Photoexcited Emission Efficiencies of Zinc Oxide

by

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Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics in the Graduate School of Duke University

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ABSTRACT

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Abstract

Optoelectronic properties of the II-VI semiconductor zinc oxide (ZnO) have been studied scientifically for almost 60 years; however, many fundamental questions remain unanswered about its two primary emission bands—the exciton-related luminescence in the ultraviolet and the defect-related emission band centered in the green portion of the visible spectrum. The work in this dissertation was motivated by the surprising optical properties of a ZnO nanowire sample grown by the group of Prof. Jie Liu, Department of Chemistry, Duke University. We found that this nanowire sample exhibited defect-related green/white emission of unprecedented intensity relative to near-band-edge luminescence. The experimental work comprising this dissertation was designed to explain the optical properties of this ZnO nanowire sample. Understanding the physics underlying such exceptional intensity of green emission addresses many of the open questions of ZnO research and assesses the possibility of using ZnO nanostructures as an ultraviolet-excited, broadband visible phosphor.

The goal of this dissertation is to provide insight into what factors influence the radiative and nonradiative recombination efficiencies of ZnO by characterizing simultaneously the optical properties of the near-band-edge ultraviolet and the defect-related green emission bands. Specifically, we seek to understand the mechanisms of ultraviolet and green emission, the mechanism of energy transfer between them, and the evolution of their emission efficiencies with parameters such as excitation density and sample temperature. These fundamental but unanswered questions of ZnO emission are addressed here by using a novel combination of ultrafast spectroscopic techniques in conjunction with a systematic set of ZnO samples. Through this systematic investigation, ZnO may be realistically assessed as a potential green/white light phosphor.
Photoluminescence techniques are used to characterize the thermal quenching behavior of both emission bands in micrometer-scale ZnO powders. Green luminescence quenching is described by activation energies associated with bound excitons. We find that green luminescence efficiency is maximized when excitons are localized in the vicinity of green-emitting defects. Subsequent photoluminescence excitation measurements performed at multiple temperatures independently verified that green band photoluminescence intensity directly correlates with the photogenerated exciton population.

The spatial distributions of green-emitting defects and nonradiative traps are elucidated by an innovative combination of quantum efficiency and time-integrated/resolved photoluminescence measurements. By combining these techniques for the first time, we take advantage of the drastically different absorption coefficients for one- and two-photon excitations to provide details about the types and concentrations of surface and bulk defects and to demonstrate the non-negligible effects of reabsorption. A comparison of results for unannealed and annealed ZnO powders indicates that the annealing process creates a high density of green-emitting defects near the surface of the sample while simultaneously reducing the density of bulk nonradiative traps. These experimental results are discussed in the context of a simple rate equation model that accounts for the quantum efficiencies of both emission bands.

For both femtosecond pulsed and continuous-wave excitations, the green band efficiency is found to decrease with increasing excitation density—from 35% to 5% for pulsed excitation spanning $1-1000 \, \mu\text{J cm}^{-2}$, and from 60% to 5% for continuous excitation in the range $0.01-10 \, \text{W cm}^{-2}$. On the other hand, near-band-edge emission efficiency increases from 0.4% to 25% for increasing pulsed excitation density and from 0.1% to 0.6% for continuous excitation. It is shown experimentally that these changes in efficiency correspond to a reduction in exciton formation efficiency. The
differences in efficiencies for pulsed versus continuous-wave excitation are described
by changes in the relative rates of exciton luminescence and exciton capture at green
defects based on an extended rate equation model that accounts for the excitation
density dependence of both luminescence bands.

In using a systematic set of ZnO samples and a novel combination of optical
techniques to characterize them, this body of work presents a comprehensive and
detailed physical picture of recombination mechanisms in ZnO. The insight provided
by these results has immediate implications for material growth/processing tech-
niques and should help material growers control the relative efficiencies of ultraviolet,
green/visible, and nonradiative recombination channels in ZnO.
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Contents

Abstract iv
Acknowledgments vii
List of Figures xii
List of Tables xviii

1 Introduction 1
1.1 Overview of Zinc Oxide 1
1.2 Green Band Luminescence 4
1.3 Overview of the Dissertation 6

2 Theory of Photoluminescence in ZnO 10
2.1 Free Carrier Generation 10
2.2 Exciton Formation and Luminescence 15
  2.2.1 Exciton Formation 15
  2.2.2 Free Exciton Luminescence 17
  2.2.3 Phonon-Assisted Exciton Luminescence 19
  2.2.4 Bound Exciton Luminescence 21
2.3 Green Defect-Related Radiative Recombination 24
2.4 Escape of Radiation from ZnO: Optical Effects 26
2.5 Summary 31

3 Optical Characterization Techniques 33
3.1 Time-Integrated Photoluminescence and Photoluminescence Excitation 33
6.4 Modeling ............................................................... 97

6.4.1 Two-Photon Excitation, Annealed Sample, 
       Bulk Region ....................................................... 98

6.4.2 Two-Photon Excitation, Unannealed Sample, 
       Bulk Region ....................................................... 99

6.4.3 One-Photon Excitation, Unannealed Sample, 
       Surface Region ................................................... 101

6.4.4 One-Photon Excitation, Annealed Sample, 
       Surface Region ................................................... 101

6.4.5 Dependence of PL Intensity on Excitation Density ............ 103

6.5 Summary ............................................................... 103

7 Influence of Photoexcitation Density on Carrier Dynamics and 
   Luminescence Efficiencies ......................................... 105

7.1 Femtosecond Pulsed Excitation .................................. 107

7.1.1 High Excitation Effects ...................................... 107

7.1.2 Time-Integrated Photoluminescence and 
       Quantum Efficiency ............................................ 111

7.1.3 Time-Resolved Photoluminescence .......................... 119

7.2 Continuous-Wave Excitation ...................................... 127

7.3 Summary and Discussion .......................................... 134

8 Conclusion .............................................................. 138

A Femtosecond Laser System ........................................... 142

Bibliography ............................................................. 144

Biography ................................................................. 157
List of Figures

1.1 Publications per year related to ZnO from 1955 to the present. (Source: Web of Science [22].) ................................................................. 4

1.2 Comparison of the ZnO:Zn emission spectrum to the dark-adapted (scotopic) human eye response [44]. ........................................... 6

2.1 Effect of surface recombination on the steady-state density of photo-generated minority carriers (holes) for (a) one-photon and (b) two-photon excitation. The sample’s front and rear surfaces are indicated by the vertical dashed lines at $z=0$ nm and $z=150$ nm, respectively. . 12

2.2 Approximate room-temperature dispersion for the transverse A- and B-exciton polaritons (solid lines). The longitudinal and transverse resonance energies (subscripts “L” and “T,” respectively) for A- and B-excitons are denoted at $k=0$. The linear dispersion of the uncoupled photon (near-vertical dashed line) as well as exemplary quadratic dispersions of uncoupled excitons are also shown. (After Lagois [70].) 17

2.3 (a) Components of ZnO’s PL spectrum at room temperature. The contributions from free exciton (X-0LO) emission and the first two phonon replicas (X-1LO and X-2LO) are shown. (b) Schematic diagram of the phonon-assisted exciton luminescence process. An exciton with wave vector $k_X$ on the exciton-like portion of the exciton polariton dispersion scatters to the photon-like portion of the dispersion by creation of LO phonons whose wave vectors $k_{LO}$ satisfy momentum conservation. (After Fig. 13.12 of Klingshirn [69].) . . . . . . . . . . . . . . . 21

2.4 Schematic diagram of relevant bound excitons in ZnO. The Coulomb binding (dashed ellipse) of the electron in the conduction band (C.B.) to the hole in the valence band (V.B.) reduces the free exciton energy ($E_X$) from that of the band gap ($E_g$). Excitons may be bound to a neutral donor (nDBE), ionized donor (iDBE), or neutral acceptor (nABE) with respective exciton localization energies $E_{loc}^{nDBE}$, $E_{loc}^{iDBE}$, $E_{loc}^{nABE}$. The binding energies $E_b$ of the donor electron to its donor site and the acceptor hole to its acceptor site are also shown. . . . . . . . . . . . . . . 22
2.5 (a) Schematic diagram of the one-dimensional configuration coordinate model. Transitions from the zero vibrational level of the excited electronic state to various vibrational levels of the ground excited state give rise to a broad, unstructured luminescence band (b). (After Reshchikov and Morkoc [80].) ........................................... 25

2.6 Room-temperature index of refraction and absorption coefficient for ZnO, as obtained by a best fit of spectroscopic ellipsometry data in Ref. 85. ............................................................. 27

2.7 Fraction of internally generated photoluminescence that emerges from a ZnO sample for (a) one-photon and (b) two-photon excitation subsequent to Fresnel reflection ($f_{\text{refl}}$), reabsorption ($f_{\text{reab}}$), and their combined effect ($f_{\text{esc}}$). The spatial distributions of minority carriers are assumed to be the same as indicated in Fig. 2.1. .............................. 28

2.8 Fraction of internally generated photoluminescence (emission energy $\hbar \omega = 3.4$ eV) that reaches the surface of a ZnO sample without being reabsorbed for increasing sample thickness $d$. For two-photon excitation, $f_{\text{reab}}$ asymptotically scales as the sample’s surface-to-volume ratio ($1/d$). ................................................................. 30

3.1 Experimental setup for time-integrated photoluminescence measurements. ......................................................... 34

3.2 Example photoluminescence (PL) and photoluminescence excitation (PLE) data for ZnO:Zn micropowder. The spectra were acquired using the setup depicted in Fig. 3.3. The PLE spectrum corresponds to a PL detection energy denoted by the arrow (2.48 eV). ............... 36

3.3 Experimental setup for photoluminescence excitation (PLE) measurements. ........................................................... 37

3.4 Experimental procedure for measuring external quantum efficiency (QE) using an integrating sphere. .......................... 38
3.5 Time-resolved photoluminescence (TRPL) data for ZnO:Zn micropowder. (a) PL intensity distribution as a function of time and wavelength, as measured by the streak camera. (b) Time-integrated PL spectrum corresponding to the temporal range bound by the pair of horizontal arrows. (c) Spectrally integrated PL decay corresponding to the wavelength range bound by the pair of vertical arrows. (d) Wavelength-dependent temporal dispersion of the streak system due to the index of refraction dispersion of the optical fiber.

4.1 SEM images of sulfur-doped ZnO nanowires. Scale bars in (a) and (b) correspond to 2 µm and 1 µm, respectively.

4.2 SEM images of (a) unannealed ZnO powder, (b) sulfur-doped ZnO powder, and (c) annealed ZnO powder. All scale bars correspond to 5 µm.

4.3 (a) Photoluminescence spectrum of ZnO:S nanowires and the very similar spectral response of the dark-adapted human eye [44]. The spectra of ZnO powders (undoped and sulfur-doped) are shown for comparison. All spectra have been normalized to the samples’ respective absorption. (b) Spectrally integrated, time-resolved photoluminescence decays for near-band-edge emission. The apparent rise times differ due to intentional changes in the streak camera’s time resolution (110 ps for undoped powder, 50 ps for doped powder, 30 ps for doped nanowires). In all cases the rise times are instrument-limited.

4.4 Low-temperature photoluminescence spectra of ZnO powders under continuous-wave excitation.

5.1 Photoluminescence spectrum of ZnO:S micropowder for a lattice temperature of 12 K. The vertical dashed line indicates the free exciton energy of 3.376 eV. The excitation source was a femtosecond pulse train at energy 3.8 eV and fluence 5 µJ cm⁻².

5.2 Arrhenius plot of the spectrally integrated photoluminescence intensities for the two primary low-temperature emission lines in ZnO:S. The energies denoted for $I_S$ and $I_0$ correspond to thermal activation energies derived from the linear slopes of the data.
5.3 Arrhenius plot of the spectrally integrated near-band-edge photoluminescence intensity above room temperature for ZnO:Zn. The excitation source was a continuous-wave HeCd laser at energy 3.81 eV and irradiance 0.002 W cm\(^{-2}\). .......................................................... 64

5.4 Broadband defect-related photoluminescence of ZnO:S micropowder at select lattice temperatures. The excitation source was a continuous-wave HeCd laser at energy 3.81 eV and irradiance 0.002 W cm\(^{-2}\). Gaussian fits are superimposed on the 11 K and 300 K curves to illustrate the asymmetry of the band. (Curves are displaced vertically for clarity.) 66

5.5 Arrhenius plot of the temperature dependence of the green band’s amplitude, as deduced from best fits to Eq. (5.1). Activation energies are denoted according to best-fit linear slopes of the data. The horizontal arrows indicate the temperatures at which the slope begins to deviate from the primary (15 meV) activation energy: at (10 meV)\(^{-1}\) and at (15 meV)\(^{-1}\). .......................................................... 67

5.6 Temperature dependence of the green band’s peak position. The vertical arrow at \(k_B T_L = 11\) meV indicates the crossover point between the linear behaviors at low (\(\sim 50–100\) K) and intermediate (\(\sim 150–300\) K) temperatures. The vertical arrow at \(k_B T_L = 15\) meV indicates the temperature at which the peak position begins its constant redshift with increasing temperature. .......................................................... 69

5.7 Arrhenius plot of the green band thermal quenching above room temperature. An activation energy of 430 meV was derived from a linear fit to the data. ................................. 71

6.1 Comparison of photoluminescence excitation spectra for detection energies near the peak of the green band (2.49 eV) and at the peak of the X-2LO transition (3.22 eV). The lattice temperature was 88 K. 80

6.2 (a) Estimated absorption coefficient of ZnO powder as derived from the photoluminescence excitation spectrum of the peak of the green defect emission. (b) Estimated photon escape depth [inverse of the curve in (a)] due to reabsorption and probability \(f_{\text{refl}}\) of photon escape due to Fresnel reflection [derived from a Kramers-Kronig transformation of the curve in (a) and use of Eq. (2.8)]. ................................. 82
6.3 (a) Time-integrated photoluminescence (TIPL) of unannealed ZnO under one-photon and two-photon excitation. Time-resolved photoluminescence spectra are also shown for one-photon excitation (b) and two-photon excitation (c). The inset of (a) demonstrates the effect of reabsorption by comparing the difference in one-photon and two-photon TIPL intensities ($\Delta PL$) to the approximate absorption coefficient derived from photoluminescence excitation (PLE) data. In (b) and (c), the bottom three spectra in each plot are scaled by a factor of two for clarity.

6.4 Time-resolved photoluminescence of unanneled ZnO under one-photon and two-photon excitation. The corresponding window of spectral integration was centered at the X-2LO transition ($3.177 \pm 0.036$ eV).

6.5 (a) Time-integrated photoluminescence (TIPL) of annealed ZnO under one-photon and two-photon excitation. Time-resolved photoluminescence spectra are also shown for one-photon excitation (b) and two-photon excitation (c). The inset of (a) demonstrates the effect of reabsorption by comparing the difference $\Delta PL$ in one-photon TIPL intensities (unannealed vs. annealed) to the approximate absorption coefficient derived from photoluminescence excitation (PLE) data. In (b) and (c), the bottom three spectra in each plot are scaled by a factor of two for clarity.

6.6 Time-resolved photoluminescence of annealed ZnO under one-photon and two-photon excitation. The corresponding window of spectral integration was centered at the X-2LO transition ($3.177 \pm 0.036$ eV).

6.7 (a) Time-integrated and (b) time-resolved green photoluminescence of annealed ZnO under one-photon and two-photon excitation. In (b) the corresponding window of spectral integration was centered near the green emission peak ($2.52$ eV), and its width ($72$ meV) was chosen to be the same as that used for near-band-edge analysis.

7.1 Time-integrated photoluminescence spectra of annealed ZnO:Zn under low ($8.3 \mu J \text{cm}^{-2}$), intermediate ($17 \mu J \text{cm}^{-2}$), and high ($110 \mu J \text{cm}^{-2}$) fluence of femtosecond pulsed excitation.

7.2 Dependence of spectrally integrated near-band-edge (UV) and green (GR) photoluminescence intensities (a) and external quantum efficiencies (b) on excitation fluence. The vertical arrows in (a) correspond to carrier densities associated with high excitation effects (Sec. 7.1.1).
7.3 Pulsed excitation power-law behavior of the ratio of spectrally integrated photoluminescence intensity to the corresponding quantum efficiency for near-band-edge (UV) and green (GR) emissions.

7.4 Time-resolved photoluminescence decays of ZnO:Zn near-band-edge emission under low (8.3 µJ cm\(^{-2}\)), intermediate (17 µJ cm\(^{-2}\)), and high (110 µJ cm\(^{-2}\)) fluence of femtosecond pulsed excitation. The corresponding window of spectral integration was centered at the X-2LO transition (3.177 eV ± 0.036 eV).

7.5 Dependence of near-band-edge photoluminescence decay parameters on excitation fluence.

7.6 Representative time-resolved photoluminescence decays of ZnO:Zn green emission under low (8.3 µJ cm\(^{-2}\)), intermediate (17 µJ cm\(^{-2}\)), and high (110 µJ cm\(^{-2}\)) fluence of femtosecond pulsed excitation. The corresponding window of spectral integration was centered at the emission peak (2.445 eV), and its width (72 meV) was chosen to be the same as that used for near-band-edge analysis.

7.7 Dependence of defect-related green photoluminescence decay parameters on excitation fluence.

7.8 Representative steady-state photoluminescence spectra of ZnO:Zn under low (∼ 0.1 W cm\(^{-2}\)), intermediate (∼ 1 W cm\(^{-2}\)), and high (∼ 10 W cm\(^{-2}\)) levels of continuous-wave excitation.

7.9 Dependence of spectrally integrated near-band-edge (UV) and green (GR) photoluminescence intensities (a) and external quantum efficiencies (b) on excitation irradiance.

7.10 Continuous-wave power-law behavior of the ratio of spectrally integrated photoluminescence intensity to the corresponding quantum efficiency for near-band-edge (UV) and green (GR) emissions.

8.1 Comparison of irradiance dependence for the total spectrally integrated external quantum efficiency of ZnO:S (0.5% S) and annealed ZnO powders.

8.2 Dependence of spectrally integrated quantum efficiency on the concentration (by weight) of sulfur present during the annealing process. Continuous-wave HeCd irradiance was ∼1 W cm\(^{-2}\).
List of Tables

2.1 Summary of bound exciton lines in ZnO at low temperature. Energy values are averaged over several reported values in the literature [76–78], as tabulated in Ref. 67. The uncertainties in parentheses indicate the standard deviations from this averaging process. A dash (−) in parentheses indicates that no averaging was performed due to a lack of data. ................................................................. 23

4.1 Peak ratio of green to ultraviolet PL intensity ($I_{pk}^{GR}/I_{pk}^{UV}$), spectrally integrated quantum efficiency $\eta = \eta_{UV} + \eta_{GR}$, and near-band-edge time-resolved photoluminescence decay parameters for undoped and S-doped powders and S-doped nanowires. ................................................ 53

5.1 Summary of thermal activation (TA) energies deduced from the temperature dependence of photoluminescence in ZnO:S and ZnO:Zn powders. ............................................................. 72

6.1 Biexponential decay best-fit parameters for the X-2LO transition in ZnO particles. Parameters for bulk single-crystal ZnO (Ref. 77) are also shown for comparison. ......................... 88

7.1 Comparison of model recombination/capture times and critical densities [Eqs. (7.4)–(7.5)]. Values denoted by an asterisk (*) were held fixed during the fitting procedure. .......................... 130
Chapter 1

Introduction

1.1 Overview of Zinc Oxide

The II-VI semiconductor zinc oxide (ZnO) is surprisingly prevalent in products of everyday life. The compound finds use as a curing agent in rubber (especially car tires), a white pigment in paint, a food additive for its zinc content, a galvanizing agent for metal (especially nails), and as an additive in cosmetics, sunscreen, and diaper rash ointment. The nature and variety of these applications speak to the fact that ZnO is low-cost, easily produced, readily available, and safe for both humans and the environment. The vast majority of these commercial applications utilize ZnO in its polycrystalline (powder) form, which is currently produced at a level of 100,000 tons per year [1].

