110</td>
<td>0.004</td>
<td>0.0035</td>
<td>2.73</td>
<td>556</td>
<td>0.98</td>
</tr>
<tr>
<td>ZSO112</td>
<td>0.013</td>
<td>0.0122</td>
<td>2.63</td>
<td>556</td>
<td>0.87</td>
</tr>
<tr>
<td>ZSO113</td>
<td>0.021</td>
<td>0.0225</td>
<td>2.55</td>
<td>556</td>
<td>0.78</td>
</tr>
<tr>
<td>ZSO116</td>
<td>0.049</td>
<td>0.0590</td>
<td>2.36</td>
<td>556</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 4.1 Data summary for ZnSe and ZnSe$_{1-x}$O$_x$ samples described in this chapter. The sample growers determined the ZnO mole fraction from XRD and the ZnO mole fraction from BAC was determined by fitting the temperature dependence of the band gap with the band anticrossing model.
Photoluminescence spectroscopy (PL) and excitation power dependant PL measurements were carried out to measure the band-gap energy and understand the carrier dynamics of the ZnSeO samples. For all measurements, the temperature was controlled by a closed cycle compressed helium cryostat with a resistance heater and varied between 15K and 280K. For the PL measurements, a chopped HeCd (325nm) or Argon ion (457nm) laser beam was used for excitation and the luminescence signals from the samples were dispersed by a 1-m double-grating monochromator and detected by a photomultiplier tube, using a phase sensitive lock-in amplification system. The HeCd laser was used for samples with oxygen mole fraction up to 0.021 so laser energy was above the band gap of the films. The Argon ion laser was used for the sample with $x = 0.049$ because this laser has a higher maximum intensity that is necessary to measure PL above 180K for the weakly emitting sample. Neutral density filters were used to tune the laser power over three orders of magnitude for the excitation power dependant PL measurements.

For the PR measurements, quasi-monochromatic light from a xenon lamp dispersed by a 0.5M monochromator was focused on the samples as the probe beam. A chopped HeCd laser beam (325nm or 441nm) was used for photo-modulation. The PR signal was detected by a Si photodiode using a phase-sensitive lock-in amplification system.

### 4.2 Results and Discussion

#### 4.2.1 Photo-modulated Reflectance Spectroscopy

Photo-modulated reflectance spectroscopy provides a direct measure of interband transitions in semiconductors and is used to determine the band gap of the ZnSe$_{1-x}$O$_x$ films at room temperature. The PR spectra are shown in figure 4.1 for the ZnSe$_{1-x}$O$_x$ films. All spectra show derivative like spectral features, typical of optical transitions from the valence band to the conduction band. There is a clear redshift in the transition energy with increased ZnO alloying. The band gap is determined by fitting the PR spectral curve to the line shape functional form of three-dimensional interband transitions [106, 107].
Figure 4.1 Photo-modulated reflectance spectra for all the ZnSeO samples in this study. Spectra are normalized and offset for clarity and labeled with the composition determined by XRD.

The composition dependence of the determined band gaps is shown in figure 4.2, along with values from literature.[43, 45] The band gap values determined in this study correspond well to previous reports. As discussed in chapter 2, the band gap change with composition can be quantitatively explained by the band anti-crossing model (BAC) for highly mismatched alloys. The interaction leads to the characteristic splitting of the conduction band into two non-parabolic sub-bands whose dispersion relations are given by:

$$E_{\pm}(k) = \frac{1}{2} \left[ E_O + E_M(k) \pm \left( \left[ E_O - E_M(k) \right]^2 + 4C_{OM}^2x \right)^{1/2} \right]$$  \hspace{1cm} (4.1)$$

where $E_O$ is the oxygen defect level, $E_M(k)$ is the conduction band dispersion relation of the matrix, both relative to the valence band. $C_{OM}$ is the coupling parameter between the oxygen defect level and the extended states of the conduction band. The transition from the valence band to the lower sub-band, $E_-$, is the new band gap of the system.

The best fit for the band gap dependence of ZnSe$_{1-x}$O$_x$ on composition is shown in figure 2. The determined values of $E_O$ and $C_{OM}$ are 2.90 eV and 1.95 eV respectively, which correspond well to the values found in the literature of 2.90 ± 0.02 eV and 1.8 ± 0.3 eV [45].
4.2.2 Photoluminescence Spectroscopy

Excitation power dependant PL measurements at 15K show a redshift and broadening of the PL peak with decreasing laser power for the alloyed samples. A representative set of the excitation power density dependant PL spectroscopy is shown in figure 4.3 for ZnSe\textsubscript{0.987}O\textsubscript{0.013}. At the highest excitation power density, 500 W/cm\textsuperscript{2}, there is a single peak that is asymmetrically broadened to the low energy side. As the excitation power density is increased, this peak red shifts and broadens. The total PL peak shift when the laser power was decreased by three orders of magnitude was, in order of increasing x, 6meV, 4meV, 6meV and 30meV. A ZnSe reference sample had no change in peak position over the same power decrease. The decrease in PL peak energy and broadening of the peak with excitation power density indicates an exponential tail to density of states from alloy fluctuations, which implies possible carrier localization [44]. Local regions of higher oxygen concentration lead to lower energy states. This phenomenon will be discussed in detail in chapter 5.
Figure 4.3 Excitation power density dependant photoluminescence spectroscopy for a single sample over five orders of magnitude. The dashed line is a guide for the eye showing the decrease in the emission peak energy with decreased excitation density.

Figure 4.4 shows a representative set of the temperature dependent PL spectra for ZnSe$_{0.987}$O$_{0.013}$ from 15K to 180K. At 15K there is one PL peak that is attributed to localized excitons (LE) from the power dependent PL measurements and previous results [104]. As the measurement temperature is increased, this peak redshifts and a high energy shoulder appears. The shoulder is attributed to free excitons (FE) thermally excited out of the localized states. Between 95K and 105K, the FE shoulder becomes the dominant peak. The LE peak decreases in emission energy and intensity and disappears at higher temperatures as all of the excitons gain enough thermal energy to be excited out of the localized states. The FE peak also redshifts with increasing temperature.
Figure 4.4 A representative set of temperature dependant PL spectra for ZnSe$_{0.987}$O$_{0.013}$ that are normalized and vertically offset for clarity. Each spectrum is labeled with the samples temperature. The localized exciton (LE) and free exciton (FE) peaks are indicated by arrows.

The analogous PL spectra for the ZnSe reference samples are shown in figure 4.5. The free exciton peak dominates the emission at all temperatures and monotonically decreases in emission peak energy with increasing temperature. Figure 4.6 shows the peak energy for the LE and FE optical transitions for ZnSe$_{0.987}$O$_{0.013}$ and the FE transition for ZnSe at all temperature measured. To determine the PL peak energies, the PL spectra were fit with a Gaussian function using a least-square optimization procedure. For ZnSe$_{0.987}$O$_{0.013}$ the energy of the LE peak decreases in energy with increasing temperature and at a higher rate than is expected from the temperature dependent shift of the band gap. This behavior can be understood in terms of exciton localization in a variable potential produced by a distribution of oxygen atoms. At the lowest temperatures, the photo-excited electrons are localized in the nearest potential wells, resulting in the smaller average optical transition energy of the LE peak relative to the extrapolated low temperatures band gap. With increasing temperature, the electrons are imparted with addition energy that allows hopping to lower energy states, resulting in a redshift of the LE peak. Also, the probability of an exciton recombining while free increases, so the FE peak increases in intensity. At even higher temperatures, the electrons are completely delocalized and free excitons dominate the emission that results in a blue shift of the emission peak.

The FE peak energies are fit with the Varshni equation, which is a common empirical fitting for the temperature dependence of semiconductor band gaps and is given by
\[ E_g(T) = E_g(0) - \frac{\gamma \times T^2}{T + \beta} \]

(4.2)

where \( E_g(0) \) is the band gap at 0K and \( \gamma \) and \( \beta \) are the Varshni fitting parameters. For the \( \text{ZnSe}_{0.987}\text{O}_{0.013} \) sample, \( E_g(0) = 2.63 \text{eV}, \gamma = 0.87 \text{meV/K} \) and \( \beta = 556 \text{K} \). The Varshni equation fits very well to the experimental data for the FE peak, supporting the FE assignment of this peak. The same \( \beta \) can be used to fit the temperature dependence of the ZnSe reference sample and the other three ZnSeO samples. We find that the \( \gamma \) parameter decreases with increasing \( x \) from 1.2 meV/K for ZnSe to 0.50 meV/K for \( \text{ZnSe}_{0.951}\text{O}_{0.049} \), indicating a decrease in the temperature dependence of the band gap. All of the fitting parameters are listed in table 4.1.

**Figure 4.5** Variable temperature PL spectra for the ZnSe reference sample showing the monotonic decrease in peak emission energy with increased temperature. Spectra are normalized and vertically offset for clarity.