Scientific investigations of the properties of ZnO generally pertain to samples that have been synthesized at a much smaller production level in a laboratory environment. Many of the earliest studies of ZnO were performed on “platelets” [2] and “whiskers” [3] grown by gas transport techniques [4,5]. These samples were generally characterized by spatial dimensions on the nanometer–micrometer scale and were the precursors to modern-day “thin-film” and “nanowire” samples, respectively. On the other hand, bulk samples with spatial dimensions on the centimeter scale may be grown by hydrothermal [6,7] and melt techniques [8,9]. In more recent years, ZnO thin films have been grown successfully using many of the standard epitaxial growth techniques, including molecular beam epitaxy, metal-organic chemical vapor deposi-
tion, metal-organic vapor phase epitaxy, pulsed laser deposition, and radio-frequency magnetron sputtering \([1,10]\). Finally, the most recent trend is to grow nanometer-scale ZnO structures of endless variety (nanowires, nanostars, nanonails, nanocombs, etc.), mostly using gas transport \([11]\) or solution-based \([12]\) techniques.

Regardless of the growth technique, ZnO naturally crystallizes in the wurtzite (hexagonal) structure.\(^1\) In this form a hexagonal close-packed lattice of Zn\(^{2+}\) ions is interlaced with a hexagonal close-packed lattice of O\(^{2-}\) ions, such that the four nearest neighbors of a given ion are a surrounding tetrahedra of ions of the other species. The ZnO lattice is characterized by an in-plane lattice constant of \(a=3.2495\ \text{Å}\) and a unit cell spacing of \(c=5.2069\ \text{Å}\) in the direction parallel to the \(c\)-axis \([16]\).

The wurtzite structure of ZnO yields a minimum direct band gap of \(\sim 3.4\ \text{eV (365 nm)}\). Transparency in the visible spectrum, combined with other properties typical of wide-band-gap semiconductors (high \(n\)-type conductivity, radiation hardness, high breakdown voltage, etc.), potentially lends ZnO to device applications such as transparent thin-film transistors, transparent ohmic contacts for solar cells, and light extraction enhancement structures for visible-wavelength light-emitting diodes \([17]\). Moreover, strong absorption and emission of light near the band gap in the ultraviolet has motivated extensive investigations into the suitability of ZnO for ultraviolet detectors, lasers, and light-emitting diodes. The most widely cited property of ZnO along these lines is a very large exciton binding energy of 60 meV, which holds promise (in the minds of many) for highly efficient exciton-based lasing at temperatures even exceeding room temperature.

Currently the largest barrier to the realization of ZnO optoelectronic devices is the inability to \(p\)-dope the material reliably and with sufficient hole concentra-

\(^1\)ZnO is also stable in the zincblende structure but only if grown on a cubic substrate \([13,14]\). It can form a metastable phase of rocksalt structure, but only under high pressure (\(\sim 10\ \text{GPa}\)) \([15]\).
tion/mobility. This inability is largely due to the intrinsic $n$-type conductivity of ZnO and is a problem for many wide-band-gap semiconductors (GaN, CdS, ZnS, ZnSe) [17]. Unintentional shallow and deep donors, mainly associated with lattice defects, compensate whatever acceptor levels are intentionally introduced and make $p$-doping very difficult. Nevertheless, achieving $p$-type ZnO is an area of intense research, and there have been limited reports of successful fabrication of all-ZnO light-emitting diodes [18–21]. Even in the case of successful device fabrication, the source of emission and the long-term stability of the $p$-type layer are the subject of much scrutiny [17].

The amount of scientific work pertaining to ZnO over the past $\sim$50 years is summarized graphically in Fig. 1.1, which indicates the number of ZnO-related publications per year during that time period [22]. Although the first scholarly publication dates back to 1935 [23], work began more fervently in the late 1950s when many semiconductors were being studied for potential use as phosphors for cathode-ray tube applications. Many physics-related developments, such as exciton theory in the early 1960s [24,25] and theories of highly excited semiconductors in the 1970s [26,27], led to a plateau of ZnO-related work in the late 1970s and early 1980s [1]. A discrete increase in publications during the early 1990s can be attributed to improved epitaxial growth techniques and the advent of sub-picosecond lasers to characterize in more detail these newly grown samples. The current renaissance in ZnO-related research (exponential rise in Fig. 1.1) began in the mid-1990s and can be attributed in large part to the experimental realization of optically pumped lasing, first at low temperature [28] and then at room temperature [29–32].
1.2 Green Band Luminescence

During the present period of intense ZnO research, the majority of work relates to the near-band-edge (ultraviolet) light-emitting properties of ZnO thin films and nanostructures. In many cases this emission band is accompanied by the infamous, defect-related “green band” of ZnO. The origin of this broad, structureless band centered at $\sim 2.5 \text{ eV (500 nm)}$ remains a matter of debate.

Vanheusden et al. provided a seemingly convincing experimental correlation between the intensity of green emission and the concentration of defects they identified as oxygen vacancies [33]. In their model, an electron trapped at an oxygen vacancy recombines with a free hole in the valence band to produce green luminescence. Since that time, other experimental results have called into question their identification of the relevant defects as oxygen vacancies, and subsequently the claim of direct involve-
ment of the oxygen vacancy in the recombination process has been questioned [17,34]. Other experimental results have also indicated the involvement of oxygen vacancies in the green luminescence process, but these results have suggested instead that the oxygen vacancy is a deep hole trap, and that green band emission originates from the recombination of free (or shallowly trapped) electrons with holes deeply trapped at oxygen vacancies (acceptors) [35,36].

Contrary to these interpretations of experimental data, state-of-the-art, first-principles calculations performed by several techniques suggest that oxygen vacancies form deep donors in ZnO and therefore are not involved in the green luminescence mechanism [37–41]. A growing consensus in the theoretical community is that zinc vacancies, which form acceptors in ZnO, are instead responsible for the green luminescence [17]. However, the more common interpretation involving oxygen-related defects continues to be discussed both theoretically [42] and experimentally [43].

Even though the microscopic origin of the green luminescence remains controversial, the green band has been exploited in technological applications. Nonstoichiometric ZnO with an excess of Zn atoms, traditionally referred to as “zinc-doped ZnO” (ZnO:Zn), has a long history of use as a green/monochrome phosphor in electron-excited vacuum fluorescent and field emission displays [45–48]. ZnO:Zn emits very efficiently in the visible portion of the spectrum; its tabulated efficiency as a green phosphor is $\sim 60\%$ [49]. Moreover, the spectral distribution of the green band is very broad and similar to the dark-adapted (scotopic) human eye response (Fig. 1.2) [44].

These desirable characteristics of the green band, combined with the increasing availability of ultraviolet light-emitting diodes which could be used to excite ZnO, have motivated the work of this dissertation to characterize the possibility of using ZnO:Zn as a photoexcited green/white-light phosphor. As part of this work, the author and his collaborators were the first to point out the overlap of ZnO:Zn emission
Figure 1.2: Comparison of the ZnO:Zn emission spectrum to the dark-adapted (scotopic) human eye response [44].

with the human eye response [50], and they have subsequently urged the optoelectronics community to reconsider the phosphor properties of ZnO:Zn and ZnO:S [51]. Based on ZnO’s many positive attributes listed at the beginning of this chapter, the material potentially offers many advantages over existing white light phosphors in terms of efficiency, cost, and personal/environmental safety.

1.3 Overview of the Dissertation

Successful development of ZnO-based optoelectronic devices—either in the ultraviolet region (near-band-edge luminescence) or in the visible spectrum (defect-related luminescence)—depends on a thorough understanding of the physics associated with these two emission bands and the energy transfer between them. The additional
presence of defects and impurities leading to nonradiative recombination must also be taken into account because these nonradiative channels reduce the efficiencies of the radiative recombination channels. The goal of this dissertation is to contribute to the understanding of what factors influence the radiative efficiencies (ultraviolet and green/white) in ZnO so that material growth/processing techniques can be tuned to control these efficiencies on demand.

The optical properties of ZnO and the underlying radiative recombination mechanisms are reviewed in Chap. 2, and the experimental techniques used in this dissertation to characterize these optical properties are described in Chap. 3. The relatively simple experiments of photoluminescence (time-integrated and time-resolved), photoluminescence excitation, and external quantum efficiency described in Chap. 3 provide surprisingly rich and compelling data to explain the relative efficiencies of radiative and nonradiative recombination in ZnO.

Several aspects of ZnO material growth and processing are discussed in Chap. 4. In particular, the relative effects of sample size/morphology, dopant concentration, and post-growth annealing on the relative intensities of ultraviolet and green luminescence are discussed. A unique ZnO nanostucture (sulfur-doped ZnO nanowires) provides an example of how the nanostructuring process introduces nonradiative surface traps while the sulfur-doping process simultaneously introduces many green-emitting defects. Implications for the efficiency of green band luminescence in this case are understood by comparing the results to those from a set of standardized ZnO powder samples subjected to various types of post-growth annealing/doping treatments. The powder samples introduced for this purpose also serve as the subjects of more extensive optical investigations in subsequent chapters.

Thermal quenching of both luminescence bands is studied in Chap. 5 by measuring the temperature dependence of the bands’ intensities throughout the range 12–525 K.
Several common donors are identified in the low-temperature photoluminescence data based on the recombination of excitons bound to them. The origin of an additional near-band-edge feature in the low-temperature PL spectra is discussed in light of its apparent correlation with green band luminescence. The most significant and unexpected result from these temperature dependence measurements was a decrease in green luminescence intensity characterized by activation energies associated with bound excitons. It was concluded that green luminescence efficiency is maximized when excitons are localized in the vicinity of green-emitting defects.

The excitation mechanism of green-emitting defects is further explored in Chap. 6. Photoluminescence excitation measurements independently verify that the green band photoluminescence intensity directly correlates with the photogenerated exciton population. The spatial distributions of green-emitting defects and nonradiative traps are elucidated by an innovative combination of quantum efficiency and time-integrated/resolved photoluminescence measurements using one-photon and two-photon femtosecond excitation sources. These measurements take advantage of the drastically different absorption coefficients for one- and two-photon excitations to provide details about the types and concentrations of surface and bulk defects and to demonstrate the non-negligible effects of reabsorption. A comparison of results for unannealed and annealed ZnO samples indicates that the annealing process creates a high density of green-emitting defects near the surface while simultaneously improving the bulk material quality by reducing the density of bulk nonradiative traps. Because the green-emitting defects are concentrated near the surface of the material, the green luminescence efficiency is largely determined by the relative densities of these defects and of the nonradiative surface traps that provide an alternate recombination channel.

The results of Chap. 6 are discussed in the context of a simple rate equation
model that accounts for the quantum efficiencies of near-band-edge luminescence and green luminescence. This model is extended in Chap. 7 to explain qualitatively the excitation density dependence of both luminescence bands. For both femtosecond pulsed and continuous-wave excitations, the green band efficiency is found to decrease with increasing excitation, while the near-band-edge emission efficiency increases. Two possible explanations—the hot phonon effect and the trap saturation model—are proposed to account for these new results. Regardless of the interpretation, it is shown that the exciton formation efficiency is reduced under high excitation. The green luminescence mechanism, which was shown in previous chapters to depend on the existence of a stable exciton population, is very sensitive to this change in dynamics.

Implications of the results from Chaps. 4–7 are briefly discussed from a phosphor/device perspective in Chap. 8. Sulfur doping is discussed as a possible technique to increase the overall quantum efficiency and to reduce the sensitivity of green luminescence efficiency to high excitation densities. Future work regarding the dependence of ZnO’s optical properties on the concentration of sulfur dopant is outlined.
Chapter 2

Theory of Photoluminescence in ZnO

Photoluminescence (PL) spectroscopy is a powerful tool for the study of carrier and energy transfer dynamics in semiconductors because meaningful information is obtained in a remote, nondestructive fashion. All of the experimental results discussed in this dissertation are based on PL measurements of ZnO nano- and microstructures. This chapter provides a theoretical framework for the mechanisms leading to radiative recombination in ZnO and thus provides context for the data presented in subsequent chapters. The creation of nonequilibrium carrier densities by means of optical excitation is discussed in Sec. 2.1. How the carriers eventually recombine radiatively is discussed in Sec. 2.2 for near-band-edge recombination (exciton-related emission), and in Sec. 2.3 for the infamous green band (defect-related emission). General optical effects which influence both types of radiative recombination are the subject of Sec. 2.4.

2.1 Free Carrier Generation

In the linear (low-intensity) regime of optical excitation, free electron-hole pairs are created by one-photon absorption of above-gap radiation. The excitation irradiance $I_{\text{exc}}$ inside the sample at a depth $z$ is well approximated by Beer’s Law,

$$\frac{dI_{\text{exc}}(z)}{dz} = -\alpha_1 I_{\text{exc}}(z) \implies I_{\text{exc}}(z) = I_{\text{exc}}(0)e^{-\alpha_1 z}, \quad (2.1)$$
where $I_{\text{exc}}(0)$ is the incident irradiance at the sample surface ($z = 0$) and $\alpha_1$ is the linear absorption coefficient at the wavelength of excitation. For the case of ZnO, $\alpha_1 \sim 2 \times 10^5 \text{ cm}^{-1}$ for excitation energies $\hbar\omega_{\text{exc}}$ higher than the band gap; incident radiation is therefore attenuated exponentially on a characteristic length scale (or “optical penetration depth”) of $\alpha_1^{-1} \sim 50 \text{ nm}$.

Because the excited carrier densities are spatially inhomogeneous and are concentrated near the surface of the material, free electrons and holes will diffuse away from the surface in an effort to achieve an equilibrium spatial charge distribution. ZnO samples similar to the ones studied in this dissertation typically exhibit $n$-type conductivity in the $10^{16} - 10^{18} \text{ cm}^{-3}$ range [33,52,53]. For low to moderate excitation densities ($n_{\text{exc}} \ll 10^{17} \text{ cm}^{-3}$), the equilibrium free-electron spatial distribution is not significantly perturbed by photoexcitation; therefore, the initial spatial distribution and subsequent diffusion of minority carriers (holes) largely determine the sample’s optical response.

The sample surface is such a strong perturbation of the lattice that some carriers diffuse to the surface and quickly recombine nonradiatively. For ZnO nanostructures in particular, the non-uniform spatial generation of free carriers and the effects of surface recombination are important because at least one dimension of the nanostructures is comparable to the optical penetration depth ($\sim 50 \text{ nm}$) and the hole diffusion-drift length ($\sim 20 \text{ nm}$).

A reasonable approximation for the photogenerated minority carrier density $p$ is obtained from a one-dimensional steady-state diffusion equation which takes into account surface recombination and the spatial profile of photoexcitation in a sample of thickness $d$ [54–56]:

$$\frac{d^2 p}{dz^2} - \frac{p}{L_p} + \frac{\alpha_1 I_{\text{exc}}(0)}{D_p \hbar \omega_{\text{exc}}} e^{-\alpha_1 z} = 0,$$

$$ \tag{2.2}$$
subject to the boundary conditions

\[ D_p \frac{dp}{dz} \bigg|_{z=0} = S_p p(z = 0), \quad D_p \frac{dp}{dz} \bigg|_{z=d} = -S_p p(z = d). \]

The solution to this equation is shown in Fig. 2.1(a) for above-gap excitation of a sample with thickness \(d = 150\ \text{nm}\), hole diffusion-drift length \(L_p = 20\ \text{nm}\), and ratio of surface recombination velocity \((S_p)\) to diffusion coefficient \((D_p)\) of \(S_p/D_p = 0.08\ \text{nm}^{-1}\). These numerical values have been chosen because they were obtained experimentally for ZnO:Zn phosphor powders very similar to those discussed in Chaps. 4–7 of this dissertation [55]. Figure 2.1(a) illustrates the significant effect of surface recombination: The hole concentration deviates drastically from the exponentially decaying irradiance \(I_{exc}\) near the surface of the material, such that the maximum hole concentration occurs at roughly a diffusion length into the sample rather than at the surface.

ZnO is essentially transparent to low-intensity radiation of energy below the band
gap; however, the regime of nonlinear absorption and multiphoton excitation is easily reached using femtosecond pulsed excitation from the optical parametric amplifier described in Appendix A. Higher-order absorption processes can be approximated by an extension of Eq. (2.1):

\[
\frac{dI_{\text{exc}}}{dz} = -\alpha_1 I_{\text{exc}} - \sum_{m\geq2} \alpha_m I_{\text{exc}}^m,
\]

where \(\alpha_m\) is the nonlinear absorption coefficient characterizing the strength of \(m\)-photon absorption [57].\(^1\)\(^2\) Both two- and three-photon absorption have been observed in ZnO for peak irradiances in the range 0.1-1 GW cm\(^{-2}\) (corresponding to moderate femtosecond excitation fluences of 10-100 \(\mu\)J cm\(^{-2}\)). For a typical excitation energy of 1.91 eV (650 nm), nonlinear absorption coefficients of bulk ZnO are \(\alpha_2 \sim 3 \times 10^{-11} \text{ m W}^{-1}\) and \(\alpha_3 \sim 1 \times 10^{-25} \text{ m}^3 \text{ W}^{-2}\) [57, 60, 61]. For reasons not yet fully understood, thin films and nanostructures of ZnO exhibit significantly higher nonlinear absorption coefficients (for example, \(\alpha_2 \sim 3 \times 10^{-9} \text{ m W}^{-1}\)) [62, 63].

Even for such strong nonlinear absorption, \(< 1\%\) of incident light is absorbed across a sample of sub-micrometer thickness \(d\). In this case, the exciting photon flux is essentially constant throughout the thickness of the sample, and the resulting minority carrier profile can be estimated by removing the exponential factor in Eq. (2.2). The result is shown in Fig. 2.1(b), where all of the other parameters are the same as in Fig. 2.1(a). For two-photon excitation, then, the photogenerated carrier

\(^1\)Equation (2.3) is obtained by solving Maxwell’s equations for the laser pulse’s complex electric field in the slowly varying envelope and thin sample approximations [58]. The former approximation is valid spatially because the laser spot size (\(\geq 100 \mu\)m) is much greater than the pulse’s center wavelength (\(< 0.1 \mu\)m), and it is valid temporally because the laser pulse width (\(\sim 100 \text{ fs}\)) is much greater than the optical period (\(\sim 0.1 \text{ fs}\)). The latter approximation is valid because the laser beam’s Rayleigh length (\(> 1,000 \mu\)m) is larger than the sample thickness (\(\sim 1 \mu\)m).

\(^2\)Absorption of exciting photons by the photoexcited free carriers themselves has been neglected because the effect is negligible for femtosecond excitation [59].
density peaks in the center of the material and is significantly reduced at both \( z=0 \) and \( z=d \) due to surface recombination.

For both continuous-wave and pulsed excitations, it is important to estimate the three-dimensional density \( n_{\text{exc}} \) of photoexcited electron-hole pairs. A reasonable estimate of \( n_{\text{exc}} \) for \( m \)-photon excitation is given by

\[
 n_{\text{exc}} = \frac{A I_{\text{exc}} \tau}{(m \hbar \omega_{\text{exc}}) l},
\]  

(2.4)

where \( A \) is the fraction of excitation irradiance \( (I_{\text{exc}}) \) at energy \( \hbar \omega_{\text{exc}} \) which is absorbed by the sample, \( l \) is the characteristic length scale over which free carriers are photogenerated, and \( \tau \) is a characteristic time scale defined as follows: For continuous wave excitation, \( \tau \) is the characteristic lifetime of the dominant free carrier recombination mechanism. In ZnO samples where the radiative quantum efficiency is low \( (\lesssim 1\%) \), free electron/hole populations decay in \( \tau \sim 10 \) ps \([55, 64, 65]\); on the other hand, in samples where the defect-related radiative efficiency is high \( (\gtrsim 50\%) \), \( \tau \) is determined by the characteristic recombination time of this radiative mechanism \( (\tau \sim 250 \) ns\). For femtosecond pulsed excitation, the duration \( \tau_{\text{exc}} \) of the exciting pulse is much shorter than all of the carriers’ relaxation time scales and \( \tau \equiv \tau_{\text{exc}} \).

The characteristic length scale \( l \) in Eq. (2.4) is different for one-photon and two-photon excitation. For one-photon excitation, one generally finds in the literature \( l \equiv \alpha_1^{-1} \) for samples with thicknesses larger than the optical penetration depth \( (d > \alpha_1^{-1}) \). However, it is more accurate to take into account minority carrier diffusion if \( L_p \gtrsim \alpha_1^{-1} \):

\[
l \equiv \alpha_1^{-1} + L_p.
\]

This definition is suitable for the ZnO samples under consideration in Chaps. 4-7. Using the previously mentioned values of \( \alpha_1^{-1} = 50 \) nm and \( L_p = 20 \) nm for ZnO yields

14
\( l \approx 70 \text{ nm}. \) For multiphoton excitation (specifically two-photon excitation in this dissertation), the effective optical penetration depth is much larger than the sample thickness \( d \), so \( l \equiv d \).

## 2.2 Exciton Formation and Luminescence

### 2.2.1 Exciton Formation

The direct nature of ZnO’s band gap yields a dipole-allowed, band-to-band transition exhibiting large oscillator strength. As a consequence, excitons form readily and couple strongly to the radiation field (the latter being characterized by electric field \( E \) and wave vector \( k \)). The valence band of ZnO is split into three levels due to crystal field and spin-orbit effects. The excitons corresponding to these valence bands are denoted A-, B-, and C-excitons in order of increasing energy gap, and their optical excitation selection rules differ according to the symmetries of the three valence bands: The A- and B-excitons are primarily transverse in nature (\( \Gamma_5 \) symmetry, polarized perpendicular to the \( c \)-axis) and are most optically active for \( E \perp c \) (either \( k \parallel c \) or \( k \perp c \)). The C-exciton is primarily longitudinal in nature (\( \Gamma_1 \) symmetry, polarized parallel to the \( c \)-axis) and is most optically active for \( E \parallel c \), \( k \perp c \) [66–68].

The energetic separation of the A- and B-excitons (\( \sim 10 \text{ meV} \)) is smaller than that of the B- and C-excitons (\( \sim 40 \text{ meV} \)), but all three excitons possess a binding energy of \( E_{\text{X}}^b \sim 60 \text{ meV} \) [67]. The samples studied in Chaps. 4–7 of this work consist of macroscopic clusters of randomly oriented ZnO particles. The angle between the \( c \)-axis of an individual particle and \( E, k \) of the excitation light is arbitrary. Therefore, for both one-photon (p-polarized) and two-photon (s-polarized) excitations, the selection rules for the creation of all three types of excitons will be satisfied. However,
in practice, the C-exciton is rarely—if ever—observed in PL experiments because it resides in the continuum states of the A- and B-excitons and is strongly damped [69].

Because excitons in ZnO possess such a strong oscillator strength, excitonic processes are understood most properly in the framework of the exciton polariton, i.e. the mixed states of excitons and photons [24,69]. Exciton polaritons arise from the coupling of the exciton’s quadratic dispersion to the linear dispersion of light propagating through a dielectric (Fig. 2.2). The experiments in this dissertation will largely be confined to a regime where both the sample/lattice temperature \((k_B T_L \sim 8-25 \text{ meV})\) and the exciton linewidth \((\sim 30-120 \text{ meV})\) are larger than the longitudinal-transverse splittings of the excitons \((\Delta_{LT} = 2 \text{ meV}, 10 \text{ meV}, 12 \text{ meV} \text{ for A-, B-, and C-excitons, respectively})\); therefore, exciton polariton effects will not be manifested directly in the luminescence measurements. However, the fundamental concept of the exciton polariton—the cyclic exchange of energy between a Coulomb-correlated electron-hole pair and a photon—remains relevant to the propagation and luminescence of free excitons, as discussed below.

Due to the polar nature of ZnO, the Fröhlich interaction between free charge carriers and longitudinal optical (LO) phonons is rather strong. The dominant LO phonon for ZnO possesses symmetry \(E_1\) (polarized perpendicular to \(c\)) and energy \(h \omega_{LO} = 72 \text{ meV}\) [66, 71]. Thus, if the energy of photoexcitation greatly exceeds the band gap \([(h \omega_{exc} - E_g) \gg h \omega_{LO}]\), then free electrons and holes initially dissipate excess energy in increments of 72 meV; once their excess energy is less than \(h \omega_{LO}\), they dissipate excess energy by emission of acoustic phonons. When the relaxing free electrons and holes have excess energy \(\lesssim E_b^X / 2\), they begin to form free excitons. In bulk ZnO, this exciton formation process occurs in \(\sim 2 \text{ ps}\) at room temperature; in ZnO nanostructures, the characteristic exciton formation time is shorter \(\sim 0.2 \text{ ps}\) due to reduced overall carrier lifetimes (increased nonradiative recombination) [64,72].
Figure 2.2: Approximate room-temperature dispersion for the transverse A- and B-exciton polaritons (solid lines). The longitudinal and transverse resonance energies (subscripts “L” and “T,” respectively) for A- and B-excitons are denoted at \( k = 0 \). The linear dispersion of the uncoupled photon (near-vertical dashed line) as well as exemplary quadratic dispersions of uncoupled excitons are also shown. (After Lagois [70].)

In any case, the excitons finally thermalize to a Boltzmann-like distribution primarily on the transverse exciton-like portions of the various exciton polariton branches (\( k \gtrsim 8 \) in Fig. 2.2). This thermalization process occurs on a time scale of \( \lesssim 10 \) ps, which is much shorter than that of radiative recombination (> 100 ps) [69]. The exciton distribution is characterized by a temperature \( T_X \) which is greater than or equal to the lattice temperature \( T_L \).

### 2.2.2 Free Exciton Luminescence

Once the exciton polariton (hereafter, simply “exciton”) has formed, it propagates through the sample and is potentially trapped by a defect or scattered by impurities
or phonons. Due to reabsorption effects, the exciton is most likely to reach the surface if it is formed near the surface of the material, within an “escape depth” defined by the inverse extinction coefficient at the exciton energy $[\alpha^{-1}(E_X) \sim 70 \text{ nm for ZnO}]$. In the event that the exciton does reach the surface of the sample, the probability of light being emitted from the material is further reduced by reflection from the sample–air interface, as described in Sec. 2.4.

The small amount of free exciton (or “zero-phonon”) luminescence that does emerge from the sample is expected to have a spectral distribution that reflects 1) the Maxwell-Boltzmann-like distribution of the excitons and 2) a shape function $S(\hbar \omega)$ corresponding to energy conservation in the radiative transition [54]:

$$I_{X-0\text{LO}}(\hbar \omega) \sim S(\hbar \omega - E_X) e^{-\hbar \omega/k_B T_X}, \quad (2.5)$$

where $E_X$ is the energy of the exciton resonance and $\hbar \omega$ is the energy of the emitted photon. As discussed in Sec. 2.2.1, technically there are two excitons (A and B) to consider for ZnO. The majority of the experimental work discussed in subsequent chapters was performed at temperatures $k_B T_L$ higher than the energy separation of the A- and B-excitons ($E_B^X - E_A^X \sim 10 \text{ meV}$), and this energy separation in turn is very small in comparison to the exciton energies themselves ($E_B^X, E_A^X \sim 3.31 \text{ eV at room temperature}$); therefore, the measured optical signals contain contributions from both excitons, and it is simpler to refer henceforth to a single, effective exciton with energy $E_X$.

For the case of moderate exciton-phonon coupling (as is the case for ZnO), the line shape function is expected to be Gaussian with standard deviation $\sigma$, thus leading to a zero-phonon exciton luminescence band that is Gaussian in shape but redshifted from the exciton resonance $E_X$ by $\sigma^2/k_B T_X$ [54, 73]. This redshift can be made
explicit by substituting the Gaussian shape function for $S(\hbar \omega - E_X)$ in Eq. (2.5) and rearranging terms:

$$I_{X-0\text{LO}}(\hbar \omega) \sim e^{-(\hbar \omega - E_X)^2/2\sigma^2} e^{-\hbar \omega/k_B T_X}$$

$$= e^{-(\hbar \omega - (E_X - \sigma^2/k_B T_X))^2/2\sigma^2} e^{-(E_X - \sigma^2/2k_B T_X)/k_B T_X}.$$ 

The Gaussian parameter $\sigma$ is a function of both temperature and phonon energy [74], but it is generally on the order of $k_B T_X$ [54]. Therefore, the X-0LO peak position is expected to lie in the range $(E_X - k_B T_X) \lesssim \hbar \omega_{\text{max}}^{X-0\text{LO}} < E_X$.

The temporal decay of free exciton luminescence is expected to be exponential in nature because the radiative emission probability is simply proportional to the exciton population (as opposed to band-to-band recombination, where the probability depends on the product of electron and hole populations). Nonradiative recombination and thermal dissociation of excitons both cause the observed exciton PL to decay faster than the intrinsic recombination lifetime of several nanoseconds, but in principle these processes do not change the shape of the luminescence decay.

2.2.3 Phonon-Assisted Exciton Luminescence

Phonon-assisted exciton luminescence is a very important aspect of near-band-edge luminescence in ZnO. For above-gap, nonresonant photoexcitation, many LO phonons are generated during the initial carrier cooling process. The moderate strength of exciton-phonon coupling in ZnO leads to a high probability that an exciton will simultaneously impart some of its energy and momentum to one or more of these LO phonons and undergo a radiative transition. Such phonon-assisted transitions are further favored from an external optical point of view because the emitted photons possess energy $\hbar \omega < E_X$ and therefore experience less reabsorption than free exciton
luminescence (Sec. 2.4).

Assuming the exciton distribution is well approximated by a Boltzmann distribution, the $m^{th}$ phonon replica $(X-m\text{LO})$ for $m>0$ has a line shape given by

$$I_{X-m\text{LO}}(h\omega) \sim \left[ \frac{\epsilon^{1/2} e^{-\epsilon/k_B T_X}}{\epsilon_p} \right] \epsilon^p,$$

(2.6)

where $\epsilon = h\omega + mh\omega_{\text{LO}} - E_X$ is the exciton’s kinetic energy, $h\omega$ is the energy of the emitted photon, $h\omega_{\text{LO}}$ is the LO phonon energy, and $E_X$ is the free exciton energy at $k = 0$ [75]. The bracketed term in Eq. (2.6) represents the product of exciton density of states and occupation probability at kinetic energy $\epsilon$, and the remaining factor in Eq. (2.6) represents a common approximation for the phonon-assisted transition probability [75]. The exponent $p$ in the transition probability is usually taken to be $p=1$ for the first phonon replica ($m=1$) since the density of LO phonon final states under momentum conservation scales with $\epsilon$ [69]. For $m>1$, one usually takes $p=0$ since many combinations of LO phonon wave vectors will satisfy momentum conservation. An important consequence of this fact is that phonon replicas for $m \geq 2$ involve excitons of all kinetic energies; therefore, the line shapes of these replicas directly reproduce the kinetic energy distribution of the overall exciton population [69,75].

Differentiation of Eq. (2.6) indicates that the $m^{th}$ LO phonon replica’s peak position should be at photon energy

$$h\omega_{\text{max}}(m>0) = E_X - mE_{\text{LO}} + (p + 1/2)k_B T_X.$$

(2.7)

Thus, the kinetic energy of the excitons causes the replica peak positions to be blueshifted from their naively expected positions at $E_X - mh\omega_{\text{LO}}$. 

20
Figure 2.3: (a) Components of ZnO’s PL spectrum at room temperature. The contributions from free exciton (X-0LO) emission and the first two phonon replicas (X-1LO and X-2LO) are shown. (b) Schematic diagram of the phonon-assisted exciton luminescence process. An exciton with wave vector $k_X$ on the exciton-like portion of the exciton polariton dispersion scatters to the photon-like portion of the dispersion by creation of LO phonons whose wave vectors $k_{LO}$ satisfy momentum conservation. (After Fig. 13.12 of Klingshirn [69].)

A graphical summary of the theoretical near-band-edge luminescence for ZnO is shown in Fig. 2.3 for $T_X = T_L = 295$ K. The X-$m$LO ($m = 0, 1, 2$) lineshapes are shown in Fig. 2.3(a), with emphasis on the deviations of their peak positions from the energies $E_X - m\hbar\omega_{LO}$ as discussed above. The phonon-assisted recombination processes are shown schematically in Fig. 2.3(b), where an exciton on the exciton-like portion of the exciton polariton dispersion curve transitions to the photon-like portion of the curve by scattering with LO phonons.

2.2.4 Bound Exciton Luminescence

The results of Secs. 2.2.2 and 2.2.3 apply in principle to ZnO luminescence at all temperatures for which excitons are stable and free to propagate through the material. However, at sufficiently low lattice temperatures ($T_L \lesssim 230$ K), excitons are frequently localized at impurity or defect sites in the lattice due to a Coulomb binding of one
carrier in the electron-hole pair to the impurity or defect. The exciton luminescence resulting from this bound exciton is therefore redshifted from the energy of a free exciton by an amount corresponding to the localization energy $E_{\text{loc}}$ of the exciton to the impurity/defect. The most common case for ZnO is an exciton bound to a defect or impurity serving as a neutral shallow donor, although excitons bound to ionized donors and neutral acceptors have also been reported.

These three types of bound exciton transitions are illustrated schematically in Fig. 2.4. The Coulomb binding (dashed ellipse) of the electron in the conduction band (C.B.) to the hole in the valence band (V.B.) reduces the free exciton energy ($E_X$) from that of the band gap ($E_g$). Excitons may be bound to a neutral donor (nDBE), ionized donor (iDBE), or neutral acceptor (nABE) with respective exciton localization energies $E_{\text{nDBE}}^{\text{loc}}$, $E_{\text{iDBE}}^{\text{loc}}$, $E_{\text{nABE}}^{\text{loc}}$. The binding energies $E_b$ of the donor electron to its donor site and the acceptor hole to its acceptor site are also shown.
electrostatically bound to a neutral donor (nDBE), ionized donor (iDBE), or neutral acceptor (nABE). The respective localization energies $E_{\text{loc}}$ of the exciton to these donors/acceptors are distinct from the binding energies $E_{\text{b}}$ of the donor electron to its donor site and the acceptor hole to its acceptor site (the latter binding energies being defined as the energetic distance between the donor/acceptor level and the conduction/valence band).

**Table 2.1:** Summary of bound exciton lines in ZnO at low temperature. Energy values are averaged over several reported values in the literature [76–78], as tabulated in Ref. 67. The uncertainties in parentheses indicate the standard deviations from this averaging process. A dash (-) in parentheses indicates that no averaging was performed due to a lack of data.

<table>
<thead>
<tr>
<th>PL line</th>
<th>photon energy (eV)</th>
<th>localization energy (meV)</th>
<th>binding energy (meV)</th>
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<td>$X$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$I_0$</td>
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<td>4.1(9)</td>
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<td>3.3711(8)</td>
<td>5.6(14)</td>
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<td>7.5(7)</td>
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</tr>
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<td>9.1(10)</td>
<td></td>
</tr>
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<td>3.3664(2)</td>
<td>10.4(9)</td>
<td></td>
</tr>
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<td>15.3(9)</td>
<td>51.9(69)</td>
</tr>
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</tbody>
</table>

The low-temperature PL spectrum of ZnO is very rich due to a large number of bound exciton complexes. The most prominent lines are labeled $I_n$ ($n=0,1,2,\ldots,11$) in order of decreasing energy according to the notation of very early work on the
subject [2]. The observed PL transition energies are summarized in Table 2.1. The values listed are averages over three of the most recent experimental works on bound excitons in ZnO [76–78]. Where available, the corresponding exciton localization and donor/acceptor binding energies are also listed. There is a surprising amount of controversy to this day on the assignment of the various lines to donor- or acceptor-bound excitons. The general consensus is that lines $I_3$ to $I_8$ are due to neutral donors, whereas $I_9$ to $I_{11}$ have variously been attributed to neutral donors [76] or acceptors [77]. Similarly, the lines $I_0$ to $I_2$ have been attributed to B-excitons bound to neutral donors and excited rotator states of A-excitons bound to neutral donors [77, 79], or alternatively to A-excitons bound to neutral and ionized donors only [76].

The study of bound exciton luminescence is important because it provides information about what impurities/defects (and their relative concentrations) are present in a given sample of ZnO. Such information will be used in Chap. 5 to draw conclusions not only about what impurities/defects are present, but also the interdependence of exciton- and defect-related luminescence bands.

## 2.3 Green Defect-Related Radiative Recombination

The defect-related green band emission studied in this dissertation is spectrally broad, unstructured, asymmetric, and peaked significantly below the band gap of ZnO. These spectral features are common to many defect luminescence bands in wide-bandgap semiconductors and ionic insulators, and they are indicative of strong electron-phonon coupling in the material. Such luminescence bands are generally described at least qualitatively in terms of a one-dimensional configuration coordinate diagram, as illustrated in Fig. 2.5(a) [80–83]. Whether the defect consists of an impurity, a lattice defect (vacancy, interstitial atom, etc.), or a complex involving both, its
Figure 2.5: (a) Schematic diagram of the one-dimensional configuration coordinate model. Transitions from the zero vibrational level of the excited electronic state to various vibrational levels of the ground excited state give rise to a broad, unstructured luminescence band (b). (After Reshchikov and Morkoç [80].)

overall potential energy is considered to depend primarily on a single mode of lattice vibration. In its relaxed state, the defect’s total potential energy (electronic plus nuclear) is approximately parabolic with an energetic minimum corresponding to zero atomic displacement. This ground electronic state is coupled to the lattice through equally spaced vibrational modes whose spacing corresponds to a local, defect-specific phonon mode.

Through interaction with photogenerated carriers (e.g., capture of a hole), the defect can be excited into its first potential energy excited state. The minimum of the excited state potential occurs at a nonzero value of atomic displacement because the capture of a photogenerated carrier has caused the complex’s atoms to shift from their relaxed positions. If the local phonon mode spacing of the excited electronic state exceeds $k_B T_L$, then radiative transitions occur from the lowest vibrational level of the excited state to a manifold of vibrational levels within the ground electronic state. As indicated in Fig. 2.5(b), the spectral width of the resulting emission band depends on the “width” of the zero vibrational level of the excited state, which in turn
affects how many ground state vibrational levels are coupled to it. The band’s peak position and amount of asymmetry are related to the extent of atomic displacement which occurs in the excited state. For cases such as ZnO, where electron-phonon coupling is relatively strong, the Stokes shift from the band edge is significant, and the band exhibits distinct asymmetry.