This decrease in temperature dependence of the band gap has been observed in other HMA’s, most notably GaAsN [108]. The change in temperature dependence can be explained by the band anti-crossing (BAC) model. To derive the temperature dependence of the band gap from BAC, we assume that the defect state, the coupling parameter and valence band are constant with temperature; only the conduction band shifts in energy with temperature. The resulting temperature dependence is:

\[ E_g(T) = \frac{1}{2} \left[ E_O + E_M(T) - \left( [E_O - E_M(T)]^2 + 4C_{OM}^2 x \right)^{1/2} \right] \]

(4.3)
In order to fit the temperature dependence of the band gaps, we use equation 4.3, the $C_{OM}$ and $E_{O}$ derived from our composition dependence of the band gaps and $E_{M}(T)$ from the Varshni equation fitting of the ZnSe reference. The Varshni fitting of the FE peak emission energy of ZnSe yielded the parameters $E_{g}(0) = 2.796\text{eV}$, $\gamma = 1.2\text{meV/K}$, and $\beta = 556\text{K}$. Only $x$, the oxygen mole fraction, is used as a fitting parameter. Figure 4.7 shows the results of the BAC fitting for the ZnSeO samples and the Varshni fitting for ZnSe with only the FE peak energies shown for clarity. The derived $x$ values are displayed with each curve and are within the experimental error of XRD. Table 4.1 lists the composition determined from the BAC temperature dependence fitting and XRD. The BAC fits match very well to the experimental data, providing additional evidence to the applicability of BAC to the ZnSeO material system. In addition, any temperature dependence added to $E_{O}$ dramatically decreased the fit quality, indicating that $E_{O}$ is indeed constant with temperature.
Figure 4.7 ZnSe and ZnSe$_{1-x}$O$_x$ free exciton (FE) peak emission energy as a function of temperature. The solid lines represent fits of the data. The ZnSe data is fit by the Varshni equation. The ZnSe$_{1-x}$O$_x$ data are fit with the band gap temperature dependence derived by the band anticrossing model. The indicated compositions are from this fitting procedure.

The decrease in the band gap temperature dependence, caused by the addition of a small amount of oxygen to ZnSe, is evident with a direct comparison between the top two fittings in figure 4.7. With less than one atomic percent of oxygen, the energy shift of ZnSe$_{0.996}$O$_{0.004}$ is clearly smaller than the ZnSe reference sample. For ZnSe and the four ZnSeO alloys, the difference between $E_g(0)$ and $E_g(295K)$ of the fit is 122meV, 96meV, 83meV, 78meV and 57meV with increasing x.

The band anticrossing model provides conceptual insight into the cause of the decreased temperature dependence of the band gaps of highly mismatched alloys. Figure 4.8a and b illustrate the decrease in the band gap temperature dependence and show the calculated conduction band structure of ZnSe$_{0.996}$O$_{0.004}$ at 10K and 300K respectively. Equations 4.2 and 4.3 show that the strength of the anticrossing interaction depends on the composition, coupling parameter and energy separation between the defect level and the conduction band edge (CBE). Only the energy separation depends on temperature. At 10K, the conduction band edge of ZnSe is about 100 meV below the oxygen defect level, but at 300K the separation is about 220meV. So at low temperature, the repulsion of $E_o$ from the defect level, $E_o$, is greater than at high temperature. This phenomenon is clearly illustrated in figure 4.7 by comparing the difference in the separation of the new conduction band edge, $E_o$, with the original conduction band edge of ZnSe. The shift is much larger at 10K than at 300K, due to the proximity of $E_o$ to the original CBE.

In summary, ZnSe$_{1-x}$O$_x$ behaves as a highly mismatched alloy, whose properties can be explained by the band anti-crossing model. The temperature dependent PL data
show a high-energy peak that increases in relative intensity with temperature and is assigned to free excitons by empirical fitting of the Varshni equation. The BAC model quantitatively explains the composition and temperature dependence of the band gap. Alloying ZnSe with ZnO allows for band gap control through the visible range of the electromagnetic spectrum and decreases the thermal sensitivity of the band gap by over 50% for x = 0.049.

**Figure 4.8** The calculated band structure of ZnSe$_{0.996}$O$_{0.004}$ at a) 10K and b) 300K from the band anticrossing model, including the original conduction band dispersion of ZnSe and the defect energy level, E$_D$. 
5 Exciton Localization and Photoluminescence Efficiency in ZnSe$_{1-x}$O$_x$

Exciton localization is a phenomenon in alloyed semiconductor thin films and superlattices that has been observed in several alloy systems, including In$_{1-x}$Ga$_x$N [109-111], GaAs$_{1-x}$N$_x$ [46, 112, 113], In$_{1-x}$Ga$_x$As$_{1-y}$N$_y$ [46], and ZnSe$_{1-x}$Te$_x$ [114, 115]. In the most cited case, the high efficiency of In$_{1-x}$Ga$_x$N light emitting diodes, despite the relatively high defect density, has been attributed to localized radiative recombination. Variation in the local indium content results in disorder induced band tails of localized states that trap excitons, isolate them from non-radiative recombination centers, and maintain the holes and electrons in close proximity [111]. In this study, the low temperature luminescence efficiency of ZnSe increases by more than an order of magnitude when alloyed with ZnO. I attribute this increase in efficiency to exciton localization.

ZnSe$_{1-x}$O$_x$ is a promising material to study carrier localization because of the strong change in the band gap of ZnSe with the addition of a small amount of the isoelectronic oxygen onto the selenium anion sites [116]. We have found a 130meV decrease in the band gap with only one atomic percent of incorporated ZnO [45]. This large band gap shift, with increased ZnO mole fraction, implies relatively large band tails from random fluctuations in the oxygen content, so that strong localization should be observed even without phase separation.

As reported in chapter 4, the effects of carrier localization can be observed with conventional photoluminescence spectroscopy (PL) through varying the excitation power or the sample temperature. The former shows a redshift in the emission peak with decreasing excitation power. The latter shows a unique “S” shape signature of the temperature dependence of the emission peak. We have observed both characteristics of localized recombination in ZnSe$_{1-x}$O$_x$ [117].

Time-resolved photoluminescence provides a direct method to measure and study the localization kinetics. A redshift in the emission peak with time and an increasing PL lifetime with decreasing emission energy has been attributed to localized exciton recombination [118, 119]. Both signatures are a product of excitons relaxing to the lower band tail energy states, where the excitons are spatially localized and radiatively recombine.

5.1 Experimental Details

Temperature dependent photoluminescence spectroscopy (PL) measurements were carried out in the same fashion as described in chapter 4. The absolute PL intensity was measured by using the same excitation and collection conditions for all samples. The PL optics were realigned before each measurement to ensure maximum collection efficiency for all spectra. Time-resolved photoluminescence spectroscopy (TRPL) measurements were carried with a frequency doubled Ti-Sapphire laser for excitation with a 76MHz repetition rate and an average power for 40mW at a wavelength of 400nm. The luminescence signals were dispersed by a 0.5m spectrometer and detected by a streak camera with a time resolution of 10 ps. Details on the TRPL system can be found in appendix A.
5.2 Experimental Results

5.2.1 Photoluminescence Spectroscopy

Temperature dependent PL measurements were taken from 10K to 310K to explore the effect of oxygen on the luminescence efficiency. Figure 5.1 shows the absolute integrated intensity for all samples in this study. A HeCd laser at 325nm and 20mW was used for photo-excitation for all samples. All integrated intensities are normalized to the value of ZnSe at 10K. At 10K, the integrated intensity for the three lowest oxygen content ZnSeO films is higher than the ZnSe film. The absolute intensity of the PL for $x = 0.004, 0.013, 0.021$, and $0.049$ compared to ZnSe is $13.4, 4.2, 2.45$, and $0.568$ respectively. For ZnSe and the three ZnSe$_{1-x}$O$_x$ samples with the lowest oxygen content, the PL intensities reach a stable values for temperatures above 250K. The highest oxygen content sample is fully quenched at around 150K, indicating a high concentration of non-radiative recombination centers. The PL spectra follow the same trends described for figure 4.4 with the high-energy peak becoming dominant as the sample temperature is increased.

![Graph showing normalized integrated photoluminescence intensity](image)

**Figure 5.1.** Normalized integrated photoluminescence intensity for all samples in this study.

Figure 5.2 shows the temperature dependent PL peak energies for all samples in this study. The ZnSe$_{0.951}$O$_{0.049}$ sample is excited with an argon-ion laser at 488nm and 500mW to probe the temperature dependence of the PL peak energies up to room temperature. The higher pumping power of the argon-ion laser was needed to detect the PL signal above 150K. As seen in figure 4.6, the ZnSe$_{1-x}$O$_x$ samples all exhibit both free exciton (FE) and localized exciton (LE) recombination. The ZnSe$_{0.996}$O$_{0.004}$ sample’s PL spectra exhibit two peaks at low temperature that are attributed to LE and FE recombination. At the lowest temperatures, the LE and FE peaks are both present. As
the temperature is increased, the LE peak decreases in emission energy and the FE peak remains constant in emission energy but decreases in intensity. Eventually, at 45K, only the LE peak remains. As the temperature is further increased, the FE peak reappears at 70K and begins to dominate the emission at higher temperatures. The LE and FE peak are both present at low temperature because of the low oxygen concentration, which means that density of localized band tail states is low compared to the other ZnSe$_{1-x}$O$_x$ samples in this study. At low temperature, the PL efficiency is high and carriers have a longer lifetime so the localized band tail states are all filled and some excitons overcome the mobility edge into extended states. This assignment is supported by power dependent PL measurements, where the high energy FE peak decreased in intensity with decreased laser power at a much higher rate than the LE peak. In order to confirm the localized and free exciton peak assignment and understand how the exciton kinetics affects the PL efficiency, we performed variable-temperature TRPL.