This model has been applied quantitatively in the case of ZnO green band emission by Leiter et al. [84]. They deduced a local phonon mode energy of $\hbar \omega_{\text{loc}} = 39 \text{ meV}$ (assumed to be the same for both ground and excited states) and an absorption peak at 3.4–3.5 eV. This direct absorption band of the defect is presumably obscured by the much stronger band-to-band absorption transition except in very pure samples and at very low lattice temperatures ($T_L < 10 \text{ K}$). In light of the continued controversy over the origin of green emission in ZnO, the interpretation of Leiter et al. is perhaps not definitive; nevertheless, it illustrates the usefulness of the simple configuration coordinate model specifically for the case of ZnO.

### 2.4 Escape of Radiation from ZnO: Optical Effects

After free electron-hole pairs are photoexcited as described in Sec. 2.1, they relax and recombine by the mechanisms discussed in Secs. 2.2 and 2.3. Regardless of the specific radiative recombination mechanism responsible for PL at a certain wavelength, there are optical effects which limit the amount of internally generated luminescence that actually emerges from the sample. Specifically considered here are the effects of reabsorption and Fresnel reflections from the sample–air interface in affecting the intensity and spectral distribution of experimentally observed PL.

Figure 2.6 illustrates the approximate spectral dependence of the absorption coefficient and index of refraction for ZnO at room temperature [85]. ZnO is moderately
birefringent ($\Delta n = 0.021$), so the curves represent average responses of light polarized perpendicular and parallel to the crystal’s $c$-axis \cite{16}.

The effect of reabsorption on the fraction of PL emerging from the sample depends on the spatial distribution of carriers $p(z)$, i.e., whether the recombining carriers are concentrated near the surface of the material (one-photon excitation) or are distributed uniformly throughout the entire thickness of the material (two-photon excitation). The fraction $f_{\text{esc}}^{\text{reab}}$ of internally generated PL that reaches the sample surface ($z = 0$) and escapes without being reabsorbed also depends on the strength of the absorption coefficient $\alpha_1$ at the emitted photon energy ($\hbar \omega$) \cite{54}:

$$f_{\text{esc}}^{\text{reab}}(\hbar \omega) = \frac{\int_0^d [p(z) e^{-\alpha_1(\hbar \omega)z}] \, dz}{\int_0^d [p(z)] \, dz},$$

where $d$ is the sample thickness.
Figure 2.7: Fraction of internally generated photoluminescence that emerges from a ZnO sample for (a) one-photon and (b) two-photon excitation subsequent to Fresnel reflection ($f_{\text{refl}}$), reabsorption ($f_{\text{reab}}$), and their combined effect ($f_{\text{esc}}$). The spatial distributions of minority carriers are assumed to be the same as indicated in Fig. 2.1.

The escape fraction $f_{\text{esc}}(\hbar\omega)$ is plotted in Fig. 2.7(a) using the minority carrier distribution derived previously for steady-state, one-photon excitation of a ZnO sample with thickness $d = 150$ nm [Fig. 2.1(a)]. Similarly, the fraction $f_{\text{esc}}(\hbar\omega)$ plotted in Fig. 2.7(b) corresponds to $p(z)$ for two-photon excitation [Fig. 2.1(b)]. Even for such a thin sample, reabsorption significantly reduces the experimentally measurable PL intensity near the band edge for both one-photon and two-photon excitations. Reabsorption attenuates the PL more for the case of two-photon excitation because the recombining free carriers are located more uniformly throughout the material, and the generated photons on average must propagate farther before reaching the sample surface. The difference in $f_{\text{esc}}(\hbar\omega)$ for one-photon versus two-photon excitation becomes more pronounced as the sample thickness increases (and therefore the surface-to-volume ratio decreases), as shown in Fig. 2.8 for photon energy $\hbar\omega = 3.4$ eV. Indeed, the fraction $f_{\text{esc}}$ asymptotically scales as the sample’s surface-to-volume ratio, $1/d$.

When the PL generated at a particular photon energy $\hbar\omega$ propagates through the
material and reaches the ZnO–air interface, it will be totally internally reflected if the angle of incidence $\theta$ is larger than the critical angle $\theta_c(h\omega) = \sin^{-1}[1/n(h\omega)]$ [86]. Light incident at angles $\theta \leq \theta_c$ comprises a cone of luminescence that may be “transmitted” and hence experimentally accessible. The transmittance of light within this luminescence cone may be estimated by integrating the relevant Fresnel equations over all angles $\theta \leq \theta_c$:

$$f_{\text{refl}}(h\omega) = \left(\frac{1}{2\pi}\right) \int_0^{2\pi} \int_0^{\theta_c(h\omega)} \left\{ \frac{\sqrt{1 - n^2 \sin^2 \theta}}{n \cos \theta} [t(\theta, h\omega)]^2 \right\} \sin \theta \, d\theta \, d\phi , \quad (2.8)$$

where $t(\theta, h\omega)$ is the angle- and polarization-dependent Fresnel equation for transmission of photons with energy $h\omega$ at a dielectric–air interface [87].

The escape fraction $f_{\text{esc}}(h\omega)$ averaged over both polarizations of emitted light is shown in Fig. 2.7. This fraction is the same for both types of excitation because it depends only on the index of refraction mismatch at the ZnO–air interface. Total internal reflection plays a dominant role in reducing the measurable PL: An index of refraction in the range $n = 2.0–2.5$ (Fig. 2.6) corresponds to a range of small critical angles $\theta_c = 24^\circ–30^\circ$. The solid angle of the corresponding cone of luminescence is therefore $\Omega_c = 2\pi(1 - \cos \theta) = 0.54 - 0.84$ sr. When normalized to the solid angle $\Omega_h = 2\pi$ sr of a hemisphere (corresponding to no index mismatch, i.e., $\theta_c = \pi/2$), the corresponding ratios are $\Omega_c/\Omega_h = 0.086 - 0.13$. The small emission cone is therefore largely responsible for the maximum value of $f_{\text{esc}} \sim 10\%$ shown in Fig. 2.7.

Also plotted in Fig. 2.7 is the overall estimated fraction of PL that escapes from the sample after taking into account the optical effects of reabsorption and Fresnel reflections:

$$f_{\text{esc}}(h\omega) = f_{\text{esc}}^{\text{refl}}(h\omega) \ast f_{\text{esc}}^{\text{reab}}(h\omega) .$$

---

$^3$The normalization factor of $2\pi$ is obtained by performing the integrals for the case $n = 1$ ($\theta_c = \pi/2$).
Figure 2.8: Fraction of internally generated photoluminescence (emission energy $\hbar \omega = 3.4 \text{ eV}$) that reaches the surface of a ZnO sample without being reabsorbed for increasing sample thickness $d$. For two-photon excitation, $f_{\text{esc}}$ asymptotically scales as the sample’s surface-to-volume ratio ($1/d$).

The experimentally measured PL is especially altered in both intensity and spectral shape near the band-edge resonances; however, the ZnO–air index mismatch also significantly limits the probability of radiation escape at visible photon energies where ZnO is transparent but, in the case of ZnO:Zn, also highly luminescent. It is important to note that the results summarized in Fig. 2.7 represent the approximate effect for a luminescence photon originating within the material during its first attempt to escape the sample. Ultraviolet photons which are internally reflected will be subject to reabsorption until they reach the ZnO–air boundary once again. For realistic ZnO samples where the majority of recombination occurs nonradiatively, luminescence photons with energy $\hbar \omega \gtrsim 3.3 \text{ eV}$ are highly likely to be reabsorbed and then recombine nonradiatively if they do not escape the material on their first “attempt.” In
this case, the fractions displayed in Fig. 2.7 are realistic upper limits on near-band-edge quantum efficiency. On the other hand, for green luminescence ($h\omega < 3 \text{ eV}$) the photons are not subject to reabsorption; if these photons experience total internal reflection on their first escape attempt, then they will simply re-propagate through the material and continue to reflect from the ZnO–air interface until escaping. Based on these elementary considerations alone, the green PL quantum efficiency has a theoretical upper limit of 100%.

2.5 Summary

Excitonic effects are very important when considering the photoluminescence (PL) properties of ZnO because the exciton binding energy is relatively large. Similarly, a large LO phonon energy implies a moderate–strong coupling of both free electrons and excitons to the LO phonons via the Fröhlich interaction. The near-band-edge recombination in ZnO is therefore dominated by free exciton emission and its LO phonon replicas. A second prominent emission band in ZnO is that of defect-related green emission. This emission is associated with a deep defect level of controversial origin. The properties of this band can be understood qualitatively in terms of a simple configuration coordinate diagram which accounts for the band’s general spectral properties through strong electron-phonon coupling.

For luminescence photons originating inside the ZnO sample, reabsorption can significantly affect the externally accessible PL signal if the photon energy lies near the exciton resonance or above the band gap. This effect is more detrimental in the case of two-photon excitation than one-photon excitation because the former excitation’s absorption profile places the photogenerated carriers farther from the surface of the sample. On the other hand, one-photon excitation creates a gradient
of carriers concentrated near the surface, where nonradiative surface recombination significantly reduces the effective carrier concentration.

For both ultraviolet and green PL photons that do reach the surface of the sample, the large index of refraction mismatch between ZnO and air leads to a small emission cone of half-angle $\sim 24-30^\circ$. Using typical parameters for ZnO in conjunction with elementary optical equations suggests an approximate upper limit of $\sim 10\%$ for near-band-edge quantum efficiency. Because the green PL photons experience negligible reabsorption, they eventually escape the sample with 100% probability, albeit after several reflections from the ZnO–air interface.
Chapter 3

Optical Characterization Techniques

The spectroscopic techniques described in this chapter allow experimental observation of the radiative recombination processes described in Chap. 2. Each experiment begins with the creation of a nonequilibrium distribution of carriers by means of optical excitation with photons of energy $\hbar\omega_{\text{exc}}$. Standard sources of optical excitation for ZnO include a continuous-wave HeCd laser ($\hbar\omega_{\text{exc}} = 3.81$ eV), the monochromatized output of a xenon arc lamp, and femtosecond pulses derived from a wavelength-tunable optical parametric amplifier (OPA).¹ While the latter two sources are typically tuned to ultraviolet excitation energies above the band gap of ZnO ($\hbar\omega_{\text{exc}} \gtrsim 3.4$ eV), it is important to note that multiphoton excitation of ZnO can be achieved by tuning the OPA to visible or infrared wavelengths such that $m\hbar\omega_{\text{exc}} \gtrsim 3.4$ eV for $m$-photon excitation ($m = 2, 3, \cdots$). The importance of this alternative to traditional one-photon excitation will be emphasized in Chap. 6.

3.1 Time-Integrated Photoluminescence and Photoluminescence Excitation

Radiative recombination of photoexcited carriers is readily observed using the setup depicted in Fig. 3.1. The exciting beam of light illuminates the sample at an angle $\sim 5^\circ$ from normal incidence.² A cone of the emitted photoluminescence (PL) is collected and collimated by an aluminum off-axis parabolic mirror (5.1 cm diameter, 33

¹The femtosecond laser system is described in more detail in Appendix A.
²The sample can optionally be placed in a liquid nitrogen or closed-cycle helium cryostat to obtain lattice temperatures from room temperature down to 88 K and 12 K, respectively.
Figure 3.1: Experimental setup for time-integrated photoluminescence measurements.

15 cm effective focal length). The exciting beam’s angle of incidence is chosen so that the specular reflection of exciting light from the sample surface is not directly collected by the mirror. The collimated PL is directed to a second, identical off-axis parabolic mirror that focuses the PL into an all-silica optical fiber (numerical aperture 0.22). The parameters of the mirrors are chosen such that the half-angle of the converging PL $[\tan^{-1}(2.5 \text{ cm}/15 \text{ cm}) = 9.5^\circ]$ is less than the fiber’s half-angle of acceptance ($13^\circ$). When possible, a color filter is placed in front of the fiber input so that scattered excitation light is absorbed by the filter and only the PL is transmitted to the detection system. The fiber provides convenient coupling of the PL into a 30 cm spectrometer, where the emission is spectrally dispersed and imaged onto a liquid-nitrogen-cooled charge-coupled device (CCD). A combination of spectrometer slit width and CCD exposure time is chosen to optimize system resolution and signal intensity while avoiding saturation of the CCD.

The use of reflective optics rather than lenses is motivated by the broadband nature of the PL from ZnO and by the need to use various wavelengths of exciting light. Chromatic dispersion in the system is thus minimized. However, the optical system’s spectral sensitivity is not constant. The correct spectral distribution of
the PL intensity is obtained as follows: A tungsten halogen lamp is placed at the sample position, and its spectrum $I_{bb\text{meas}}(\lambda)$ is measured using the same parameters as were used to measure the sample’s PL. To a good approximation, the lamp’s actual spectrum is that of an ideal black body, $I_{bb\text{ideal}}(\lambda)$. Deviations of the lamp’s measured spectrum from an ideal black body spectrum indicate the spectral response of the optical system. The relative system response at wavelength $\lambda$ is therefore

$$I_{\text{resp}}(\lambda) = \frac{I_{bb\text{meas}}}{I_{bb\text{ideal}}} \propto \frac{I_{bb\text{meas}}}{\lambda^5(e^{hc/\lambda k_B T} - 1)},$$

where $T = 2800$ K is the color temperature of the lamp as specified by the manufacturer.\(^3\) The corrected PL spectrum is then obtained by normalizing the measured PL spectrum to $I_{\text{resp}}(\lambda)$.

A second noteworthy element of processing PL data correctly is conversion of the spectrum from units of wavelength ($\lambda$) to units of energy ($E$). In addition to rescaling the abscissa according to $E = hc/\lambda$, the PL intensity $I_{\text{PL}}(\lambda)$ must be rescaled in order to maintain proper spectral weighting:

$$E \propto \frac{1}{\lambda} \implies dE \propto \frac{d\lambda}{\lambda^2}.$$

Thus, the scaling factor is the square of the wavelength and

$$I_{\text{PL}}(E) \propto \lambda^2 I_{\text{PL}}(\lambda)$$

to satisfy the requirement that $I_{\text{PL}}(E)dE \propto I_{\text{PL}}(\lambda)d\lambda$ [88]. An example PL spectrum processed using these techniques is presented in Fig. 3.2.

\(^3\)The variables $h$, $c$, and $k_B$ have their usual definitions of the Planck constant, the speed of light in vacuum, and the Boltzmann constant, respectively.
Figure 3.2: Example photoluminescence (PL) and photoluminescence excitation (PLE) data for ZnO:Zn micropowder. The spectra were acquired using the setup depicted in Fig. 3.3. The PLE spectrum corresponds to a PL detection energy denoted by the arrow (2.48 eV).

Once a feature of interest has been identified in a PL spectrum, it is natural to address the question of what excitation wavelength most efficiently produces that PL feature. Such an excitation profile is obtained by performing a photoluminescence excitation (PLE) experiment as outlined in Fig. 3.3. The monochromatized output of a 300 W xenon lamp photoexcites the sample. An aluminum-coated spherical mirror collects the resultant PL and focuses it into a 0.75 m monochromator. The detection wavelength of this monochromator is fixed at the position of the PL feature of interest while the excitation wavelength is scanned. The intensity of the PL feature for each excitation wavelength is measured by a photomultiplier tube on the exit port of the monochromator using standard lock-in amplifier detection techniques. The lamp’s spectral intensity distribution varies smoothly throughout ultraviolet/visible
wavelengths; however, the magnitude of variation is significant enough that it must be taken into account. A properly measured spectrum of the lamp intensity is therefore used as a normalization for the raw PLE data. Fig. 3.2 also shows an illustrative PLE trace for the detection energy denoted by an arrow on the corresponding PL spectrum (defect emission from ZnO:Zn micropowder).

### 3.2 External Quantum Efficiency

An important metric for optoelectronic applications of materials such as ZnO is the efficiency with which absorbed energy is converted to useable light. In the case of optical excitation, external quantum efficiency (QE) is defined as

\[
\eta = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}.
\]

Measuring QE for samples such as thin films and powders is not trivial because the emission is not isotropic. Placing the sample inside an integrating sphere for PL measurements overcomes this problem because the emitted PL is redistributed isotropically across the interior surface of the sphere.

Figure 3.4 depicts a method for measuring QE using an integrating sphere as
Figure 3.4: Experimental procedure for measuring external quantum efficiency (QE) using an integrating sphere.

described by de Mello, Wittmann, and Friend [89]. An excitation laser beam is introduced through the input port of a 10 cm diameter sphere. Light impinging on a small exit aperture in the wall of the sphere is fiber-coupled to the spectrometer–CCD detection system described in Sec. 3.1. A reflective cone baffle prevents direct illumination of the optical fiber. The baffle, sample holder, and interior of the sphere are coated with Spectraflect®, a diffuse reflectance coating with >95% reflectance from 300–1300 nm.

Quantum efficiency is calculated from the results of a sequence of three measurements depicted in Fig. 3.4: First, before placing the sample inside the integrating sphere, the excitation beam is introduced and its spectrum is measured [Fig. 3.4(a)]. Upon converting this spectrum to energy units, the spectrally integrated laser intensity $L_a$ represents the total amount of excitation light entering the sphere. The sample is then placed inside the sphere but not in the beam path of the exciting light [Fig. 3.4(b)], and a spectrum spanning both excitation and emission wavelengths is acquired. The spectrally integrated laser intensity, $L_b$, is less than $L_a$ by the amount of diffuse excitation light that has been scattered by the sphere wall and subsequently absorbed by the sample. This absorbed excitation light produces a small amount of PL with integrated intensity $P_b$. Finally, the sample is rotated so that the excitation
source directly illuminates it, and a third spectrum is acquired [Fig. 3.4(c)]. In this case, the integrated laser intensity $L_c$ is significantly reduced because the majority of the excitation is directly absorbed by the sample to produce PL with integrated intensity $P_c$. From this sequence of measurements, the absorption coefficient $A$ and the external quantum efficiency $\eta$ can be deduced [89]:

$$A = \left(1 - \frac{L_c}{L_b}\right) \quad \text{and} \quad \eta = \frac{P_c - (1 - A)P_b}{AL_a}.$$ 

The range of QEs that can be measured with this technique is primarily limited by the dynamic range of the CCD. For the CCD used in this work, an individual pixel has a depth of 16 bits (maximum signal 65,536 counts) and a noise floor of $\sim 100$ counts, corresponding to a minimum detectable efficiency of $\eta_{\text{min}} \approx 0.0015$. Because the PL spectrum is generally much broader than that of the exciting laser, the PL signal is distributed over a larger number of pixels and $\eta_{\text{min}} \lesssim 0.001$ in practice.

Random error in the measurement of $\eta$ is largely determined by the stability of the laser used for excitation and is typically $< 0.1\eta$. The absolute accuracy of $\eta$ deduced from the integrating sphere technique was originally assessed by comparing the results to those obtained by other techniques for measuring QE, and the absolute values were found to agree within 5% [89]. Similar bounds on the systematic errors in this work are expected based on a difference of 5% in the measured and previously reported values of $\eta$ for sulfur-doped ZnO powder [50].

### 3.3 Time-Resolved Photoluminescence

Both the time scale and shape of the decay of a PL feature provide insight into the corresponding physical recombination mechanism. Such information is easily ob-
tained from a streak camera for PL features that decay on time scales $\gtrsim 10$ ps. The time-resolved PL (TRPL) data presented in this dissertation were acquired using an analog streak system (model C4780) manufactured by Hamamatsu. The experimental setup is virtually identical to that described in Sec. 3.1 for time-integrated PL measurements, except 1) the collected PL is instead fiber-coupled to the streak system and 2) the excitation source is restricted to being pulsed (to allow observation of the PL decay between exciting pulses).

Details of the streak camera’s operating principles and specifications are available elsewhere [90]. In short, the streak system disperses the incoming PL horizontally according to wavelength and vertically according to time. The result is a $640 \times 480$ pixel$^2$ intensity distribution of the PL intensity, where the 640 horizontal pixels span $\sim 50–100$ nm (depending on grating selection) and the 480 vertical pixels span a selectable, fixed time window in the range 1 ns–1 ms. An example is shown in Fig. 3.5. The entire PL intensity distribution is shown in Fig. 3.5(a), whereas Figs. 3.5(b)–(c) indicate spectral and temporal “slices” of the PL at the indicated time delay and spectral position, respectively.

The streak system’s overall temporal response to an input optical delta function is $\sim 10$ pixels (full width at half-maximum) regardless of the time window being used. For example, on a 2 ns window, each pixel in the time direction corresponds to approximately $2$ ns/480 pixels $= 4.2$ ps, so the time resolution is approximately 42 ps.

The system’s static spectral response can be taken into account using the black body correction technique described in Sec. 3.1. In addition, the index of refraction dispersion for the optical fiber introduces a wavelength-dependent time delay which becomes relevant for blue/ultraviolet PL wavelengths [Fig. 3.5(d)]. The resultant “tilting” of the TRPL data can be corrected in software using a best-fit polynomial to characterize the fiber’s dispersion.
Figure 3.5: Time-resolved photoluminescence (TRPL) data for ZnO:Zn micropowder. (a) PL intensity distribution as a function of time and wavelength, as measured by the streak camera. (b) Time-integrated PL spectrum corresponding to the temporal range bound by the pair of horizontal arrows. (c) Spectrally integrated PL decay corresponding to the wavelength range bound by the pair of vertical arrows. (d) Wavelength-dependent temporal dispersion of the streak system due to the index of refraction dispersion of the optical fiber.

A specific TRPL feature is generally characterized as a single- or multi-exponential decay,

\[ I_{\text{PL}}(t) = \sum_{i \geq 1} A_i e^{-t/\tau_i}, \]  

(3.1)

where \( \sum A_i = 1 \). If one of these decay components occurs on a time scale comparable to the streak system’s instrument response time, then one must perform a decon-
volution procedure to obtain accurate values for the decay parameters \( \{A_i, \tau_i\} \). In the usual case that the pulse width of exciting light (\( \sim 100 \) fs) is much less than the time resolution of the streak system (\( \geq 25 \) ps), the streak system’s response function is obtained by measuring the time profile of exciting laser light scattered from the sample’s surface. The response \( I_{\text{resp}}(t) \) is well characterized by a Gaussian profile of width \( w \) and area \( A_G \). Therefore, the measured TRPL signal, \( I_{\text{PL}}^{\text{meas}}(t) \), is taken to be a convolution of this Gaussian instrument response with the ideal PL decay, \( I_{\text{PL}}(t) \) [Eq. (3.1)]:

\[
I_{\text{PL}}^{\text{meas}}(t) = [I_{\text{resp}} * I_{\text{PL}}](t) = \int_0^t \left[ \frac{A_G}{w} \sqrt{\frac{2}{\pi}} e^{-2(x-\delta)^2/w^2} \right] \left[ \sum_{i \geq 1} A_i e^{-(t-x)/\tau_i} \right] dx \\
= \frac{A_G}{2} \sum_{i \geq 1} A_i e^{-(t-\delta)/\tau_i} e^{z_i^2/8} \left\{ \text{erf} \left[ \sqrt{2} \left( \frac{\delta}{w} + \frac{z_i}{4} \right) \right] + \text{erf} \left[ \sqrt{2} \left( \frac{t - \delta}{w} - \frac{z_i}{4} \right) \right] \right\},
\]

where \( \delta > 0 \) is an arbitrary time delay between absolute \( t=0 \) and the experimental onset of the PL signal, and \( z_i \equiv w/\tau_i \).

To obtain the decay parameters \( \{A_i, \tau_i\} \), the analytical solution \( I_{\text{PL}}^{\text{meas}}(t) \) is iteratively compared to the experimentally obtained TRPL trace. The decay parameters and the delay \( \delta \) are adjusted using a standard Levenberg-Marquardt nonlinear least squares algorithm, where the instrument response parameters \( w \) and \( A_G \) have been determined independently beforehand and are fixed. This iterative reconvolution technique has been applied successfully in the more general situation that the instrument response is not well characterized by an analytical function; even in this case, it has been demonstrated that decay times up to one order of magnitude less than the instrument resolution can be extracted reliably [91,92].

42
Chapter 4

Control of Optical Properties by Material Growth and Processing

In bulk ZnO and in thin films of sufficient quality, the intensity of defect-related visible/green emission ($I_{GR}$) is several orders of magnitude weaker than that of the ultraviolet near-band-edge emission, $I_{UV}$ [84, 93–95]. For ZnO nanostructures, the intensity of the defect emission is often comparable to or stronger than UV emission. The peak intensity ratio ($I_{pk}^{GR}/I_{pk}^{UV}$) of the defect emission to the band-edge emission has been reported as large as $\sim 3$, but because the visible emission is broader, the spectrally integrated ratio is as large as $\sim 12$ [96–98].

The significant contribution of surface defects to visible emission is evident from the observation that $I_{pk}^{GR}/I_{pk}^{UV}$ is much higher in ZnO nanostructures than in bulk or thin films due to the nanostructures’ increased surface-to-volume ratio. Indeed, Shalish et al. demonstrated that the intensity of defect emission in an array of ZnO nanowires was directly proportional to the wires’ average surface-to-volume ratio [98]. Measurements of the polarization of band-edge versus defect emission [96], studies involving surfactant treatments in ZnO nanostructures [99, 100], and depth-resolved cathodoluminescence experiments [43] also indicate that the visible emission originates from surfaces states, thus lending further support to the claim that surface defects are primarily responsible for the visible emission.

Furthermore, it is well established that sulfur doping enhances the green emission from ZnO nanostructures, with $I_{pk}^{GR}/I_{pk}^{UV} \lesssim 5$ at room temperature [101, 102] and $I_{pk}^{GR}/I_{pk}^{UV} \sim 160$ at 10 K [103]. In these reports it has been suggested that sulfur substitutes for oxygen within the ZnO lattice, and the enhanced green emission is
due to the commensurate increase in oxygen vacancies presumably responsible for green band PL.

The experimental work comprising this dissertation was motivated by the optical properties of a sulfur-doped ZnO (ZnO:S) nanowire sample embodying these effects and exhibiting unusually intense green emission characterized by $I_{pk}^{GR}/I_{pk}^{UV} \sim 400$, i.e., two orders of magnitude more intense than what is commonly observed in either undoped or sulfur-doped ZnO nanowires. Understanding the reasons for this large ratio—and the possibility of then being able to control it by altering growth conditions in a systematic way—could have enormous consequences for both UV optoelectronic applications ($I_{pk}^{GR}/I_{pk}^{UV} \ll 1$ desirable) and green/white light phosphor applications ($I_{pk}^{GR}/I_{pk}^{UV} \gg 1$ desirable).

The growth, morphological, and optical properties of this unique sulfur-doped ZnO sample are briefly summarized below as a way of demonstrating that several growth-related variables influence the radiative quantum efficiencies (QEs) of UV and GR emission bands in ZnO. In particular, the nanostructuring process (i.e., the growth of ZnO with large surface-to-volume ratio) and the sulfur-doping process are shown to affect the efficiencies of radiative and nonradiative recombination channels. The relative contribution of these processes in affecting the QEs is further analyzed by studying a standardized set of samples derived from commercially available ZnO powder.

### 4.1 Sample Growth and Morphology

The sample growth and structural characterization measurements described in this section were performed by the author’s collaborators in the Department of Chemistry, Duke University, under the supervision of Prof. Jie Liu. The ZnO:S nanowire sample
was grown by his post-doctoral associate Dr. Jianye Li in 2004 using a procedure documented in Ref. 50. Subsequent powder samples were variously prepared by Prof. Liu and his students (Jianqiu Yang, Tom McNicholas, Gee Simmons) using techniques documented in Ref. 51.

The system used to grow the sulfur-doped ZnO nanowires is similar to that designed to prepare GaN nanowires [104]. Growth was carried out in a fused quartz tube inside a horizontal tube furnace. A mixture of ZnS powder (99.99%, Alfa Aesar) and graphite carbon powder (99.9995%, Alfa Aesar) with a weight ratio of 2:1 was the source material. (Graphite carbon powder was used to lower the growth temperature by decreasing the vaporizing temperature of the source material.) The substrate used to deposit the ZnO nanowires was a silicon wafer (Silicon Quest) patterned with a gold film; the gold pattern was generated by standard photolithography and thermal evaporation.

The source material and the gold-coated substrate were loaded into an alumina boat, and the boat was located in the tube such that the source material was at the center of the tube/furnace. Then the furnace was heated under a steady flow of argon (99.99%, National Specialty Gases). When the furnace temperature reached 900 °C, the temperature was kept constant for ~8 hours. The furnace was then switched off and allowed to cool to room temperature. During the growth process, the tube was not sealed tightly so that air (oxygen) could enter the tube to oxidize ZnS into ZnO.

Figure 4.1 shows scanning electron microscope (SEM) data for the nanowire sample. The sample consists of a mixture of nanowires and nanoribbons but will hereafter be referred to simply as “nanowires.” The nanowires are very long (> 20 µm) and uniform along their length, with an average cross section of ~300×100 nm² for the nanoribbons and an average diameter of ~100 nm for the nanowires. All of the strong diffraction peaks in the x-ray diffraction data (not shown) correspond to ZnO.
Figure 4.1: SEM images of sulfur-doped ZnO nanowires. Scale bars in (a) and (b) correspond to 2 µm and 1 µm, respectively.
Two small peaks corresponding to ZnS were also observed, indicating the existence of a small amount of ZnS impurity in the material. However, the characteristic UV emission from ZnS was not observed in any optical measurements; the amount of ZnS is deemed negligible and does not contribute significantly to the overall emission spectrum. This assertion was further validated by the results of energy-dispersive x-ray spectroscopy, which indicated only a trace amount (∼1%) of sulfur present in the nanowires.

The extraordinary optical properties of the ZnO:S nanowires grown in this fashion may be attributed in part to the fact that the wires have large surface-to-volume ratio and that they are sulfur-doped. A unique aspect of the systematic work presented in this dissertation was the design of a standardized set of ZnO samples which could be produced easily and reliably, and whose optical properties could be compared to those of the ZnO:S nanowires. Commercially available ZnO powder was a natural choice for a starting point because it is readily available in large quantities and it possesses an average diameter comparable to the cross-sectional dimensions of the ZnO:S nanowires. The relative effects of doping and nanostructuring on the optical properties of ZnO could then be explored systematically by subjecting the commercial ZnO powder to various treatments that mimic different aspects of the ZnO:S nanowire growth technique.

The size distribution of the commercially available undoped powder (99.999%, Alfa Aesar), hereafter referred to as “unannealed ZnO,” is characterized by a median diameter of 340 nm and a standard deviation of 183 nm [Fig. 4.2(a)]. To simulate the sulfur-doping growth process of the ZnO:S nanowires, a portion of the unannealed powder was sealed with 0.5% by weight of sulfur in an evacuated quartz tube and annealed at 1000 °C for one hour. The morphology of this nominally “S-doped ZnO” (ZnO:S) powder is illustrated in Fig. 4.2(b). The doping/annealing process causes the
Figure 4.2: SEM images of (a) unannealed ZnO powder, (b) sulfur-doped ZnO powder, and (c) annealed ZnO powder. All scale bars correspond to 5 µm.
nanoparticles to coalesce into much larger particles characterized by a median diameter of 2280 nm and a relatively large size distribution (standard deviation 1690 nm). A third “annealed ZnO” sample was prepared following the procedure used for the ZnO:S powder, except no sulfur was present during the annealing process. The image in Fig. 4.2(c) indicates that, in the absence of sulfur, the annealing process still causes the undoped nanometer-scale particles to coalesce into larger particles. The annealed ZnO particles (median size 1800 nm) are comparable in size to the ZnO:S particles but are more uniform in their size distribution (standard deviation 855 nm).

It is worth noting that both the annealed ZnO and the S-doped ZnO powder samples are similar to commercially available ZnO:Zn phosphor powders, which are typically activated by mixing undoped ZnO powder with ZnS or S powder and firing the mixture at high temperature (900−1100 °C) [49, 105]. Sulfur improves the efficiency of the reducing process regardless of how much sulfur is actually incorporated into the ZnO powder. In particular, the “S-doped” designation of the powder sample in this work refers to its preparation conditions; the amount of actual sulfur incorporation in the ZnO lattice is unknown.

The unannealed powder exhibits negligible green defect emission under UV excitation and is visually white to the eye under ambient illumination. The powders annealed with and without sulfur exhibit very strong green emission under UV excitation and are visually pale yellow/green to the eye under ambient illumination. Though this effect has not yet been quantified, it appears that the extent of this yellowing increases with sulfur concentration; e.g., the powder annealed in vacuum has only a slight yellow color, whereas the 0.5% S powder is noticeably more yellow–green. Under less controlled conditions where ZnO is simply heated and then cooled in air, it exhibits thermochromic behavior: The powder becomes yellowish green upon heating and then reverts to a white color upon cooling [106–108]. A possibly related
but longer-term behavior has been observed in the powders studied throughout the course of this dissertation work, namely that the green defect emission’s QE is maximum for freshly prepared samples and then declines on the time scale of months when the powders are continuously exposed to air. The extent of degradation appears to be more severe for samples of increasing sulfur concentration (samples which initially are increasingly yellow to the eye). This aging effect requires further study in order to understand its origin and to prevent it for the purpose of phosphor/device applications.

The ZnO:S nanowire sample was inherently ready for optical characterization by virtue of being grown on a substrate. The powder samples were prepared for optical characterization by mixing $\sim 70$ mg of each sample with 1 ml methanol, dropping the mixtures onto microscope slides, and allowing the methanol to evaporate. A portion of each powder was alternatively pressed between two fused silica plates to confirm that the solvent had no effect on the samples’ optical properties.

### 4.2 Consequences of Nanostructuring, Sulfur Doping, and Annealing

The room-temperature, continuous-wave photoluminescence (PL) spectra of spontaneous emission from the ZnO:S nanowires, the commercially available undoped ZnO powder, and the sulfur-doped ZnO powder are shown in Fig. 4.3(a). The spectra were acquired sequentially in a single day using the same experimental setup; therefore, apart from a normalization to account for the samples’ absorption, the relative PL intensities are unaltered and their differences are quantitatively meaningful. As discussed in Sec. 1.2, the broad emission spectra of the sulfur-doped ZnO nanowires and powder very closely match the dark-adapted response of the human eye [44]; moreover, their brightness and large spectrally integrated (345–650 nm) quantum ef-
iciencies ($\eta = \eta_{UV} + \eta_{GR} = 30\%$ and $\eta = 65\%$, respectively) make them compelling UV-excited phosphors. The $\eta \approx \eta_{GR} = 65\%$ quantum efficiency of the S-doped ZnO powder is consistent with a previously reported value of 60\% [49]. There have been no prior measurements of the quantum efficiency $\eta_{GR}$ of defect emission from ZnO nanowires under photoexcitation, although a band-edge quantum efficiency of $\eta_{UV} \sim 10\%$ has been reported for spontaneous emission of undoped ZnO nanowires [109].

In general, the ratio of defect to near-band-edge emission, $I_{GR}^{pk}/I_{UV}^{pk}$, depends on growth technique and can be increased through nanostructuring. However, the very large $I_{GR}^{pk}/I_{UV}^{pk}$ of the S-doped nanowires reported here cannot be explained by nanostructuring alone. The analysis of Shalish et al. regarding undoped ZnO nanowires [98] predicts $I_{GR}^{pk}/I_{UV}^{pk} \sim 0.45$ for an undoped version of our nanowires, not the $I_{GR}^{pk}/I_{UV}^{pk} = 400$ observed. The factor of $\sim 900$ difference in these ratios is attributed to sulfur doping. By way of proof, we note that $I_{GR}^{pk}/I_{UV}^{pk}$ changes from 0.02 to 80 when comparing undoped to sulfur-doped powders—a factor of 4000 change.

As noted above, there is experimental evidence that the visible/green emission originates from surface states in both undoped and sulfur-doped ZnO. It is therefore somewhat unexpected that the sulfur-doped micropowders with small surface-to-volume ratio exhibit twice the quantum efficiency and more than four times the improvement in $I_{GR}^{pk}/I_{UV}^{pk}$ (relative to the corresponding undoped case) compared to the sulfur-doped nanowires with larger surface-to-volume ratio. It is likely that the greater surface-to-volume ratio in the sulfur-doped nanowires corresponds to a greater density of nonradiative traps that directly compete with the green radiative relaxation.

To confirm this hypothesis, the time-resolved photoluminescence (TRPL) decay of the near-band-edge emission was measured for each ZnO sample [Fig. 4.3(b), Table 4.1]. The undoped powder exhibits the strongest band-edge emission and the
Figure 4.3:  (a) Photoluminescence spectrum of ZnO:S nanowires and the very similar spectral response of the dark-adapted human eye [44]. The spectra of ZnO powders (undoped and sulfur-doped) are shown for comparison. All spectra have been normalized to the samples’ respective absorption. (b) Spectrally integrated, time-resolved photoluminescence decays for near-band-edge emission. The apparent rise times differ due to intentional changes in the streak camera’s time resolution (110 ps for undoped powder, 50 ps for doped powder, 30 ps for doped nanowires). In all cases the rise times are instrument-limited.
Table 4.1: Peak ratio of green to ultraviolet PL intensity ($I_{pk}^{GR}/I_{pk}^{UV}$), spectrally integrated quantum efficiency $\eta=\eta_{UV}+\eta_{GR}$, and near-band-edge time-resolved photoluminescence decay parameters for undoped and S-doped powders and S-doped nanowires.

<table>
<thead>
<tr>
<th>sample</th>
<th>$I_{pk}^{GR}/I_{pk}^{UV}$</th>
<th>$\eta$</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped powder</td>
<td>0.02</td>
<td>0.07</td>
<td>0.20</td>
<td>1.1</td>
<td>0.48</td>
</tr>
<tr>
<td>S-doped powder</td>
<td>80</td>
<td>0.65</td>
<td>0.11</td>
<td>0.48</td>
<td>0.37</td>
</tr>
<tr>
<td>S-doped nanowire</td>
<td>400</td>
<td>0.30</td>
<td>$&lt;0.040$</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

Weakest defect emission. Although it has the slowest biexponential decay lifetimes $\tau_1$ (where $I_{UV}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$, $A_1 + A_2 = 1$), the low quantum efficiency indicates that nonradiative recombination dominates band-edge relaxation. Doping the powder with sulfur significantly enhances energy transfer from the band edge to the defect states responsible for green emission, resulting in reduced band-edge emission, faster band-edge decay, much brighter visible/green emission, and dramatically increased green quantum efficiency. Clearly the defect-mediated decay channel responsible for visible emission favorably competes with nonradiative decay channels. However, when the S-doped ZnO is formed into nanowires, the band-edge emission decay accelerates and the spectrally integrated quantum efficiency drops. Nanostructuring therefore increases nonradiative carrier recombination and decreases energy transfer to green-emitting defects. It is surmised that as the nanostructure’s surface-to-volume ratio increases, the nonradiative recombination pathways increasingly compete with the defect states responsible for the bright visible emission.