![Figure 5.2 Peak energies for all PL spectra for all ZnSe$_{1-x}$O$_x$ samples in this study. All PL spectra for each sample are measured on the same spot of each sample.](image)

**5.2.3 Time-resolved Photoluminescence Spectroscopy**

Time resolved photoluminescence spectroscopy provides a direct measure of the photogenerated carrier kinetics in semiconductor samples. Figure 5.3 shows the TRPL data from the streak camera at 15K for ZnSe$_{0.987}$O$_{0.013}$. The data is shown with false color and a linear scale. The laser pulse is at about 100ps where the PL intensity begins. There is a single asymmetric peak, as found in the PL spectroscopy shown in figure 4.4. The peak emission energy and lifetime appear to be essentially constant with time.
Figure 5.3 The raw TRPL data for ZnSe$_{0.987}$O$_{0.013}$ at 10K. The false color has a linear scale.

Figure 5.4 shows the TRPL data for the same sample at 65K. There is a clear difference in the TRPL character with temperature. This data shows a shorter carrier lifetime and decrease in PL peak emission energy with increased time. The two dimensional TRPL data can be quantitatively analyzed by taking horizontal integrations for time dependent spectra at a narrow range of emission energies and vertical integrations for energy dependent spectra at a narrow range of times.
Figure 5.4 The raw TRPL data for ZnSe$_{0.987}$O$_{0.013}$ at 65K. The false color scale is a linear scale.

The TRPL measurements for the ZnSeO films show three temperature regimes with different photoexcited exciton dynamics. Figure 5.5 shows the total change in emission peak energy ($E_p$) as a function of temperature for ZnSe$_{0.987}$O$_{0.013}$. The total change in $E_p$ is taken to be $E_p$ at laser excitation minus the peak at the latest time at which a reliable measurement can be made with each curve integrated over 5ps. We define the regime 1 as the low temperature range where the peak shift remains small, below 10meV, and almost constant. This regime ranges from 14K to 35K in ZnSe$_{0.987}$O$_{0.013}$. Regime 2 shows a monotonic increase in peak shift with temperature (from 40K to 115K) from about 10meV to 50meV for x=0.013. Regime 3 begins where the peak shift shows a dramatic drop and then decreases to about 5meV. This regime starts at about 105K for this sample.
Figure 5.5 The total peak shift with time as a function of temperature for ZnSe$_{0.987}$O$_{0.013}$. The peak shift with time is taken to be the peak emission energy at the laser excitation minus the latest possible measure of the peak emission.

Figure 5.6 shows $E_p$ as a function of time for ZnSe$_{0.987}$O$_{0.013}$ at three characteristic temperatures, one in each regime: 15K, 65K and 250K. This data is taken at 5ps increments for the entire range of data that is above the noise. The peak energy is taken to be the maximum value from each curve. In addition, I have marked the bulk band gap energy with a horizontal line at each characteristic temperature determined in chapter 4. The band gap indicating lines are in decreasing temperature from top to bottom. In regime 1, the bulk band gap value is higher than the TRPL peak value at all times, indicating that the electrons are localized below the average conduction band edge. There is a small change in peak emission energy, but the change is very gradual over 800ps, which indicates that the electrons are immediately trapped by potential fluctuations and remain mostly fixed as they recombine.
The time dependence of the peak emission energy for ZnSe$_{0.987}$O$_{0.013}$ at three characteristic temperatures. The horizontal dashed lines indicate the average band gap for each temperature.

The $E_p(t)$ data in regime 2 shows dramatically different features. For the first 20ps, the $E_p$ values are at or above the average band gap. Then the peak sharply redshifts until about 50ps after the laser pulse, where it then gradually redshifts for the remainder of the carrier lifetime. This behavior is attributed to photogenerated electrons with sufficient energy to redistribute through hopping to the lowest energy states. At early times, the highest energy excitons quickly find the many small perturbation in the band edges. After 500ps, most of these states are filled and the carriers slowly redistributed to the few still lower energy states; the probability of having a lower energy state decreases the further it is from the average band gap value. There is the same trend for all curves in regime 2, although the degree and speed of localization increase with temperature.

The $E_p(t)$ values in regime 3 are just above the band gap values at all times, as expected for free carrier recombination. The carrier lifetime is very short at this temperature; peak values can only be determined for the first 100ps, which is still enough time for localization in regime 1 or 2. In this temperature regime, the carriers have too much thermal energy to be trapped by the band tail states.

The other important manifestation of localized carriers is the emission energy dependence of the PL lifetime. Figure 5.7 shows the decay curves of the TRPL at 15K from ZnSe$_{0.987}$O$_{0.013}$ for several emission energies, spanning the width of the PL peak. The decay curves are from an emission energy range of less than 5meV and are normalized and vertically offset for clarity. The highest energy curve, 2.66eV, has double exponential character with two clear linear regions on the semi-log plot. This curve can be fit using a double exponential equation given by:

$$I(t) = I_o \left[ I_1 \exp \left( -\frac{t}{\tau_1} \right) + I_2 \exp \left( -\frac{t}{\tau_2} \right) \right]$$

(5.1)
where $I_1$ and $I_2$ are constants that define the relative contribution of each recombination mechanism and $\tau_1$ and $\tau_2$ define the characteristic recombination lifetime of each mechanism. The two characteristic lifetimes for the 2.66eV decay curve are 21 and 245ps respectively with the double exponential fitting shown in figure 5.8.

![Figure 5.7](image)

**Figure 5.7** Emission energy dependent decay curves for ZnSe$_{0.987}$O$_{0.013}$ at 15K. Curves are normalized and vertically offset for clarity.

The short lifetime regime is dominated by the relaxation of photogenerated electrons to states with lower energy caused by local regions with higher oxygen content. The long lifetime regime is dominated by the radiative recombination rate of the electrons localized 2.66eV above the valence band edge. The 2.64eV decay curve also has a slight double exponential character with the long lifetime regime dominating the decay. The decay curves of 2.63eV and below all show single exponential character with similar lifetimes. The single exponential lifetime comes from the radiative recombination of localized excitons. These lower energy decay curves show exciton lifetimes on the same order as the long lifetime state at 2.66eV. The lower emission energy decay curves also have a later maximum because of the time it takes for electrons to relax to the lower energy states. The time of maximum intensity shifts from 5 to 10ps relative to the highest emission energy, increasing with decreasing emission energy. This is consistent with the picture of regime 1 behavior, where carriers are quickly localized, but do not have enough thermal energy to find the lowest possible energy levels.
Figure 5.8 Double exponential fitting of the decay curve of sample ZnSe_{0.987}O_{0.013} at 15K at the emission energy 2.66eV.

Figure 5.9 plots the normalized PL intensity and effective carrier lifetime against the emission energy. The effective PL lifetime is defined as the time it takes for the intensity to equal 1/e of the maximum intensity and is used for convenient comparison between the single and double exponential decay curves. For the single exponential decay curves at this temperature, the effective carrier lifetime is the radiative lifetime. For the double exponential decay curves, the effective PL lifetime is dominated by exciton relaxation to lower energy states and is very similar to the short lifetime derived from the double exponential fitting. The effective lifetime increases by more than an order of magnitude as excitons are localized in low energy states from alloy fluctuations. The normalized PL intensity curve shows an asymmetric shape with an exponential tail, characteristic of recombination from disorder induced band tail states.
Figure 5.9 Effective lifetime and intensity from TRPL for ZnSe$_{0.987}$O$_{0.013}$ at 15K. The blue squares are the effective lifetime at a given emission energy and the black line is the PL intensity just after the laser pulse.

Figure 5.10 shows the PL intensity decay curves for ZnSe$_{0.987}$O$_{0.013}$ at 65K for several emission energies. The 2.66eV, 2.64eV and 2.63eV decay curves in figure 5.10 all have double exponential behavior. The shorter lifetime mechanism shows an increasing effective lifetime with decreasing emission energy and the long lifetime state stays essentially constant. Again, the short lifetime state is limited by carriers relaxing to lower energy states. This lifetime gets longer with decreasing energy because it is simultaneously fed with additional carriers from higher energy states. The remaining decay curves, 2.61eV-2.55eV, all show single exponential decay. In addition, the peak time shifts by between 2 and 24ps, increasing with decreasing emission energy. The maximum shift is more than double the 10ps for this sample at 15K, which is expected from the additional time it would take for carriers to hop to the lower available states.
Figure 5.10 Emission energy dependent decay curves for ZnSe$_{0.987}$O$_{0.013}$ at 65K. Curves are normalized and vertically offset for clarity.