The data in Fig. 4.3 indicate that the nanostructuring process does not guarantee enhanced green emission; however, it is clear that the presence of sulfur enhances the efficiency of this radiative recombination channel for both nanowires and micropowders. To understand the sulfur doping process in more detail, the op-
Figure 4.4: Low-temperature photoluminescence spectra of ZnO powders under continuous-wave excitation.

tical properties of the powder annealed without sulfur were compared to those of the undoped/annealed and the sulfur-doped powders. Figure 4.4 shows the low-temperature PL spectra of these three samples under continuous-wave excitation. The spectra are plotted on a semi-logarithmic scale to demonstrate that even the nanometer-scale unannealed sample exhibits defect emission centered at $\sim 2.5$ eV. The annealed sample, whose micrometer-scale particle sizes are comparable to those of the sulfur-doped powder, exhibits intense green emission of the same spectral shape and position even though no sulfur was present during the firing process. This result is consistent with assertions that the defect emission is due to an intrinsic defect (possibly oxygen vacancies) rather than an impurity band. Moreover, the enhancement of the green emission comes at the expense of near-band-edge emission intensity, again demonstrating a competition for carriers between the two emission mechanisms. Apart from the further quenching of near-band-edge emission and the commensurate increase in defect emission intensity, the PL spectrum for the S-doped
sample is almost identical to that of the annealed sample. Sulfur doping therefore enhances carrier capture by the radiative defects responsible for the broadband visible emission, but it does not fundamentally alter the emission mechanism itself.

4.3 Summary

ZnO samples of various sizes, geometries, and dopant concentrations can be grown using standard and inexpensive vapor deposition techniques. These samples’ structural properties, as well as their ultraviolet and visible optical properties, are very sensitive to growth parameters such as starting materials, growth temperature, and ambient environment during growth. The sulfur-doped ZnO nanowire sample discussed in this chapter provides an extreme example of how one aspect of growth (doping) can enhance green band emission through creation of favorable defects while a second aspect of growth (nanostructuring) can simultaneously inhibit ultraviolet emission—and, to some extent, green emission—through creation of a high density of nonradiative defects.

In an attempt to decouple these competing effects, a set of reference powder samples was derived from commercially available ZnO nanopowder. The commercial powder intrinsically exhibits strong UV emission and weak visible emission despite its small size (and therefore large surface-to-volume ratio). The strong enhancement of green emission observed in ZnO:S nanowires was reproduced by annealing the commercial nanopowder with and without sulfur present during the anneal. Therefore, it was the high-temperature annealing process itself more than the presence of sulfur that significantly enhanced green emission at the expense of near-band-edge emission. It was concluded that the green emission mechanism is intrinsic in nature but is significantly enhanced under certain anneal conditions. Sulfur doping does appear to
improve the efficiency of green emission without significantly affecting particle size; however, it does not appear to affect the intrinsic nature of the emission mechanism.

Some of the competing factors affecting radiative recombination efficiencies in ZnO have been discussed very briefly in this chapter. Details of the energy transfer process to green-emitting defects, the competition between radiative and nonradiative recombination, and the influence of doping/annealing will be discussed in more detail in the subsequent chapters. The samples used in these subsequent optical investigations are the three powder samples described in this chapter. They were chosen primarily based on the ease and reproducibility with which they can be created, but also because they are representative of the cases $I_{GR}^{pk} \ll I_{UV}^{pk}$ (unannealed), $I_{GR}^{pk} \gtrsim I_{UV}^{pk}$ (annealed), and $I_{GR}^{pk} \gg I_{UV}^{pk}$ (S-doped).
Chapter 5

Characteristic Defect and Impurity Energies Obtained from the Temperature Dependence of Photoluminescence

The temperature dependence of defect-related “green band” photoluminescence (PL) in ZnO is not predictable because the emission mechanism is not well understood. In general the temperature dependence of PL intensity readily yields thermal activation energies for processes which compete with or destroy a given PL mechanism and therefore reduce its intensity. By quantifying this temperature dependence for the case of green band emission, we hope to extract characteristic energies which may hint at the underlying emission mechanism and/or the energy transfer process from the band edge to green-emitting defects. Along these same lines, it is well known that near-band-edge ultraviolet (UV) PL of ZnO is typically dominated by bound exciton luminescence at low temperature; with increasing lattice temperature, the bound excitons become increasingly less localized, so bound exciton emission weakens and free exciton luminescence increases. Monitoring these changes in PL intensities with increasing temperature provides information about the bound exciton luminescence mechanisms, i.e., the localization energies of the impurities/defects to which excitons are bound (Sec. 2.2.4).

This chapter presents measurements of the temperature dependence of PL intensities for the UV and green emission bands of ZnO. The temperature evolution of each band is studied at low temperature (12–300 K) and high temperature (300–525 K) to extract as many activation energies as possible. There are several unanticipated correlations between the thermal behaviors of these bands. Taken together, the cor-
relations suggest an intimate connection between exciton localization (existence of donor- or acceptor-bound excitons) and the efficiency of green band PL. Moreover, it is useful from a device perspective to know the temperature dependence of a potential phosphor such as ZnO, especially at temperatures above room temperature.

5.1 Near-Band-Edge Luminescence

5.1.1 Low-Temperature UV Photoluminescence

Figure 5.1 shows the band-edge PL of the 0.5% S powder sample at a lattice temperature of $T_L = 12$ K. As discussed in Sec. 2.2.4, features in the energy range 3.34–3.40 eV consist of bound exciton emissions typically observed in ZnO [76–78]. The most prominent peak at 3.361 eV in Fig. 5.1 is assigned to the $I_6$ neutral DBE based on its location (Table 2.1) and the fact that this emission line is often the dominant DBE in low-temperature ZnO PL [67]. The peak position is redshifted from the free exciton energy by an amount 15 meV, corresponding to the localization energy required to bind the exciton to the neutral donor site. The donor impurity presumably responsible for $I_6$ is aluminum [76].

At least two other DBE lines are evident in this energy region—the $I_9$ line at 3.355 eV on the low-energy shoulder of $I_6$, and the $I_3$ line at 3.366 eV on the high-energy shoulder of $I_6$. Magneto-optical studies have shown conclusively that $I_9$ originates from neutral DBEs and $I_3$ from ionized DBEs [110]. Recent experimental and theoretical work suggests very strongly that the exciton localization energy of 10 meV for $I_3$ and 21 meV for $I_9$ both correspond to a donor binding energy of $\sim 65$ meV [111].$^1$ Thus, it appears that the same donor is responsible for both

$^1$For ZnO, the relationship between exciton localization energy ($E_{\text{loc}}$) and donor binding energy ($E_{\text{D}}^d$) appears to obey the empirical Haynes’ rule (linear relationship) according to $E_{\text{loc}} = \ldots$
emission lines, either in its neutral ($I_9$) or ionized ($I_3$) charge state. A positive identification has not yet been made for the donor impurity responsible for $I_3/I_9$, but the presence and intensity of these lines appear to correlate with the presence of nitrogen acceptors in bulk ZnO [76].

The origin of the second feature (or set of features) located in the energy range 3.30–3.33 eV of Fig. 5.1 is very controversial. Bound excitons are not observed at such low energies (Table 2.1), but their two-electron satellite peaks sometimes are—albeit with very low intensity [67]. The expected position of the free exciton’s first LO phonon replica [X-1LO, Eq. (2.7)] is 3.309 eV for this lattice temperature, which is very close to the observed peak position of 3.311 eV. However, there appear to

$-4.2 \text{ meV} + 0.37 E_b^D$ for neutral donors and $E_{\text{inc}} = -23 \text{ meV} + 0.50 E_b^D$ for ionized donors [76,111].
be additional mechanisms responsible for the commonly observed “3.31 eV emission band” of ZnO. Frequently cited emission mechanisms include free electron to acceptor [72,112–114], donor-acceptor pair [115], and acceptor-bound exciton recombination [116–120]. Clearly, it is generally agreed that an acceptor level is somehow involved in the emission process. An emerging consensus, based in part on particle size dependence and spatially resolved optical studies, suggests that the emission band is related more specifically to surface acceptors [113, 117, 119, 120]. Further controversy lies in whether the emission band is associated with an acceptor level of structural origin (likely stacking fault defects) or of a chemical impurity (likely nitrogen). For the purpose of this work, the exact emission mechanism of 3.31 eV PL is not as important as the fact that this surface-related PL is present with intensity comparable to that of bound exciton PL. For lack of identification beyond its correlation to surface features, it is hereafter referred to as $I_S$ for convenience.

We expect that the intensities of $I_6$ and $I_S$ will decrease as the lattice temperature is increased above $T_L = 12$ K because of exciton delocalization. The rate at which each PL line is thermally quenched depends on the localization energy of the exciton to the corresponding defect or impurity. This effect is typically quantified—and the corresponding trapping/localization energy identified—by monitoring the PL intensity of each line as a function of temperature and generating a so-called Arrhenius plot defined as follows: The radiative efficiency $\eta$ (and therefore the PL intensity) of a given recombination channel is given by the ratio of radiative transition probability $P_r$ to total transition probability ($P_r + P_{nr}$), where $P_{nr}$ is the probability of nonradiative recombination. Generally speaking $P_{nr}$ has the form $P_{nr} \propto P_{nr0} \exp(-E_a/k_BT_L)$, where $E_a$ is the activation energy characterizing the nonradiative process (for example, the localization energy characterizing thermal delocalization of an exciton from an impurity) [121]. As a result, the radiative
efficiency behaves as \( \eta \propto [1 + (P_{nr0}/P_t) \exp(-E_a/k_BT_L)]^{-1} \). For typical values of \((P_t/P_{nr0} \ll 1)\) and \((E_a/k_BT_L \lesssim 1)\), the PL intensity exhibits an Arrhenius behavior: 

\[
\ln(\eta) \propto -E_a \cdot (k_BT_L)^{-1}
\]

Therefore, when the temperature dependence of PL intensity is plotted as in Fig. 5.2, the linear slope between any two points gives the activation energy of whatever thermal quenching process is dominating in that temperature regime. Throughout this chapter, the lattice temperature \(T_L\) [K] may equivalently be expressed in energy units as \(k_BT_L\) [eV] or as an “inverse temperature” \((k_BT_L)^{-1}\) [eV\(^{-1}\)], the latter being more natural units in the context of an Arrhenius plot.\(^2\)

A coarsely sampled Arrhenius plot of PL intensities for \(I_S\) and \(I_6\) is shown in Fig. 5.2. The highest temperature points were excluded from analysis because the two PL peaks had thermally broadened and merged to the extent of being indistinguishable. Otherwise, the high-temperature points (100–200 eV\(^{-1}\)) indicate a thermal activation energy (i.e., slope) of \(~55\) meV for \(I_6\). This value is consistent with the donor binding energy of 50–55 meV previously reported for \(I_6\) (Table 2.1). Therefore, we attribute this quenching of \(I_6\) PL intensity to thermal ionization of donor electrons from the relevant shallow donor sites.

In this same temperature regime, the \(I_S\) line is quenched with an activation energy of \(~43\) meV—a value significantly less than the acceptor binding energies of 120–200 meV often associated with this emission [113, 120]. However, this value is large enough to be consistent with examples in the literature where \(I_S\) emission persists and even dominates the near-band-edge PL spectrum up to room temperature \((k_BT_L = 25\) meV\) [119, 120, 122]. In only one of these cases was the thermal quenching of \(I_S\) quantified; the value of 56 meV deduced in that case clearly differs from the value of

\(^2\)For example, a lattice temperature of \(T_L = 100\) K corresponds to a temperature in energy units of \(k_BT_L = 8.62\) meV and to an inverse temperature of \((k_BT_L)^{-1} = 116\) eV\(^{-1}\).
Figure 5.2: Arrhenius plot of the spectrally integrated photoluminescence intensities for the two primary low-temperature emission lines in ZnO:S. The energies denoted for $I_S$ and $I_6$ correspond to thermal activation energies derived from the linear slopes of the data.

43 meV deduced from Fig. 5.2 [122].

The physical meaning of the 43 meV activation energy is not immediately apparent because the precise emission mechanism responsible for $I_S$ is unknown. If we consider the possibility that this activation energy corresponds to a neutral donor binding energy analogous to the case of 55 meV for $I_6$, then the analysis of Meyer et al. [76, 111] suggests a corresponding exciton localization energy of $\sim 12$ meV. This localization energy is very consistent with that of the hydrogen-related $I_4$ neutral DBE which, though not explicitly observed in our PL data, could perhaps be involved in the $I_S$ emission process.

---

3At this point it appears coincidental that the literature value of 56 meV for the thermal activation of surface-acceptor-related $I_S$ is equivalent to our measured value for the thermal activation energy of neutral-donor-related $I_6$ (Fig. 5.2).
In the intermediate temperature regime (200–300 eV$^{-1}$), the PL intensities decrease with increasing temperature according to activation energies of $\sim$15 meV for $I_6$ and $\sim$10 meV for $I_S$. This thermal quenching corresponds to exciton delocalization for the case of $I_6$ (neutral DBE emission), as the localization energy of the exciton to this neutral donor is generally found to be 15–16 meV [67, 76]. Similarly, depending on the interpretation of the $I_S$ line, the 10 meV activation energy could be ascribed to the localization energy of the exciton to a shallow impurity involved in the 3.31 eV emission of ZnO. This measured activation energy is very close to the generally accepted exciton delocalization energy of $\sim$10 meV for the $I_3$ ionized DBE line [76], which possibly suggests a connection between $I_S$ and $I_3$.

Finally, in the intermediate–low temperature regime of 300–400 eV$^{-1}$, the Arrhenius plot of $I_6$ suggests a third activation energy of $\sim$2 meV. A similar quenching for $I_S$ is not observed. While the identification of this activation energy—and those of exciton delocalization and dissociation—is perhaps debatable given the sparseness of the data in Fig. 5.2, the temperature dependence of defect-related PL (Sec. 5.2) exhibits striking correlations in terms of its thermal quenching behavior. These correlations lend credence to the activation energies identified thus far.

### 5.1.2 High-Temperature UV Photoluminescence

At lattice temperatures exceeding $k_B T_L \sim 20$ meV ($T_L \sim 230$ K), excitons have become completely delocalized from shallow impurity sites. Free exciton emission and/or its LO phonon replicas are then expected to exist up to temperatures approaching the exciton binding energy of 60 meV (corresponding to $T_L = 700$ K). While the high-temperature limit of this regime is beyond the operating range of our experimental apparatus, we were able to study the band-edge PL intensity as a function of tem-
perature for $T_L=300-525$ K.

The integrated band-edge PL intensity for the annealed ZnO:Zn powder sample is shown in the Arrhenius plot of Fig. 5.3 for this regime. The PL appears to be quenched with a thermal activation energy of $\sim 160$ meV, which is much larger than the free exciton binding energy. However, this value is very similar to the 165 meV nitrogen acceptor binding energy observed when nitrogen substitutes on an oxygen site [76,123]. This value is also in line with the estimated acceptor binding energy of 180–200 meV reported by Fallert et al., who claim that ZnO nanoparticle PL is dominated by excitons bound to surface acceptor sites (possibly nitrogen-related) even at room temperature [120]. In any case, acceptors appear to be involved either directly or indirectly in the band-edge PL of our samples at low temperature (evidenced by the observation of $I_S$) and at high temperature (evidenced by the 160 meV activation energy).

![Figure 5.3](image)

**Figure 5.3:** Arrhenius plot of the spectrally integrated near-band-edge photoluminescence intensity above room temperature for ZnO:Zn. The excitation source was a continuous-wave HeCd laser at energy 3.81 eV and irradiance 0.002 W cm$^{-2}$. 

64
5.2 Defect-Related Green Luminescence

5.2.1 Low-Temperature Green Photoluminescence

The defect-related green band PL of ZnO:S is plotted in Fig. 5.4 for several lattice temperatures in the range of 12–300 K. The sample was continuously excited by a HeCd laser with irradiance $\sim 0.002 \text{ W cm}^{-2}$ to maximize the intensity of green PL, whereas the low-temperature results discussed in Sec. 5.1.1 (UV PL of the same sample) were obtained using femtosecond pulsed excitation to maximize UV PL intensity. The general presence and spectral shape of the defect PL are essentially independent of excitation source. The following discussion will demonstrate striking similarities between the temperature dependence of this PL band and that of the band-edge PL discussed in Sec. 5.1, despite the difference in excitation conditions.

In Sec. 2.3 the one-dimensional configuration coordinate model describing defect luminescence was introduced, and it was established that for intermediate–large atomic displacements of the defect complex in its excited state, the resulting luminescence band is asymmetric. The extent of atomic displacement and the corresponding band asymmetry correlates with the strength of the electron-phonon interaction, which in ZnO is quite large. Thus, the green band PL in Fig. 5.4 exhibits asymmetry at all lattice temperatures. Gaussian fits are superimposed on the 11 K and 300 K curves of Fig. 5.4 to illustrate this asymmetry. The degree of asymmetry decreases with increasing temperature, and the band becomes more approximately Gaussian. This behavior is consistent with quantitative theories of defect-related PL described by the one-dimensional configuration coordinate model [82].

To analyze the temperature dependence of the green PL, the spectrum $I_{GR}(\hbar\omega)$

4The relative intensities of UV and green emissions under pulsed versus continuous-wave excitations are explored in detail in Chap. 7.
Figure 5.4: Broadband defect-related photoluminescence of ZnO:S micropowder at select lattice temperatures. The excitation source was a continuous-wave HeCd laser at energy $3.81 \text{ eV}$ and irradiance $0.002 \text{ W cm}^{-2}$. Gaussian fits are superimposed on the 11 K and 300 K curves to illustrate the asymmetry of the band. (Curves are displaced vertically for clarity.)

at each temperature was fit using the fronted extreme function,

$$I_{\text{GR}}(\hbar \omega) = I_0 + A \exp \left[ \frac{1}{s} (-ez^2 + z + 1) \right], \quad z \equiv (\hbar \omega - \hbar \omega_c)/w, \quad (5.1)$$

where $I_0$ is the offset (baseline), $A$ is the amplitude, $\hbar \omega_c$ is the peak position, and $w$ is the width [124]. In addition to affecting the function’s spectral width, the shape parameter $s > 0$ characterizes the amount of deviation from a symmetric band. Because the underlying physical mechanism (and therefore the appropriate modeling equation) of the defect emission is unknown, this fit function was chosen because it describes well the asymmetric nature of the green band PL with a minimum num-
ber of parameters. The function is also somewhat of a natural choice because it is approximately Gaussian in the vicinity of its peak \((\hbar \omega - \hbar \omega_c \ll \omega)\),

\[
I_{GR}(\hbar \omega) = I_0 + A \exp \left[ \frac{1}{s} \left( -\frac{z^2}{2!} - \frac{z^3}{3!} - \frac{z^4}{4!} \cdots \right) \right] \approx I_0 + A \exp \left[ -\frac{z^2}{2s} \right],
\]

while the higher-order terms in the expansion of the exponent yield the asymmetry in the wings of the distribution.