Figure 5.11 shows the effective lifetime and PL intensity as a function of emission energy for ZnSe$_{0.987}$O$_{0.013}$ at 65K. The peak at $t = 0$ in figure 5.11 has the same shape as that of figure 5.9; the asymmetry and exponential tail of the figure are further indication of exciton localization. The decrease in emission energy it takes for the lifetime to saturate is about 50meV, exhibiting a more gradual increase than at 15K, which occurs in about 20meV. This lower energy of lifetime saturation reflects the additional band tail states available for redistribution from the additional thermal energy. The maximum lifetime has also decreased from about 600ps to 150ps.
Figure 5.11 Effective lifetime and intensity from TRPL for ZnSe$_{0.987}$O$_{0.013}$ at 65K. The blue squares are the effective lifetime at a given emission energy and the black line is the PL intensity just after the laser pulse.

The corresponding data for the same sample at 250K, in regime 3, are in figures 5.12 and 5.13. The decay curves in Figure 5.12 are all single exponential and the peaks all occur at the same time, indicating free exciton recombination. Figure 5.13 shows the lifetime and PL intensity against emission energy. The change in lifetime with emission energy is within the error of the measurement. The PL peak is symmetric and does not have the exponential tail from the localization of excitons. The lifetime dependence on emission energy, the symmetry of the PL spectra and the single exponential decay curves are indicative of free exciton recombination.
Figure 5.12 Emission energy dependent decay curves for ZnSe$_{0.987}$O$_{0.013}$ at 250K. Curves are normalized and vertically offset for clarity.

Figure 5.13 Effective lifetime and intensity from TRPL for ZnSe$_{0.987}$O$_{0.013}$ at 250K. The blue squares are the effective lifetime at a given emission energy and the black line is the PL intensity just after the laser pulse.

Figure 5.14 shows the magnitude of the peak shift with time for all ZnO containing samples in the study. Samples with $x = 0.013$, 0.021 and 0.049 all show the same trend with the three distinct regimes discussed above. The ZnSe reference sample shows no peak shift with time at all temperatures. The ZnSe$_{0.996}$O$_{0.004}$ sample shows a
different trend, as in the case with the PL peak shift with temperature in figure 5.2. In the low temperature regime, there is a large peak shift because the localized states are full, so the emission peak at early times is dominated by free exciton recombination. The free excitons recombine more efficiently than the localized excitons and are captured when lower energy states become available from localized exciton recombination, so the peak emission shifts to the localized states at longer time. As the temperature increases, the free exciton peak no longer dominates the emission at early times because more non-radiative recombination centers are active and the localized states are no longer saturated. This shift occurs at 50K where there is a decrease in the peak shift. This sample is then similar to the behavior of the others, where the peak shift with time trends to higher values with increasing temperature as excitons have additional thermal energy to redistribute to lower energy states. At 160K, the majority of the excitons are free and the peak shift is small and almost constant with temperature.
Figure 5.14 The total peak shift with time for all for ZnSeO samples in this study. Note the change in scale for the sample with highest ZnO mole fraction.

Figure 5.15 shows the temperature dependence of the effective PL lifetime for all samples. For each temperature, the full TRPL spectrum is integrated over the full energy range to get a single time dependent intensity curve. The effective lifetime is the time it takes for the intensity to decrease to 1/e of the maximum value.
5.3 Discussion

The temperature dependence of the photoluminescence integrated intensity for the series of ZnSe\textsubscript{1-x}O\textsubscript{x} compared to that of ZnSe shows a number of interesting features. At room temperature, where the intensity of the PL is an indication of material quality, the PL of the ZnSe reference sample is about an order of magnitude stronger than ZnSe\textsubscript{0.996}O\textsubscript{0.004}, which is the strongest emitting ZnSe\textsubscript{1-x}O\textsubscript{x} sample. The relative intensities at 300K are listed in table 1. As the ZnO content increases, the integrated intensity decreases, indicating decreasing material quality and quantum efficiency. This decrease in quality is expected as the films are grown on a relaxed ZnSe buffer layer so the lattice mismatch is monotonically increasing with ZnO alloying. The highest oxygen content sample, with x = 0.049, does not have any detectable PL at 300K when excited by the HeCd laser. All samples show an increase in PL integrated intensity as the temperature is decreased, but the ZnO containing samples show a much larger effect. The ZnSe sample shows a factor of 83 increase in its integrated PL intensity when cooled to 10K. The ZnSe\textsubscript{1-x}O\textsubscript{x} samples show an effect that is amplified by about two orders of magnitude. With increasing oxygen, the increase in intensity from 300K to 10K is 7000, 11250, 11500 and > 6000 respectively. The full enhancement of the highest oxygen content sample is not known because the signal is too weak to record at room temperature. The factor of 6000 is calculated from the increase between 140K and 10K. I attribute this increase in the low temperature PL intensity enhancement to the localization of excitons at low temperature, which can isolate excitons from non-radiative recombination centers.

![Graph showing temperature dependence of effective lifetime for ZnSe and ZnSe\textsubscript{1-x}O\textsubscript{x} samples.](image)

Figure 5.15 Temperature dependence of the effective lifetime for all samples in this study.
Table 5.1: Data summary for the films studied in this work.

<table>
<thead>
<tr>
<th>x [% ZnO]</th>
<th>(E_g(300\text{K})) [eV]</th>
<th>(\eta(300\text{K}))</th>
<th>(\eta(10\text{K}))</th>
<th>(\eta(10\text{K})/\eta(300\text{K}))</th>
<th>A [meV]</th>
<th>E_A [meV]</th>
<th>B [meV]</th>
<th>E_B [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.68</td>
<td>1.2x10^{-2}</td>
<td>1</td>
<td>83</td>
<td>400</td>
<td>50±4</td>
<td>40</td>
<td>1.5±1</td>
</tr>
<tr>
<td>0.004</td>
<td>2.62</td>
<td>2.0x10^{-3}</td>
<td>14</td>
<td>7,000</td>
<td>30,000</td>
<td>45±2</td>
<td>2</td>
<td>3±0.5</td>
</tr>
<tr>
<td>0.013</td>
<td>2.54</td>
<td>4.0x10^{-4}</td>
<td>4.5</td>
<td>11,250</td>
<td>30,000</td>
<td>45±2</td>
<td>2</td>
<td>3±0.5</td>
</tr>
<tr>
<td>0.021</td>
<td>2.45</td>
<td>2.0x10^{-4}</td>
<td>2.3</td>
<td>11,500</td>
<td>30,000</td>
<td>48±2</td>
<td>2</td>
<td>3±0.5</td>
</tr>
<tr>
<td>0.049</td>
<td>2.31</td>
<td>--</td>
<td>0.58</td>
<td>&gt;6,000</td>
<td>30,000</td>
<td>44±2</td>
<td>7</td>
<td>6±1.0</td>
</tr>
</tbody>
</table>

The temperature dependence of the integrated PL intensity can be understood in terms of activated non-radiative recombination centers. A single activation energy cannot explain the temperature dependence for these samples so a fit with two activation energies must be used. This fit is given by the equation

\[
I_{\text{int}}(T) = \left[1 + Ae^{\frac{E_A}{k_BT}} + Be^{\frac{E_B}{k_BT}}\right]^{-1}
\]

where \(I_{\text{int}}\) is the integrated PL intensity, A and B are constants that are related to the efficiency of each non-radiative recombination mechanism, and \(E_A\) and \(E_B\) are the respective activation energies [120-124]. The fits for ZnSe and ZnSe_{0.996}O_{0.004} are shown in figure 5.16 and the fitting parameters for all samples are given in table 1. The two activation energies are almost identical for all samples in this study, indicating a similar mechanism for PL quenching. The constants that represent the efficiency for each mechanism are very different for the ZnSe reference sample and the ZnSe_{1-x}O_{x} samples. The constant A, which is the efficiency of the high temperature non-radiative recombination mechanism, is 400 for ZnSe and 30,000 for the alloy samples. This implies that there is about a two order of magnitude greater PL quenching effect from non-radiative recombination centers due to the alloying with ZnO. The constant B, which is the efficiency of the low temperature non-radiative recombination mechanism, however, shows the opposite trend where B is 40 for ZnSe and 2 for \(x < 0.049\) and 7 for \(x = 0.049\). This shows that low temperature non-radiative recombination mechanism is much weaker in the ZnSe_{1-x}O_{x} samples, which is the temperature region where the excitons are localized.
Figure 5.16 Two representative samples for best fit of the PL quenching with a two-activation energy model.

The temperature dependence of the PL lifetime, shown in figure 5.15, provides further evidence of the enhancement from localization. At room temperature, ZnSe has a longer lifetime than all of the ZnSe\textsubscript{1-x}O\textsubscript{x} samples. At room temperature, it is expected that the lifetime will be limited by non-radiative recombination for all samples. This is an additional indication that the ZnSe is of higher crystalline quality than the ZnSe\textsubscript{1-x}O\textsubscript{x} samples. As the temperature is decreased, the ZnSe lifetime initially decreases, then increases, where as the ZnSe\textsubscript{1-x}O\textsubscript{x} samples show a monotonic increase to their lifetime with decreased temperature. The onset of the increase in lifetime for the ZnSe\textsubscript{1-x}O\textsubscript{x} samples is also shifted to higher temperature than the ZnSe film.

Figure 5.17 A schematic of the band edge of ZnSe\textsubscript{1-x}O\textsubscript{x}. The band edge fluctuations are a consequence of the random distribution of oxygen on the anion site.

At 10K, the ZnSe\textsubscript{1-x}O\textsubscript{x} samples all have at least a factor of five longer lifetimes than the ZnSe reference sample. The ZnSe\textsubscript{1-x}O\textsubscript{x} samples also show an increasing lifetime with additional oxygen content, which is the opposite trend of the integrated intensity. The large increase in lifetime relative to ZnSe and the lifetime and integrated intensity trends can be explained by exciton localization.
Figure 5.17 shows a schematic of the band edges for a ZnSe_{1-x}O_x alloy. Local regions of high oxygen content have a smaller band gap and lower conduction band edge, as explained by the band anti-crossing model. Areas with lower oxygen content have a larger band gap and higher conduction band edge. The effect of oxygen on the valence band edge is expected to be small as has been seen in GaAs_{1-x}N_x [125]. At low temperatures, electrons are trapped by the potential fluctuations in the conduction band edge and holes are coulombically bound to the electrons to form a localized exciton. These trapped excitons can not move through the crystal, as they can at high temperatures in ZnSe_{1-x}O_x or at all temperature in ZnSe, assuming they are not bound to a defect. If the excitons are trapped in a region with a low concentration of non-radiative defects, then the exciton will live until it radiatively recombines. Similar effects have been observed in In_{1-x}Ga_xN alloys, where localization of excitons is suggested to be the cause for high quantum efficiency despite a high concentration of defects [111].

At 10K in ZnSe_{1-x}O_x, where the excitons are localized and do not have enough thermal energy to hop to lower energy states, the PL lifetime at lower emission energies is dominated by radiative recombination. Figure 5.9 shows the emission energy dependence to the PL lifetime, with the low energy, high lifetime plateau being the radiative lifetime of localized excitons. At higher temperature, as in figure 5.11, excitons are only trapped at lower emission energies. The higher temperature results in more thermal energy, which allows excitons trapped in shallow wells or in close proximity to areas with higher oxygen content to relax to the lower energy states. As temperature is increased in the ZnSe_{1-x}O_x samples, the PL signal is less dominated by the recombination of localized excitons. The temperature dependence of the PL lifetime in figure 5.15 shows that the lifetime increase in the alloyed samples occurs between 100K and 150K. This is also the temperature range for the onset of localization as shown by the peak shift with time data in figure 5.14. The integrated PL intensity for the ZnSe_{1-x}O_x samples also shows a sharp increase between 100K and 150K. In aggregate, this data show that the increase in PL lifetime and integrated intensity are a consequence of exciton localization where excitons are trapped away from non-radiative recombination centers and recombine radiatively.

Localized exciton recombination can also explain how additional oxygen in ZnSe_{1-x}O_x samples can result in lower integrated PL intensity but longer lifetimes at low temperature. All of the ZnSe_{1-x}O_x films show localized exciton recombination at low temperatures and free exciton recombination at high temperatures. The high temperature PL efficiency is an indication of material quality and shows that density of non-radiative recombination centers increases with oxygen content. As temperature is decreased, excitons are localized and can be trapped away from these PL quenching defects, but the excitons can also be trapped close to a defect, which lowers the probability of radiative recombination of that exciton. The higher oxygen content samples have lower integrated PL intensity at low temperature because more of the localized excitons are lost to non-radiative recombination as the chance of being localized close to a defect increases with the decrease in material quality. The PL is still greatly enhanced as the temperature decreases because there are still many excitons localized away from defects. So the integrated PL intensity indicates the quantum efficiency of all excitons where as the lifetime is dominated by the lifetime of localized excitons recombining radiatively.

In conclusion, the addition of oxygen to ZnSe leads to exciton localization below 150K, which results in the anomalous “S” shift in the PL peak energy from temperature
dependent PL, the PL peak shift with time and the emission energy dependence of the lifetime from TRPL. The localized exciton recombination results in an enhancement of the integrated PL intensity at low temperature despite the decrease in materials quality with alloying.
6 GaN$_{1-x}$As$_x$ Alloys Through the Full Composition Range

Previous works have synthesized GaN$_{1-x}$As$_x$ alloys with $x < 0.06$ or $x > 0.94$, showing the alloy system to have a band gap range from 3.4eV to 1.0eV [50, 65]. The properties of these alloys have been well described by the band anticrossing model (BAC), which predicts a minimum band gap of 0.8eV [65]. This alloy system could provide continuous tuning of the band gap through almost the full solar spectrum, making it a potential candidate for photovoltaic applications.

GaNAs films have been successfully synthesized across the full composition range in collaboration with Dr. S. Novikov of the Foxon Group at the University of Nottingham through low-temperature molecular beam epitaxy. The structural and optical properties have been characterized to determine the crystal structure and band gap dependence on composition.

6.1 Experimental Details

The GaN$_{1-x}$As$_x$ samples were grown on 2 inch Pyrex or c-plane sapphire substrates by plasma-assisted MBE in a MOD-GENII system equipped with an HD-25 Oxford Applied Research RF-activated plasma source to provide active nitrogen. Elemental gallium from a Knudsen cell was used as the group III source; a Veeco arsenic valved cracker produces arsenic in the form of As$_2$. The film composition is controlled by changing the substrate temperature between 100-700°C. Details of the growth can be found elsewhere [126, 127].

Dr. Kin Man Yu determined the composition and thickness of the films with Rutherford backscattering spectrometry (RBS) and particle induced x-ray emission (PIXE) using a 3 MeV He ion beam. The crystallinity and microstructural properties of the films were measured by transmission electron microscopy, selected area electron diffraction and x-ray diffraction. The electron microscopy and selected area electron diffraction measurements were performed and analyzed by Dr. Zuzanna Liliental-Weber.

The band gap of the films was determined by absorption spectroscopy (AS) and photo-modulated reflectance spectroscopy (PR). Transmission spectroscopy was measured in the dual-beam configuration with a Perkins Elmer Lambda 950 NIR-UV-Vis spectrophotometer and converted to absorption as described in chapter 3. For the PR measurements, quasi-monochromatic light from a xenon lamp dispersed by a 0.5m monochrometer was focused on the samples as a probe beam. A chopped HeCd laser (325nm or 441nm) was used for photo-modulation. The PR signal was detected by a silicon or germanium photodiode using a phase-sensitive lock-in amplification system.

6.2 Determination of alloy composition and crystallinity

The incorporation of non-equilibrium concentrations of arsenic on the anion site of GaN has been accomplished by low temperature growth. Typical high quality MBE-grown GaN is synthesized at a substrate temperature of at least 700°C [127]. We have found homogeneous films for the full composition range, but with a transition from single crystal to polycrystalline to amorphous microstructure with the decrease in substrate temperature and increase in arsenic composition.
Figure 6.1 A representative set of RBS data. The arrows indicated the energy of backscattered He⁺ from Ga and As atoms at the film surface. (Data courtesy of Dr. K. M. Yu)

Figure 6.1 shows a representative RBS spectrum for a GaN₁₋ₓAsₓ film. The expected energy loss for scattering from surface Ga and As are marked on the spectrum. Nitrogen cannot be measured directly with RBS, but can be determined by the absence of arsenic. The high-energy shoulder is due to He⁺ scattering off of arsenic; the increased intensity of this shoulder indicated increased arsenic content in the films. In addition, PIXE has been used to confirm the composition determined from RBS. A representative set of PIXE data are shown in figure 6.2.

Figure 6.2 A representative set of PIXE data. (Data courtesy of Dr. K. M. Yu)

Figure 6.3 indicates the temperature dependence of the arsenic concentration in the GaNAs films. The only variable that has been changed is the substrate temperature;
the beam equivalent pressure (BEP) of Ga, As\textsubscript{2} and N are constant. For this set of films, the Ga BEP was fixed at 1.5\times10^{-7} Torr, the As\textsubscript{2} BEP was 7.5\times10^{-6} Torr and the nitrogen BEP was 1.5\times10^{-5} Torr. The arsenic concentration increases with decreasing substrate temperature.

![Graph showing substrate temperature dependence of As content and film microstructure of GaN\textsubscript{1-x}As\textsubscript{x} alloys with fixed beam equivalent pressures for Ga, As\textsubscript{2} and N.]

**Figure 6.3** The substrate temperature dependence of As content and film microstructure of GaN\textsubscript{1-x}As\textsubscript{x} alloys with fixed beam equivalent pressures for Ga, As\textsubscript{2} and N.