An Arrhenius plot of the best-fit amplitude using Eq. (5.1) is shown in Fig. 5.5. Several activation energies (slopes obtained by linear fits) are evident: The PL in-

![Arrhenius plot](image_url)

**Figure 5.5:** Arrhenius plot of the temperature dependence of the green band’s amplitude, as deduced from best fits to Eq. (5.1). Activation energies are denoted according to best-fit linear slopes of the data. The horizontal arrows indicate the temperatures at which the slope begins to deviate from the primary (15 meV) activation energy: at \((10 \text{ meV})^{-1}\) and at \((15 \text{ meV})^{-1}\).
tensity first begins to roll off at low temperature (inverse temperature 230–130 eV$^{-1}$) with an activation energy of 2 meV. A more significant rolloff begins at inverse temperature 100 eV$^{-1}$ ($T_L = 115$ K), after which the PL intensity decreases monotonically with increasing temperature up to inverse temperature 48 eV$^{-1}$ ($T_L = 230$ K). After this point, the intensity is approximately constant up to room temperature. The substantial, monotonic decrease in intensity from 100–48 eV$^{-1}$ is best fit with a slope (activation energy) of 15 meV; however, closer examination of this decrease (inset of Fig. 5.5) reveals a distinct change in slope from 55–48 eV$^{-1}$ before the intensity levels off at 48 eV$^{-1}$. This “kink” in the otherwise smooth decrease of PL intensity is characterized by an activation energy of 44 meV.

There appear to be several correlations between these characteristic energies of the green band PL and those of the band-edge PL (Sec. 5.1). The two smaller activation energies for the green band (2 meV and 15 meV) correspond to activation energies associated with the $I_6$ neutral DBE, while the highest green band activation energy (44 meV) corresponds to an activation energy associated with $I_S$. Moreover, it is interesting to note in Fig. 5.5 that the green band PL deviates from the overall 15 meV slope beginning at an inverse temperature of 100 eV$^{-1} = (10$ meV$)^{-1}$ and again at 67 eV$^{-1} = (15$ meV$)^{-1}$ prior to the “kink” 55 eV$^{-1}$. The two energies 10 meV and 15 meV correspond, respectively, to the measured exciton localization energies associated with $I_3$ and $I_6$ (Fig. 5.1 and Table 2.1). The 10 meV energy also characterizes the thermal quenching of $I_S$ in Fig. 5.2.

Further evidence of a change in the green band PL at temperatures of $k_B T_L = 10$ meV and $k_B T_L = 15$ meV is manifested in the temperature dependence of the band’s peak position (Fig. 5.6). After first blueshifting for temperatures of 10–35 K, the band’s peak position remains constant until $T_L \sim 90$ K. There then appears to be a transition region where the band begins to redshift. Beginning at a temperature of
Figure 5.6: Temperature dependence of the green band’s peak position. The vertical arrow at $k_B T_L = 11$ meV indicates the crossover point between the linear behaviors at low ($\sim 50-100$ K) and intermediate ($\sim 150-300$ K) temperatures. The vertical arrow at $k_B T_L = 15$ meV indicates the temperature at which the peak position begins its constant redshift with increasing temperature.

170–180 K ($\sim 15$ meV), the redshift becomes constant with increasing temperature. Based on the intersection of linear fits to these two regimes (no shift at low temperature, constant redshift at high temperature), the “knee” of the transition region occurs at a temperature of 130 K (11 meV).

Thus, the temperature dependences of both the amplitude (Fig. 5.5) and peak position (Fig. 5.6) of the green band depend directly on a 15 meV process that is likely related to the neutral DBE $I_6$. The same data also indicate the involvement of $I_S$ by way of a 44 meV process (inset of Fig. 5.5) and a 10 meV process, the latter being associated with the thermal quenching of $I_S$ in the same way that the 15 meV
activation energy is associated with $I_6$ (Fig. 5.2).

### 5.2.2 High-Temperature Green Photoluminescence

Thermal quenching of the green PL above room temperature was studied using a ZnO:Zn powder sample as described in Sec. 5.1.2. As indicated in Fig. 5.7, the activation energy in this case is $\sim 430$ meV. This energy is much larger than the shallow energies discussed thus far ($\sim 10 - 55$ meV) and is likely related to a deep level involved in the green PL emission process. Given the large Stokes shift of $\sim 900$ meV between the exciton resonance (3.38 eV) and the peak position of the green PL (2.46 eV), we expect that at least one deep level is involved in the defect-related radiative recombination process. For the similar case of yellow defect-related emission in GaN, the analogous deep level has been associated with a hole trapped at a deep acceptor [125].

We have mentioned already the possibility that a 165 meV acceptor is involved in the near-band-edge PL of our ZnO samples, but that the acceptor-related $I_S$ emission mechanism is unclear. In light of the large activation energy associated with green emission—and the apparent correlation between green emission and $I_S$—we consider here the possibility that $I_S$ originates from neutral acceptor-bound exciton (nABE) recombination. The exciton localization energy in this case would be $\sim 65$ meV based on the separation between $I_S$ at 3.311 eV and the free exciton energy of 3.376 eV (for $T_L = 12$ K). Theory suggests that for the case of ZnO, the ratio of exciton localization energy to acceptor binding energy is $E_{nABE}^{\text{loc}} / E_b^{\text{A}} = 0.10 - 0.15$ [126,127]. Thus, for a hypothetical ABE localization energy of 65 meV, theory predicts an acceptor binding energy in the range 430–650 meV. The observed activation energy of 430 meV for green emission falls at the lower end of this range and perhaps suggests that thermal
ionization of holes from the \( I_5 \) acceptor is what causes the green PL intensity to drop so drastically with increasing temperature.

![Figure 5.7: Arrhenius plot of the green band thermal quenching above room temperature. An activation energy of 430 meV was derived from a linear fit to the data.](image)

### 5.3 Summary and Discussion

Table 5.1 summarizes the thermal activation energies for both near-band-edge ultraviolet (UV) and defect-related green (GR) emissions in our ZnO samples. It is important to note that almost every energy listed in the table was evident in *both* emission bands, which suggests very strongly that green PL occurs most efficiently when an exciton is localized at a donor site that also happens to be in the vicinity of the deep 430 meV acceptor level. In the following summary, we consider in more detail how each activation energy listed in Table 5.1 supports this physical picture.
Table 5.1: Summary of thermal activation (TA) energies deduced from the temperature dependence of photoluminescence in ZnO:S and ZnO:Zn powders.

<table>
<thead>
<tr>
<th>Energy (meV)</th>
<th>UV Manifestation</th>
<th>GR Manifestation</th>
<th>Physical Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$I_6$ TA</td>
<td>TA</td>
<td>$I_6$ rotator state (?); polariton splitting (?)</td>
</tr>
<tr>
<td>10</td>
<td>X–I₃ separation;</td>
<td>A slope change;</td>
<td>$I_3$ exciton localization</td>
</tr>
<tr>
<td></td>
<td>$I_S$ TA</td>
<td>$h\omega_c$ “knee”</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>X–I₆ separation;</td>
<td>TA ;</td>
<td>$I_6$ exciton localization</td>
</tr>
<tr>
<td></td>
<td>$I_6$ TA</td>
<td>$A$, $h\omega_c$ slope change</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>$I_S$ TA</td>
<td>TA</td>
<td>$I_4$ donor binding energy (?); $I_S \rightarrow I_9$ transfer (?)</td>
</tr>
<tr>
<td>56</td>
<td>$I_6$ TA</td>
<td>——</td>
<td>$I_6$ donor binding energy</td>
</tr>
<tr>
<td>160</td>
<td>TA</td>
<td>——</td>
<td>acceptor binding energy (?)</td>
</tr>
<tr>
<td>430</td>
<td>——</td>
<td>TA</td>
<td>acceptor binding energy (?)</td>
</tr>
</tbody>
</table>

The activation energy of 2 meV is smaller than any of the reported exciton localization energies for donor-bound excitons in ZnO. Its correlation with the $I_6$ neutral DBE could indicate the presence of the excited rotator state of $I_6$. This excited state of the netural DBE is analogous to an excited rotational state of the H₂ molecule, but in our case it is interpreted as the exciton rotating around the donor site. The energy of this excited state is generally found to be 1–2 meV for excited rotator states of DBEs in ZnO [76,128]. In this interpretation of the 2 meV activation energy, thermal excitation of $I_6$ into an excited rotational state would reduce the probability that the exciton recombines radiatively and would also reduce the coupling of the localized exciton to the green-emitting defect (thus lowering the green PL intensity as well).

An alternative explanation of the 2 meV activation energy is the longitudinal-transverse A-exciton-polariton splitting, $\Delta_{LT}$, which occurs in ZnO at low temperature (Sec. 2.2). Experimentally, this splitting is usually measured to be 1.5–2 meV [129–131]. At very low temperature ($k_B T_X \leq \Delta_{LT}$), the majority of excitons
thermalize on the lower-energy, transverse branch of the A-exciton-polariton. At temperatures exceeding the splitting energy, excitons also thermalize on the longitudinal branch. Because these longitudinal excitons on average have slightly higher kinetic energy, they are less prone to localization at defect sites. Again, a lower probability for bound exciton formation would lead to reduced intensity of $I_6$ PL and less efficient energy transfer from bound exciton states to green-emitting defects.

The assignment of 10 meV as the localization energy of $I_3$ is consistent with its peak separation from the free exciton energy and with similar assignments in the literature (Table 2.1). The low intensity and partial spectral overlap of the $I_3$ line with the stronger $I_6$ line prevented the direct observation of this same activation energy in the temperature dependence of the near-band-edge photoluminescence. However, this activation energy was clearly evident in the spectrally distinct $I_5$ line. We have already noted that both $I_9/I_3$ (neutral/ionized versions of the same donor) and $I_5$ (surface-related acceptor) appear to correlate with the presence of acceptors, especially nitrogen. It has further been suggested [110] that these acceptors may ionize shallow donors in their vicinity, which in our case would explain the observation of ionized DBE PL at the $I_3$ position. More importantly, the reduction in PL intensity of $I_5$ with an activation energy equal to the $I_3$ localization energy suggests an energy transfer mechanism whereby excitons localized at $I_9/I_3$ donor sites induce photoluminescence of nearby $I_5$ surface acceptor sites. That the properties of green emission depend characteristically on this same activation energy is further evidence that green emission correlates with the localization of excitons at donor sites—either neutral or ionized.

Similar to the case of $I_3$, the 15 meV exciton localization energy of $I_6$ is given by its separation from the free exciton energy. In this case, the $I_6$ PL intensity was strong enough that its thermal quenching behavior could be measured, and it
nicely reproduced this localization energy. The most significant thermal quenching of
the green band PL likewise occurred with this same activation energy. Even though
the donor associated with $I_6$ is almost certainly different from the one for $I_9/I_3$,
the conclusion is the same: green band PL intensity is reduced dramatically when
excitons become thermally delocalized from donor binding sites, regardless of the
donor species.

There is a distinct non-parallel between bound exciton emission and green emis-
sion when it comes to the higher (56 meV) activation energy associated with thermal
ionization of the $I_6$ donor’s electron. At temperatures exceeding the exciton local-
ization energy, there is still a small but nonzero number of excitons bound to the
neutral donor sites. The number of such excitons is large enough to measure the
quenching of $I_6$ PL, but evidently very few of these excitons transfer their energy
to the green-emitting defects. This lack of energy transfer at higher temperature
explains the lack of a corresponding 56 meV thermal activation in the green PL.

On the other hand, the green band does exhibit a thermal activation of some-
what less energy: 44 meV. The near-band-edge $I_S$ line exhibits this same activation
energy, and we have already discussed the possibility that a neutral donor (whose
binding energy is 44 meV) could be involved in the $I_S$ emission process. However, the
corresponding DBE would have a localization energy of only 12 meV, which is not
sufficient to explain the spectral shift of $\sim 65$ meV between the free exciton and the
$I_S$ peak position; something more complicated than bound exciton emission would
have to be responsible for $I_S$.

If we instead reconsider the possibility of acceptor-bound exciton recombination
(briefly discussed in Sec. 5.2.2), we can maintain the trend of green PL intensity
being correlated with bound excitons since it shares with $I_S$ the thermal activation
energy of 44 meV. What that would imply for an exciton localized at $I_S$ is that an
energy of only 44 meV—not the full 65 meV by which it is separated from the free exciton energy—is sufficient for delocalization. We therefore note that

\[ I_S + 44 \text{ meV} = 3.311 \text{ eV} + 0.044 \text{ eV} = 3.355 \text{ eV} = I_9. \]

Thus, it is possible that the 44 meV activation of \( I_S \) corresponds physically to an acceptor-bound exciton gaining enough excess energy to “transfer” to a nearby donor-bound exciton (\( I_9 \)) and become bound there instead. In becoming bound to a more shallow defect site, the transfer of energy to a green-emitting defect is reduced accordingly, such that the green PL again shares a thermal activation energy with \( I_S \).

Finally, we consider the two large activation energies which are potentially associated with acceptor binding energies. Their appearances are mutually exclusive regarding near-band-edge versus green PL. The lack of correlation between the two emission mechanisms for these large energies is not surprising since both activation energies greatly exceed all relevant bound exciton localization energies and even the free exciton binding energy of 60 meV. The dependence of the near-band-edge PL on an acceptor level of 160 meV depth is consistent with previous reports in the literature, but it is not fully understood. The interpretation of the 430 meV activation energy as a deep acceptor level is more straightforward and is very consistent with one of the primary theories on green emission in ZnO—that deeply trapped holes are involved in the emission process [35,37]. An aspect of the emission process which does not appear to have been appreciated prior to this work is that exciton localization at certain shallow donors (\( I_6, I_3 \)) in the vicinity of the deep acceptor level (\( I_S \)) is largely responsible for efficient transfer of energy to green-emitting defects.
Chapter 6

Effects of Reabsorption and Spatial Trap Distributions on Radiative Quantum Efficiencies in ZnO

In this chapter, we attempt to elucidate how the interplay between radiative and nonradiative recombination mechanisms in ZnO depends on reabsorption and the spatial distributions of green defects and traps. This interplay has already been illustrated dramatically by comparing the photoluminescence (PL) properties of ZnO:S nanowires to ZnO:Zn micropowder (Chap. 4). In both cases the defect-related green emission dominated the PL spectrum; however, the exciton lifetime was much shorter in the case of nanowires (larger surface-to-volume ratio) because of increased competition from nonradiative surface traps. Clearly we need to understand the relative densities of radiative defects versus nonradiative traps—as well as their locations relative to the photoexcitation profile—to understand the resulting efficiencies of the various recombination channels. Equipped with this knowledge, material growers may then intelligently adjust the ZnO growth/treatment parameters to improve material quality.

To this end, both unannealed and annealed ZnO powder samples are selectively excited primarily in the surface region or throughout the entire particle volume using femtosecond one-photon excitation or two-photon excitation, respectively. A comparison of the time-integrated quantum efficiencies (QEs), PL spectra, and time-resolved photoluminescence (TRPL) intensities for both types of samples and excitation conditions allows us for the first time to draw very specific conclusions about the competing recombination mechanisms, the spatial distributions of the associated recombination
centers, and the influence of reabsorption.

The ZnO samples studied in this chapter were derived from commercially available ZnO powder, as described in Sec. 4.1. A reference sample, hereafter referred to as “unannealed ZnO,” underwent no additional treatment. A second sample (“annealed ZnO”) was prepared by sealing a portion of the unannealed ZnO in a quartz tube under vacuum and firing it for one hour at 1000 °C in a horizontal tube furnace. SEM images indicate that the unannealed powder particles have a median diameter of 340 nm, whereas the annealed powder exhibits a much larger median size of 1800 nm. As discussed in Chap. 4, the annealed ZnO sample exhibits optical properties virtually identical to those of typical ZnO:Zn phosphor powders; i.e., the photoluminescence spectrum is dominated by highly efficient, defect-related emission centered at \( \sim 2.5 \) eV with a full width at half-maximum of \( \sim 450 \) meV. In the unannealed ZnO sample, this “green band” defect emission is almost three orders of magnitude weaker than the ultraviolet, near-band-edge emission.

Optical excitation was provided by \( \sim 100 \) fs pulses from a tunable 1 kHz optical parametric amplifier (OPA). Above-gap excitation at 3.84 eV (323 nm) was generated using the fourth harmonic of the OPA’s signal. Due to the large absorption coefficient of ZnO at this excitation energy (\( \alpha_{\text{exc}} \sim 2 \times 10^5 \) cm\(^{-1}\)), creation of electron-hole pairs occurs primarily near the surface of the particles (\( \alpha_{\text{exc}}^{-1} \sim 50 \) nm) [132, 133]. The samples were also excited below the band gap at 1.92 eV (646 nm) using the second harmonic of the OPA’s signal. In this case, electron-hole pairs are generated via two-photon absorption, but the carriers have the same initial energy distribution as for one-photon excitation since the two-photon excitation energy is half that of the one-photon excitation. Assuming a two-photon absorption coefficient of \( \beta_{\text{exc}} \sim 3 \) cm GW\(^{-1}\) for ZnO [57, 60], the effective penetration depth of two-photon excitation is \( \sim 1 \) cm; thus, the carriers are generated uniformly throughout the volume.
of the nanometer- and micrometer-scale particles. The incident laser fluences were approximately $3 \, \mu J \, \text{cm}^{-2}$ and $80 \, \mu J \, \text{cm}^{-2}$ for one-photon (“surface”) and two-photon (“volume”) excitation, respectively. After taking into consideration the actual number of photons absorbed by the samples (96% and 8% for one-photon and two-photon excitation, respectively\(^1\)) and the fact that two photons of volume excitation lead to a single photoexcited electron-hole pair, the effective fluence for both one-photon and two-photon excitation is $\sim 3 \, \mu J \, \text{cm}^{-2}$.

6.1 Excitation Mechanism for the Emission Bands: Implications for Reabsorption

In the exciton-polariton picture, the coherent mixed state of exciton and photon propagates through the material until its coherence is destroyed by an interaction with another entity (free carrier, phonon, impurity, lattice defect, etc.). This interaction defines a reabsorption event if it imparts additional energy to the exciton and thereby creates a free electron-hole pair. The characteristic length scale over which the exciton polariton can travel before undergoing reabsorption is approximately equal to the inverse absorption coefficient at the exciton energy, $\alpha^{-1}(\hbar \omega = E_X)$. The majority of zero-phonon exciton luminescence therefore originates from within this optical escape depth of the sample surface. For ZnO the escape depth is $\alpha^{-1}(E_X) \sim 45 \, \text{nm}$; excitons which are formed more than $\sim 45 \, \text{nm}$ from the surface are unlikely to emerge from the sample as luminescence photons because they will first undergo a reabsorption event, which in many cases will lead to nonradiative recombination of the electron-hole pair.