The microstucture of the films has a clear temperature dependence. Figure 6.4 shows a representative set of 2θ-ω XRD data for the same set of films. The high temperature film with no arsenic shows the 0002 diffraction peak of GaN. As the temperature is decreased and the arsenic beam is turned on, the peak shifts to lower angle, indicating an increasing lattice parameter from the incorporation of arsenic into the anion site of the lattice. Below 450°C and above x = 0.10, there is no more XRD diffraction peak. The composition determined from Vegard’s law for the shifted 0002 diffraction peak corresponds well to the composition determined by RBS and PIXE.
The microstructure of the films was further studied, through transmission electron microscopy and selected area diffraction, by Dr. Liliental-Weber. Figure 6.5 shows a bright field electron micrograph for a film with $x = 0.45$. This image shows that the film is homogeneous with no voids or phase separation. The selected area electron diffraction pattern is also shown, which exhibits the diffuse ring pattern typical of amorphous materials indicating the absence of any nano-scale crystalline phases. By comparing the thickness determined by TEM and RBS, the amorphous films are between 0.75 and 0.80 as dense, as would be predicted taking the linear interpolation for the density of GaAs and GaN. These results are typical for the amorphous GaNAs films used in this study.

Figure 6.4 A representative set of XRD data showing the substrate temperature dependence of the microstructure and diffraction peak shift.

Figure 6.5 Low and high magnification TEM images and SAD pattern of GaN$_{0.55}$As$_{0.45}$ showing a homogeneous amorphous film. (Data courtesy of Dr. Z. Liliental-Weber)
6.3 Optical Properties

The optical properties of the GaNAs alloys have been studied by optical absorption spectroscopy and photo-modulated reflectance spectroscopy. The band restructuring that is a consequence of replacing nitrogen with arsenic complicates the interpretation of the absorption spectra. A quantitative model of the absorption has been utilized to determine the BAC fitting parameters for nitrogen-rich GaNAs films and to understand how to determine the band gap from absorption spectroscopy. The model is based on the band anti-crossing model and has been adapted for GaN\textsubscript{1-x}As\textsubscript{x} from the work of M. Mayer, who developed a model for the analysis of the absorption spectroscopy of ZnO\textsubscript{1-x}Se\textsubscript{x} [128]. Photo-modulated reflectance spectroscopy (PR) provides a direct measure of the band gap of films in the middle composition ranges (x > 0.15) from fitting by Aspnes' third-derivative fitting approach [106, 107].

6.3.1 Photo-modulated Reflectance Spectroscopy

Figure 6.6 shows a representative set of the PR data for GaNAs alloy thin films. The third-derivative-like signature is typical for the inter-band transition between the valence and conduction bands and can be used to determine the band gap with the Aspnes' third-derivative fitting [106, 107]. This method provides a direct measure of the band gap. The PR data show a clear red shift in the band gap with an increase in arsenic content. These films are amorphous, as determined by XRD, TEM and SAD, but show the clear PR signature. The presence of the strong PR signature is an indication of material quality and a high degree of short-range order.

Figure 6.6 Photo-modulated reflectance spectroscopy for a representative set of GaN\textsubscript{1-x}As\textsubscript{x} films. The spectra are normalized and vertically offset for clarity. The arrows indicated the band gaps of the thin films determined by the Aspnes' third-derivative fitting.

6.3.2 Absorption Spectroscopy and Modeling

Figure 6.6 shows a representative set of the absorption spectroscopy data for GaNAs alloys. The absorption spectra show a clear large red shift in the absorption edge with increased arsenic content, consistent with the PR data. The absorption
becomes sharper with increasing arsenic content, despite the transition from crystalline to amorphous phase that occurs around $x = 0.14$. The low energy undulations in the data are Fabry-Perot oscillations from interference effects, indicating smooth surfaces and high quality interfaces.

Figure 6.6 A representative set of absorption spectroscopy data for GaN$_{1-x}$As$_x$. The film with $x = 0.05$ is crystalline and the remaining films are amorphous.

The valence band restructuring, which is a consequence of the interaction of the localized arsenic level with the extended states of the valence band, invalidates the standard approach for band gap determination. As discussed in chapter 3, the typical approach to determine the band gap for a direct band gap semiconductor is to take a linear fit of $\alpha^2$ and extrapolate it to the energy axis. The intersection of the linear extrapolation with the energy axis is the band gap of the material. This approach assumes that the conduction and valence bands are parabolic in the energy region probed during absorption, which is a good assumption for most direct band gap semiconductors, including GaAs and GaN.

The band anticrossing model has been shown to quantify the effect of alloying highly mismatched alloys, like GaN:As [65, 66]. The theory predicts that two nonparabolic bands form from the alloying of GaN with GaAs. The nonparabolic bands make the standard approach for band gap determination invalid. Figure 6.7 shows the band structure for GaN$_{0.90}$As$_{0.10}$ from a simplified version of VBAC, including a band formed by the interaction of the spin orbit energy of the As level with the valence bands. The simplified version of VBAC will be discussed below. All of the resulting valence bands ($E_v$, $E_{v\text{SO}}$, and $E_v$) in figure 6.7 are nonparabolic.
A model of the absorption spectroscopy was used to determine the coupling parameter and defect energy level for VBAC of GaN:As. The model quantified the optical density of states for three transitions: from $E_+$ to the CB, from $E_{+}^{SO}$ to the CB and from $E_-$ to the CB. The dispersion relations for each of the valence bands are determined by a simplified version of the valence band anticrossing model. The simplified version ignores spin effects and separates the remaining 6 x 6 problem into three 2 x 2 problems that has been shown to be an effective treatment of the anticrossing interaction for the valence band [128, 129].

Each of the 2 x 2 problems are treated by the simple BAC model, described in chapter 2. For GaNAs, the dispersion relationship for the valences bands is then give by

$$E_{\pm}(k, x) = \frac{1}{2} \left\{ E_{GaN}(k) + E_{As} \pm \sqrt{\left( E_{GaN}(k) - E_{As} \right)^2 + 4C_{GaN-As}^2 \cdot x} \right\}$$  \hspace{1cm} (6.1)

where $E_{GaN}(k)$ is the dispersion relationship of the unperturbed GaN valence band, $E_{As}$ is the arsenic defect level and $C_{GaN-As}$ is the empirically determined coupling parameter between the extended states of the GaN valence bands and the localized states of the arsenic level [56, 65]. The density of states effective mass is used to determine $E_{GaN}(k)$ to account for the light hole, heavy hole and spin orbit band in a single effective mass.

This calculation is performed for both the defect level of arsenic and the spin orbit level, which is 0.3eV below the arsenic level. The density of states effective hole mass of GaN is 1.5m_e [130] and the electron effective mass of GaN is 0.2m_e [4], which is used to determine the dispersion relation of the parabolic conduction band. The electron effective mass is assumed to remain constant with alloying. The conduction band edge is shifted with alloying as prescribed by the band anticrossing model for the full composition range, described in chapter 2. This treats the shift of the conduction

Figure 6.7 Calculated band structure of GaN$_{0.90}$As$_{0.10}$ from a simplified version of the valence band anticrossing model.
band edge as a linear interpolation of the position of the CBE of GaN with the CBE shift predicted for GaAsN (GaAs-rich) from BAC. The CBE of GaN and GaAs are assumed to be 4.0eV and 4.02eV below the vacuum level, respectively [131]. The literature values of \( C_{\text{GaAs-N}} = 2.7eV \) and \( E_N = 1.62eV \) (relative to the VBE of GaAs) are used to calculate the CBE of \( \text{GaAs}_{\text{x-N}} \) [56, 57]. For the composition range considered, the CBE decreases by about 25meV per percent arsenic mole fraction.

The joint optical density of states depends on the dispersion relation of the valence bands and conduction bands, extrinsic and intrinsic broadening of the band states and the distribution of localized and extended states in the valence bands. The broadening from random composition fluctuations and broadening inherent to BAC [58] are accounted for by convoluting a Gaussian function at each \( k \) value with the joint density of states. Only extended valence band states participate efficiently in the optical absorption; but the interaction of the localized arsenic defect states with the extended states of the valence bands results in a distribution of the localized and extended states in \( E_c \) and \( E_v \). The localized and extended density of states can be calculated from the two-state perturbation theory and are included in the model, so that only the extended states are included in the joint density of states.

The expression for the optical absorption from one of the valence bands, \( E_c(k) \), to the conduction band can be written as

\[
\alpha_+ (\hbar\omega) = \frac{1}{4\Delta_+ \pi \sqrt{\pi}} \int \left(-\sin \left(\frac{\theta}{2}\right)\right)^2 \exp \left(-\frac{\hbar\omega - \left[E_c(k) - E_+(k)\right]}{\Delta_+}\right)^2 k^2 dk
\]

where \( E_c(k) \) is the dispersion relation for the conduction band, \( E_v(k) \) is the dispersion relation for the \( E_v \) band as determined by equation (6.1), \( \Delta_+ \) is the Gaussian broadening parameter for the higher energy bands [128]. The factor

\[
\left(-\sin \left(\frac{\theta}{2}\right)\right)^2
\]

determines the fraction of the density of states that are delocalized and contribute to absorption where [129]:

\[
\theta(k) = \tan^{-1} \left(\frac{2C_{\text{GaAs-N}}}{{E_{\text{GaN}}}(k) - E_{\text{As}}}\right)
\]

The other two transitions involved in the absorption model are given by

\[
g_+^{SO} (\hbar\omega) = \frac{1}{4\Delta_+ \pi \sqrt{\pi}} \int \left(-\sin \left(\frac{\theta}{2}\right)\right)^2 \exp \left(-\frac{\hbar\omega - \left[E_c(k) - E_+^{SO}(k)\right]}{\Delta_+}\right)^2 k^2 dk
\]

and

\[
g_- (\hbar\omega) = \frac{1}{4\Delta_- \pi \sqrt{\pi}} \int \left(\cos \left(\frac{\theta}{2}\right)\right)^2 \exp \left(-\frac{\hbar\omega - \left[E_c(k) - E_-(k)\right]}{\Delta_-}\right)^2 k^2 dk
\]

where \( \Delta_+ \) is the Gaussian broadening parameter for the lower-energy matrix like band. The full expression for the absorption coefficient in this model is given by

\[
\alpha(\hbar\omega) = \alpha_0 \left(\frac{2}{3} g_+ (\hbar\omega) + \frac{1}{3} g_+^{SO} (\hbar\omega) + g_- (\hbar\omega)\right)
\]

where \( \alpha_0 \) is a scaling constant and the transitions are weighted by a degeneracy factor [128]. Figure 6.8 shows the best fits to the absorption spectroscopy data for three
samples with compositions ranging from 0.02 to 0.15. The same processing conditions were used to convert the transmission spectroscopy data to absorption spectroscopy, including the method of baseline subtraction to account for scattering and reflection as discussed in chapter 3.

The model matches well to the experimental data for all three arsenic concentrations when $C_{\text{GaN-As}} = 1.3\text{eV}$ and $E_{\text{As}} = 0.62\text{eV}$. The $E_{\text{As}}$ is the same value determined in previous studies, but the $C_{\text{GaN-As}}$ is a revised value from the 0.75eV previously determined [65]. The previous study used photo-modulated transmission for a set of films up to $x = 0.06$. A self-consistent fit of the absorption data is achievable with a coupling parameter of 0.75eV for our films up to $x = 0.06$, but it breaks down at higher arsenic concentrations and 1.3eV must be used. The high-energy bands’ broadening parameter, $\Delta_+\text{r}$, ranges from 0.20-0.28eV and the low energy band’s broadening parameter, $\Delta_-\text{r}$, ranges from 0.40-0.80eV. These ranges are of similar value to the modeling of the absorption of ZnO$_{1-x}$Se$_x$ [128]. The fits were optimized to the $\alpha$ range above $2\times10^4\text{ cm}^{-1}$, where the effect of the Fabry-Perot oscillations is minimized. At lower values of $\alpha$, variation in the fit from the data is due to these interference effects.

The model can be verified by comparing the band gap determined by absorption modeling and by fitting the PR spectra for the same film. Figure 6.8 shows the absorption data and modeling and the PR data for GaN$_{0.85}$As$_{0.15}$. The band gap, determined by each method, is marked by an arrow. The upward pointing arrow marks the band gap from PR and the downward pointing arrow marks the band gap determined by modeling the AS data, which are 2.01 and 1.98eV, respectively.

Figure 6.7 Results of the best fit of the absorption model to the absorption spectroscopy data. The data points are experimentally determined and the solid lines are calculated.
Figure 6.8 Comparison between the band gap determined by PR and absorption spectroscopy modeling. The arrows indicate the band gap location for each method. The blue arrow pointing upward is the band gap from PR and the red arrow pointing downward is the band gap from absorption modeling.

The standard method to determine the band gap, extrapolating a linear fit of $\alpha^2$ to the energy axis provides a reasonable estimate of the band gap when the proper $\alpha^2$ range is used. Figure 6.9a and b show the absorption spectroscopy data and model for two ranges of $\alpha^2$. Figure 6.9a and b show the data and model up to $5 \times 10^9$ cm$^{-2}$ and $6 \times 10^{10}$ cm$^{-2}$, respectively, along with the band gap determination from a linear extrapolation. The data ranges in figure 6.9a and b yield a band gap of 2.2 and 2.7 eV, respectively, whereas the model and PR yield a band gap of about 2 eV. The error in the linear extrapolation of $\alpha^2$ increases with increasing $\alpha^2$ range. Figure 6.9b shows the full experimentally determined $\alpha^2$ data range for this sample.

Figure 6.9 Absorption spectroscopy data and modeling for GaN$_{0.85}$As$_{0.15}$ for $\alpha^2$ up to a) $5 \times 10^9$ cm$^{-2}$ and b) $6 \times 10^{10}$ cm$^{-2}$. The dashed line indicates the band gap determination from a linear extrapolation of $\alpha^2$ to the energy axis.
The estimation of the band gap from a linear extrapolation of $\alpha^2$ improves with the decreasing range of $\alpha^2$ used in the determination. This follows from the band structure of GaNAs in two ways. The first reason is that the new valence band edge, defined by $E_v$, has a small relatively delocalized density of states so the absorption from $E_v$ to the conduction band will be relatively weak compared to a typical direct band gap semiconductor or $E$ to the conduction band. The second reason is that at small enough wavevector, $k$, the valence bands can be approximated as parabolic. The error between the band gap determined by the absorption model and linear extrapolation of $\alpha^2$ ranges from 50 to 200meV. Figure 6.10 shows the band gap summary for all GaNAs films in this study. The modeling of the absorption has been used to determine the position of the arsenic level and the coupling parameter between the arsenic defect level and the extended states of the valence band. The band gap dependence over the full composition range can then be calculated by linearly interpolating the GaN-rich VBAC range with the GaAs-rich CBAC range, as described in chapter 2 and in reference [65]. The conduction band edges of GaN and GaAs are assumed to be 4.0eV and 4.2eV below the vacuum energy, respectively [131]. The defect energy levels relative to vacuum used in the BAC model for the full composition range parameters are $E_{As} = -6.78$eV (0.62eV relative to the VBE of GaN) and $E_{N} = -3.97$eV (1.63eV relative to the VBE of GaAs). The coupling parameters are $C_{GaN-As} = 1.3$eV and $C_{GaAs-N} = 2.7$eV.

Figure 6.10 The band gaps determined for all GaNAs alloys in this study. The band gaps are experimentally determined by absorption spectroscopy and/or photo-modulated reflectance spectroscopy. Literature values for GaN-rich and GaAs-rich alloys are also included. The BAC model quantifies the band gap dependence across the full composition range.

The band gaps, indicated in figure 6.10, are determined by fitting the PR spectra and/or a linear extrapolation of $\alpha^2$ to the energy axis for the proper range of $\alpha^2$. The error bars account for variation in the band gap determined by the two methods or for curvature in the considered low $\alpha^2$ range. The BAC model provides a quantitative
explanation of the band gap for the full composition range, including the amorphous films in the middle composition range.

In conclusion, for the first time high quality and homogeneous GaN$_{1-x}$As$_x$ alloys have been fabricated across the full composition range. The films are crystalline for $x < 0.15$ and $x > 0.80$ and amorphous for the remaining range, as determined by x-ray diffraction, transmission electron microscopy and selected area electron diffraction. The composition was determined by Rutherford backscattering spectrometry and particle induced x-ray emission. The band gap has been quantified by photo-modulated reflectance and absorption spectroscopy. An absorption spectroscopy model, based on the valence band anticrossing model, has been used to determine the arsenic defect energy level and the coupling parameter of the defect level to the valence band of GaN. The band anticrossing model quantifies the band gap dependence across the full composition range, even for amorphous films.
7 Conclusion

7.1 Summary of the Dissertation

The effects of alloying on the optical and structural properties of the semiconductor alloy systems In$_{1-x}$Al$_x$N, ZnSe$_{1-x}$O$_x$ and GaN$_{1-x}$As$_x$ have been studied. These novel alloys are promising materials for photovoltaic or light-emitting applications because their band gaps can be controlled in the visible energy spectrum. Additional understanding of how alloying affects the band structure will aid in future device fabrication and design.

The band gap bowing parameter of InAlN was quantified through determination of the band gap as a function of composition. The composition of the films was determined using x-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS). The thin film quality was quantified with channeling-RBS and XRD. The band gap was determined through modeling the absorption spectroscopy to account for the nonparabolicity of the conduction and light hole bands and the Burstein-Moss shift. This work resulted in the most accurate band gap bowing parameter to date, with $b = 4.7\text{eV}$ and $5.1\text{eV}$ when the composition is determined by RBS and XRD, respectively.

The effect of oxygen on the band structure of ZnSe was studied in several ways. The change in the band gap and the temperature dependence of the band gap were quantified through photo-modulated reflectance spectroscopy and photoluminescence spectroscopy, respectively. Both phenomena can be quantitatively explained by the band anti-crossing model, which provides a framework for understanding why the band gap and temperature dependence of the band gap change drastically with alloying. These properties are important for designing thermally stable light emitting devices.

The alloying of ZnSe with ZnO has also been shown to have a large effect on the exciton kinetics in ZnSeO, which results in a low temperature enhancement of the photoluminescence (PL) intensity and an increase in the temperature dependence of the PL intensity. This phenomenon is explained by exciton localization, which has been measured as a function of temperature by time-resolved photoluminescence spectroscopy. The exciton localization results from fluctuations in the local oxygen concentration, causing disorder induced conduction band tailing of localized states that can trap electrons.

The final section reports on the study of GaN$_{1-x}$As$_x$ alloys across the full composition range. This set of thin films are wurtzite (crystalline) for $x < 0.15$, amorphous for $0.15 < x < 0.80$, and zinc blend (crystalline) for $x > 0.80$. The amorphous films are homogeneous and have no voids. The optical properties were studied with photo-modulated reflectance spectroscopy and absorption spectroscopy. A model of the absorption spectroscopy based on the band anticrossing model was used to determine the coupling constant between the arsenic defect level and the valence bands of GaN and the energy level of arsenic. The band gaps for all of the films were determined using absorption spectroscopy. When possible, PR was also used to determine the band gap. The band gap dependence on composition for the full alloy range can be quantitatively understood in terms of a linear interpolation of conduction band anticrossing model for GaAs:N and valence band anticrossing model for GaN:As.
7.2 Future Work

The utility of In-rich In$_{1-x}$Al$_x$N alloys depends on the ability to contact p-type alloys. The electron accumulation at the surface, due to the high electron affinity of InN, must be overcome. To date, p-type conductivity has only been measured with the aid of an electrolytic interface or through thermopower [132-134]. Novel methods of contacting the p-type materials or passivating the n-type surfaces are needed.

ZnSeO growth is still in its early stages. Additional growth optimization can improve film homogeneity and increase the oxygen incorporation beyond 6% to allow for further decrease of the band gap. Growth of the alloy system across the full composition range, similar to the study of GaNAs in chapter 6, would be an interesting additional test of the applicability of the band anticrossing model for a highly mismatched II-VI semiconductor alloy system across the full composition range. In addition, recent work on ZnO$_{1-x}$Se$_x$ (ZnO-rich) has shown promise for use in photo-electrochemical cells [128].

There are two significant challenges for the GaNAs alloy system. The first is to control the electrical properties. Early studies of doping amorphous GaNAs through ion-implantation of Ge, Si, Zn or Mg have shown limited success. Only the implantation of Ge resulted in any measurable conductivity ($\sim 10^4$ Ohm-cm) and any thermal treatment decreased the conductivity (rapid thermal annealing or pulsed laser melting). There may be a limit to the substitutional incorporation of dopants through ion-implantation due to the amorphous phase, so doping during growth should be attempted. The film growers at the University of Nottingham will be trying this method soon.

The second interesting challenge for GaN$_{1-x}$As$_x$ is to understand the effect of the amorphous phase on the band structure. At $x = 0.15$, we have an amorphous film and crystalline film with the same composition. This was achieved by using a glass and sapphire substrate, respectively. Within error, these two films have the same band gap, indicating that the amorphous phase has a limited effect on the valence band and conduction band edges of GaNAs. Crystallizing the amorphous films in the middle composition range would provide an additional method to understand the effect of microstructure on the band structure.

Attempts to use rapid thermal annealing (RTA) and pulsed laser melting (PLM) to crystallize the amorphous films have both resulted in phase separation. It appears that RTA results in phase separation into GaN-rich and GaAs-rich crystalline phases, where as PLM results in GaAs-rich crystalline phases and GaN-rich amorphous phases. Further study into the effects of PLM on amorphous GaNAs is necessary to understand the structural properties. Higher laser energy or shorter pulse times may be necessary for crystallization into a homogenous phase.

In summary, all three alloy system have remaining challenges to enable device fabrication, but remain scientifically interesting and potentially useful materials for photovoltaic and light emitting applications.
Appendix A Time-Resolved Photoluminescence Spectroscopy

A.1 Experimental System

Adding time resolution to photoluminescence spectroscopy is accomplished by utilizing a pulsed laser to allow for decay in the PL signal and a time sensitive detection system. Figure A.1 shows a schematic of the time-resolve photoluminescence spectroscopy (TRPL) system in the electronic materials program of the Materials Sciences Division, Lawrence Berkeley National Laboratory. This system consists of an Nd-YAG pumped Titanium-Sapphire (Ti-Sapp) laser. The pump laser is a doubled diode laser that is capable of 5.5W pumping power at 532nm. The Ti-Sapp laser has a 76 MHz repetition rate (pulses every 13.6ns) with laser emission tunable between 720-930nm. Emission at 800nm provides the maximum average power of about 800mW. The Ti-Sapp laser can be used in continuous wave (CW) and mode locked (ML, pulsed) modes. The typical pulse width when ML is about 200 fs.

The system is equipped with a “doubler box,” which includes non-linear optics that convert the primary Ti-Sapp laser beam to its second and third harmonics. Pumping with the maximum 800nm laser pulse, results in a 400nm beam of about 40 mW average power and a 266nm beam of about 20mW average power. Tuning the Ti-Sapp laser provides a laser wavelength pumping range of about 240-306nm for the third harmonic ($3\omega$) and 360-460nm for the second harmonic ($2\omega$), although the average power decreases as the Ti-Sapp is tuned away from 800nm.

![Figure A.1 Schematic of the time-resolved photoluminescence spectroscopy system.](image)

The optics are arranged in the backscattering geometry so that the excitation laser and PL signal travel along the same optical axis. This set up provides easy alignment and is ideal for use with a cryostat because of its narrow windows. Care should be taken to minimize scattered and reflected laser light into the monochrometer that will interfere with data collection.
The PL is dispersed by a spectrometer and focused into the streak camera. The typical grating setting results in a wavelength window of about 80nm. The streak camera system allows for time sensitivity. Figure A.2 shows a schematic of a streak camera. The streak camera has a photocathode that converts the dispersed light into electrons, while keeping the spatial distribution of the signal. These electrons are accelerated through two parallel plates across which a time varying electric field is applied. The electric field increases with time so electrons that pass through the parallel plates at later times will be accelerated downwards with greater force. The electrons then strike a microchannel plate (MCP) that consists of hundreds of microchannels that are biased to result in secondary electrons when the signal electrons strike them. The MCP provides signal amplification, while maintaining the spatial distribution that provides the wavelength and time information. These amplified electrons then strike a phosphor screen that converts the electrons back to photons. This signal is collected by a CCD array and transmitted to the computer for data acquisition and analysis.

![Schematic of Streak Camera](image)

Figure A.2 A schematic of the streak camera detection system.

There are two sweeping systems for the streak camera: a “slow sweep” and a “fast sweep” model. The slow sweep model has time windows from 5ns up to 50ns. The time scale limitation on the long side is the pulse separation of the laser, which is 13.6 ns. The “fast sweep” model has windows of 2ns down to 0.5ns. The maximum possible time resolution is 5ps.

### A.2 TRPL Data Processing

The TRPL data are collected in a two-dimensional (2D) array, with the wavelength data on the x-axis and time data on the y-axis. It is typically displayed as a false color image. Figure A.3 shows typical TRPL data with a linear color scale.
Figure A.3 An example of TRPL data with a linear color scale. The sample here is ZnSe$_{0.987}$O$_{0.013}$ at 10K excited by the 400nm laser line. The horizontal red box marks the area of vertical integration for figure A.4a. The vertical blue box marks the area of horizontal integration for figure A.4b.

The 2D image is useful for displaying the full data, but should be processed to facilitate data analysis. The data analysis software provided with the steak camera provides an easy way to take horizontal or vertical integrations of the data to produce intensity vs. time or intensity vs. wavelength (energy) spectra. Figure A.4 show an example of each. Data processing software, such as Matlab, can also be used to automate the analysis.

Figure A.4 Examples of a) vertical and b) horizontal integration from the raw TRPL data shown in figure A.3.
The intensity vs. energy data can be analyzed in the same fashion as typical PL spectroscopy, with the additional benefit of tracking the peak position, intensity and full width at half max as a function of time. The intensity vs. time data provides information on the PL lifetime. The decay in figure A.4b is exponential, which is given by the equation:

$$I(t) = I_o \exp \left[ -\frac{t}{\tau_{PL}} \right]$$  \hspace{1cm} (A.1)

where $I_o$ is the maximum intensity and $\tau_{PL}$ is the PL lifetime that is given by

$$\frac{1}{\tau_{PL}} = \frac{1}{\tau_{Rad}} + \frac{1}{\tau_{Non-Rad}}$$  \hspace{1cm} (A.2)

where $\tau_{Rad}$ is the radiative lifetime and $\tau_{Non-Rad}$ is the non-radiative lifetime. The radiative and non-radiative lifetimes depend on the excitation power density. At high excitation density, Auger recombination dominates the non-radiative lifetime and the radiative lifetime depends on bimolecular recombination. At low excitation densities for a doped film, the minority carrier lifetime dominates the radiative lifetime and Shockley-Read-Hall (defect) dominates non-radiative recombination. Details on radiative and non-radiative recombination can be found in chapter 2 of reference [135].
References

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