After photoexcitation of an exciton population in ZnO, luminescence is also generated at energies $\hbar \omega$ below the exciton resonance $E_X$, for example through

\(^1\)The number of photons absorbed by the sample is measured as a part of the quantum efficiency measurement procedure described in Sec. 3.2.
phonon-assisted exciton annihilation. The corresponding exciton polaritons are on
the “photon-like” portion of the polariton dispersion curve \( k \lesssim 5 \) in Fig. 2.2; i.e.,
their wave functions are described almost completely in terms of the eigenstates of
the uncoupled photon field \([69]\). These photons have energies lying in the absorption
(or “Urbach”) tail below the exciton resonance \( E_X \) and the band gap \( E_g \). Though the
absorption coefficient \( \alpha \) is quickly decreasing at these energies, it is certainly nonzero;
the photons may be reabsorbed and thus re-create free electron-hole pairs \([134–138]\).
However, the smaller value of \( \alpha \) means that these photons may travel a longer dis-
tance before undergoing reabsorption. The escape depth for luminescence at \( h \omega < E_X \)
is therefore larger than for zero-phonon exciton luminescence \( (h \omega \sim E_X) \).

The preceding discussion may be summarized as follows: Any luminescence pho-
ton with energy \( h \omega < E_g \) is subject to reabsorption according to the strength of \( \alpha(h \omega) \).
On average the photon will reach the sample surface without undergoing reabsorption
if it originates within the optical escape depth \( \alpha^{-1} h \omega \) of the surface. Whenever a
reabsorption event does occur, a free electron-hole pair is re-created. This electron-
hole pair is then subject anew to the possibilities of exciton formation and/or energy
transfer to “traps” (either radiative or nonradiative).

The data presented in Chap. 5 strongly suggest a correlation between localized
excitons and efficient excitation of green-emitting defects. In the physical picture
outlined above, excitation of the green-emitting defect could occur through a reab-
sorption event as follows: The exciton polariton becomes trapped by the defect itself
or is localized at a nearby impurity; interaction of the exciton polariton with either of
these localized states destroys the coherence of the exciton and transfers the energy
of the electron-hole pair to the defect, thus inducing it to an excited electronic state.
In this sense “reabsorption” of an exciton leads to excitation of the green-emitting
defect.
Figure 6.1: Comparison of photoluminescence excitation spectra for detection energies near the peak of the green band (2.49 eV) and at the peak of the X-2LO transition (3.22 eV). The lattice temperature was 88 K.

To confirm this excitation mechanism of the green PL, photoluminescence excitation (PLE) measurements were performed for detection wavelengths near the peak of the green PL and at the X-2LO near-band-edge transition for the annealed ZnO sample. The results for a lattice temperature of $T_L = 88$ K are shown in Fig. 6.1, where the two curves have been normalized to their intensities at the band gap ($E_g = 3.43$ eV).\(^2\) The excitation profiles for exciton luminescence and green luminescence are almost identical. This result indicates that efficient energy transfer to green-emitting defects depends directly on a pre-existing exciton population.

The X-2LO PLE data can be used to estimate the effective absorption coefficient spectrum $\alpha(\hbar\omega)$ because the exciton luminescence PLE spectrum effectively maps out

\(^2\)The details of the PLE traces (fine structure, peak locations, etc.) are beyond the scope of the current discussion and are the subject of a more detailed future investigation.
the exciton and band-to-band absorption resonances. Furthermore, because the green band PLE is identical to that of exciton luminescence for photon energies \( \hbar \omega \gtrsim E_g \), the green band PLE can also be used to estimate \( \alpha(\hbar \omega) \) [94]. An approximation of the room-temperature absorption spectrum specific to the ZnO samples studied in this chapter is shown in Fig. 6.2(a). The absorption spectrum was approximated by measuring the annealed sample’s green PLE spectrum and scaling the spectrum’s intensity so that typical values of \( \alpha \sim 2 \times 10^5 \text{ cm}^{-1} \) were obtained directly above the band gap in the range \( \hbar \omega = 3.5 - 3.8 \text{ eV} \). There is an apparent enhancement in absorption at 3.26 eV, which is below the exciton resonance \( E_X = 3.31 \text{ eV} \). A similar enhancement was observed previously in the PLE of ZnO nanorods and was attributed to enhanced exciton-phonon coupling at room temperature [122].

The estimated photon escape depths \( \alpha^{-1}(\hbar \omega) \) at energies relevant to our luminescence measurements were derived from the absorption spectrum in Fig. 6.2(a) and are plotted in Fig. 6.2(b). The fraction of exciton polaritons with \( \hbar \omega \sim 3.1 - 3.3 \text{ eV} \) have a high probability of escaping as luminescence photons if they are generated within \( \lesssim 100 \text{ nm} \) of the particle surface. The probability of escape is higher for the X-2LO transition \( (\hbar \omega_{X-2LO} = 3.18 \text{ eV}) \) compared to X-1LO and X-0LO \( (\hbar \omega_{X-1LO} = 3.26 \text{ eV} \) and \( \hbar \omega_{X-0LO} = 3.29 \text{ eV} \), respectively) because the lower photon energy of X-2LO is less susceptible to reabsorption.

As discussed in Sec. 2.1, one-photon excitation primarily generates carriers (and therefore excitons) within 50–70 nm of the particle surface, but the effective carrier concentration is reduced at the surface due to nonradiative surface recombination. Therefore, for one-photon excitation we expect the luminescence to originate near the particle surface, to undergo minimal reabsorption, and to experience competition

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3Room-temperature PLE was also performed on the X-2LO emission peak near the band edge, and the excitation profile was virtually identical to that shown in Fig. 6.2(a), except the “enhancement” at 3.26 eV was not as pronounced.
Figure 6.2: (a) Estimated absorption coefficient of ZnO powder as derived from the photoluminescence excitation spectrum of the peak of the green defect emission. (b) Estimated photon escape depth [inverse of the curve in (a)] due to reabsorption and probability $f_{esc}^{ref}$ of photon escape due to Fresnel reflection [derived from a Kramers-Kronig transformation of the curve in (a) and use of Eq. (2.8)].
primarily from nonradiative surface recombination.

Two-photon excitation generates the same number of carriers, but over the entire thickness of the sample ($\gtrsim 350$ nm) rather than only near the surface. In this case, many excitons will form within the sample at distances exceeding the optical escape depth. As these exciton polaritons propagate through the sample in the direction of the PL collection optics, they will on average undergo one reabsorption event every $\alpha^{-1}(h\omega_X) \sim 45$ nm. Many of them will therefore be reabsorbed and lost through non-radiative recombination in the bulk of the sample. Similarly, excitons which undergo phonon-assisted recombination in the bulk of the material will yield photons undergoing reabsorption every $\alpha^{-1}(h\omega_{X-1LO}) - \alpha^{-1}(h\omega_{X-2LO}) = 35-80$ nm, with subsequent high probability of nonradiative recombination for the electron-hole pairs. The measured luminescence signal will therefore consist primarily of luminescence from the small fraction of excitons photogenerated near the surface of the sample.

The above considerations apply to near-band-edge photoluminescence because the material absorption coefficient is quite large at those energies. However, the absorption coefficient is negligible at visible wavelengths where the majority of green luminescence originates. The green PL should therefore be independent of the distribution of excitation (one-photon versus two-photon) from a reabsorption standpoint.

Both emission bands are further subject to the constraints of Fresnel reflections at the ZnO–air interface, as described in Sec. 2.4. An emission cone of half-angle $\sim 25-30^\circ$ (compared to $90^\circ$ for the case of no index of refraction mismatch) dictates that $>60\%$ of the luminescence photons incident on the interface will be totally internally reflected. If the photon energy is close to the exciton or band-to-band absorption resonances, then the continued internal propagation subsequent to total internal reflection may lead to reabsorption even for photons originating within the escape depth. The fraction $f_{\text{esc}}(h\omega)$ of photons in this energy region which are trans-
mittet through the ZnO–air interface is shown in Fig. 6.2(b). The escape probability was calculated according to Eq. (2.8) using an index of refraction \( n(\hbar \omega) \) derived from a Kramers-Kronig transformation of the estimated absorption spectrum in Fig. 6.2(a). Green luminescence photons with \( \hbar \omega < 3 \text{ eV} \) will continually propagate through the material and reflect from the ZnO–air interface until successfully escaping the material \( (f_{\text{refl}} \sim 1.0) \).

6.2 Photoluminescence of Unannealed ZnO: The Distribution of Nonradiative Traps

The time-integrated PL (TIPL) spectra for surface (one-photon) and volume (two-photon) excitation of the unannealed ZnO powder are shown in Fig. 6.3(a). The relative PL intensities are as-measured and have not been normalized. Near-band-edge emission consists of a superposition of free exciton luminescence and its longitudinal-optical (LO) phonon replicas, as discussed in Sec. 2.2.

For surface excitation of the unannealed ZnO, reabsorption effects are minimal, as evidenced by the fact that the luminescence extends non-negligibly to energies above the exciton resonance. The high-energy tail of the X-0LO line shape yields a reasonable effective temperature of \( T_X \sim 330 \text{ K} \) for the Boltzmann-like exciton population [Eq. (2.5)]. Significant reabsorption at the exciton resonance would increase the slope of the high-energy tail and yield an effective exciton temperature that is unrealistically low (less than room temperature). The spectrally integrated external quantum efficiency (QE) \( \eta_{\text{UV}} \) for near-band-edge emission, also denoted in Fig. 6.3(a), is highest for this sample and excitation condition. However, the low value of \( \eta_{\text{UV}} = 1.4\% \), consistent with other reported values for ZnO [51, 69], indicates the overall dominance of nonradiative recombination in the ZnO nanoparticles. Because the majority of carriers are excited within \( \alpha_{\text{exc}}^{-1} \sim 50 \text{ nm} \) of the particle surface, nonradiative surface
Figure 6.3: (a) Time-integrated photoluminescence (TIPL) of unannealed ZnO under one-photon and two-photon excitation. Time-resolved photoluminescence spectra are also shown for one-photon excitation (b) and two-photon excitation (c). The inset of (a) demonstrates the effect of reabsorption by comparing the difference in one-photon and two-photon TIPL intensities ($\Delta$PL) to the approximate absorption coefficient derived from photoluminescence excitation (PLE) data. In (b) and (c), the bottom three spectra in each plot are scaled by a factor of two for clarity.
recombination is expected to play a particularly significant role in depleting carriers and reducing the QE (Sec. 2.1).

In comparing the PL spectra for surface and volume excitation of the unannealed ZnO, it is clear from Fig. 6.3(a) that the high-energy side of the spectrum is suppressed for volume excitation; furthermore, $\eta_{\text{UV}}$ is lower by an order of magnitude. For volume excitation, reabsorption of the exciton is more likely because on average the photogenerated exciton must travel a longer distance to reach the surface of the particle. Subsequent to reabsorption, nonradiative recombination is possible with a probability proportional to the density of bulk nonradiative centers. For the unannealed sample, the density of bulk nonradiative traps throughout the volume of the particle is evidently significant because the QE drops so dramatically compared to the case of surface excitation.

While one would expect reabsorption to be strongest at energies $\hbar\omega > E_X$, the estimated absorption coefficient trace of Fig. 6.2(a) confirms that the Urbach tail of the absorption—possibly enhanced by an additional resonance near the X-1LO energy—extends non-negligibly to the X-1LO transition energy $\hbar\omega_{X-1LO} = 3.26$ eV at room temperature. Thus, for volume excitation, the suppression of the high-energy edge of the PL spectrum for $\hbar\omega \gtrsim (E_X - E_{1LO})$ and the overall reduction in QE can be attributed to reabsorption and subsequent nonradiative recombination in a high density of bulk traps. This reabsorption effect is dramatically illustrated in the inset of Fig. 6.3(a), where the difference in one-photon and two-photon PL intensities is virtually identical to the sub-band-gap absorption resonance derived from photoluminescence excitation data [Fig. 6.2(a)].

Figure 6.4 shows the decay of the unannealed ZnO PL spectrally integrated about the X-2LO transition (3.177 eV±0.036 eV). This decay is representative of the overall exciton population decay because many combinations of phonon wave vectors satisfy
Figure 6.4: Time-resolved photoluminescence of unannealed ZnO under one-photon and two-photon excitation. The corresponding window of spectral integration was centered at the X-2LO transition (3.177 eV ± 0.036 eV).

the momentum conservation rule associated with 2-LO-assisted exciton annihilation (Sec. 2.2.3). There is no significant change in the PL dynamics for surface versus volume excitation because in both cases the collected PL signal originates within the optical escape depth near the particle surface (α−1 ∼ 80 nm at the X-2LO transition energy). What is different is the number of excitons that either are photoexcited near or have propagated to the surface region of the sample where photon escape is possible, as indicated by the QE values and the relative PL intensities.

The PL decays of Fig. 6.4 are well described by a biexponential function, $I_X(t) = A_f \exp(-t/\tau_f) + A_s \exp(-t/\tau_s)$, where $A_f + A_s = 1$. The best-fit decay parameters, obtained by taking into account the streak system response function, are shown in Table 6.1. For both excitations of unannealed ZnO, the fast component of the PL
Table 6.1: Biexponential decay best-fit parameters for the X-2LO transition in ZnO particles. Parameters for bulk single-crystal ZnO (Ref. 77) are also shown for comparison.

<table>
<thead>
<tr>
<th>Sample/Excitation</th>
<th>$\tau_f$ [ns]</th>
<th>$\tau_s$ [ns]</th>
<th>$A_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed/one-photon</td>
<td>0.40</td>
<td>1.6</td>
<td>0.72</td>
</tr>
<tr>
<td>Unannealed/two-photon</td>
<td>0.38</td>
<td>1.5</td>
<td>0.69</td>
</tr>
<tr>
<td>Annealed/one-photon</td>
<td>0.33</td>
<td>1.7</td>
<td>0.77</td>
</tr>
<tr>
<td>Annealed/two-photon</td>
<td>0.45</td>
<td>2.1</td>
<td>0.47</td>
</tr>
<tr>
<td>Bulk/one-photon [77]</td>
<td>0.43</td>
<td>3.0</td>
<td>0.29</td>
</tr>
</tbody>
</table>

decays on a time scale $\tau_f \sim 400$ ps and with a dominant relative amplitude of $A_f \sim 0.7$. The slow component decays on a much longer time scale of $\tau_s \sim 1.5$ ns.

The fast decay component is comparable to what has been measured for bulk single-crystal ZnO ($\tau_f^{\text{bulk}} \sim 430$ ps) and has been associated with predominantly non-radiative recombination [77]. Given the shallow escape depth of near-band-edge luminescence in ZnO, the similarity of fast decay times for bulk single-crystal and nanometer-scale samples suggests more specifically that nonradiative surface recombination competes heavily with exciton-related luminescence during the first few hundred picoseconds following femtosecond excitation. The fast decay component is much more dominant for ZnO nanoparticles ($A_f \sim 0.7$) compared to bulk single-crystal samples ($A_f^{\text{bulk}} \sim 0.3$) because the surface-to-volume ratio is much larger in the former case.

The slow decay component for bulk single-crystal ZnO is characterized by $\tau_s^{\text{bulk}} \sim 3$ ns (Table 6.1) and has been attributed to the intrinsic radiative lifetime of the free exciton [77]. The reduction in $\tau_s$ by a factor of $\sim 2$ for nanoparticles is likely due to increased competition for carriers within the volume of the material because of a higher density of bulk nonradiative recombination centers.

88
Associating the fast/slow PL decay components with competition between exciton luminescence and recombination at nonradiative surface/bulk traps is supported by an analysis of the time-resolved PL spectra [Fig. 6.3(b)–(c)]. The differences in time-integrated PL spectra [Fig. 6.3(a)] for surface and volume excitation are manifested in temporal windows of 125 ps width on the sub-nanosecond scale (nonradiative surface recombination dominant) and for temporal windows of 500 ps width on the nanosecond time scale (nonradiative bulk recombination dominant). Neither spectral distribution exhibits a shift in energy as a function of time.

Absence of a time-dependent energy shift in surface-excited PL of the unannealed ZnO eliminates the possibility that the biexponential decay of the PL is explained by free excitons competing with nonradiative surface recombination (fast component) and localized excitons (slow component) [139]. If exciton localization were occurring, then the spectrum would redshift as a function of time: At very early times, the PL would primarily correspond to free excitons that have not yet become localized. After a delay characterized by the exciton localization time, the PL would primarily correspond to localized excitons which, by definition, would emit photons of lower energy upon annihilation.

Moreover, if exciton localization were responsible for the biexponential decay, then the decay characteristics would depend sensitively on the relative densities of localized states and nonradiative surface traps; generally speaking, as the sample’s surface-to-volume ratio increases, the relative density of nonradiative surface traps would increase and the fast decay component (associated with free exciton plus nonradiative surface recombination) would become more dominant than the slow component (associated with localized exciton recombination). However, because the fast decay amplitudes for both unannealed and annealed ZnO are $A_f \sim 0.75$ (Table 6.1) while the samples’ surface areas differ by a factor of $\sim 30$, it is unlikely that exciton
localization is responsible for the observed biexponential decay.

Absence of a time-dependent energy shift in the surface-excited PL also eliminates the possibility that the biexponential decay of the PL is explained by exciton diffusion from the surface region to the bulk region. Compared to volume excitation, where the excitons are generated uniformly throughout the particle, surface excitation creates a strong gradient in the spatial distribution of excitons. One might expect the excitons to diffuse away from the surface while simultaneously undergoing nonradiative surface recombination and emitting exciton luminescence. These processes would presumably occur on a fast time scale and would correspond to the fast component of the PL decay, whereas the slow component would correspond to relaxation once the excitons have diffused and equilibrated throughout the volume of the particle. If this type of diffusion were occurring in our sample, then the PL spectrum would redshift during the decay; it would evolve from the spectrum observed for surface excitation [the one-photon curve in Fig. 6.3(a)] to the spectrum observed for volume excitation [the two-photon curve in Fig. 6.3(a)]. However, the spectra plotted in Fig. 6.3(b) show that this is not the case.

Similarly, the spectra in Fig. 6.3(c) indicate that when the excitons are uniformly generated throughout the sample, there is no net migration of excitons toward the surface as a function of time. If this were the case, then the two-photon-excited PL would blueshift during the decay; it would evolve from the spectrum observed for volume excitation to the spectrum observed for surface excitation. Because neither spectral distribution shifts in energy during the course of PL decay, there is no large-scale spatial redistribution of excitons occurring via surface–bulk or bulk–surface diffusion. The data indicate that the distribution of excitons in the sample is relatively unchanged from the moment of photoexcitation to the completion of the decay process, regardless of whether surface or volume excitation is used.
The time-resolved PL spectra thus support the claims that 1) the differences in time-integrated PL spectra and QEs are due to differences in initial carrier distributions (the extent of reabsorption and bulk nonradiative recombination being much more significant for volume excitation) and 2) the biexponential decays are explained by distinct surface and bulk nonradiative recombination mechanisms rather than exciton localization and/or surface–bulk diffusion.

6.3 Photoluminescence of Annealed ZnO: The Distribution of Green-Emitting Defects

6.3.1 Near-Band-Edge Luminescence

The near-band-edge PL spectra for the annealed ZnO sample are shown in Fig. 6.5(a). As described in Sec. 4.1, the annealing process creates a large number of green-emitting defects. The presence of these defects, whose excitation profile is given by the absorption trace of Fig. 6.2(a), has a pronounced effect on the near-band-edge PL when the annealed sample is excited primarily near the surface. The inflection point at $\sim 3.26$ eV in the one-photon PL spectrum [Fig. 6.5(a)] lies near the peak of the effective absorption coefficient derived from the green defect excitation profile, suggesting that the change in PL compared to the case of unannealed ZnO (negligible green-emitting defects) is due to additional reabsorption, possibly caused by the presence of green-emitting defects. The inset of Fig. 6.5(a) compares the difference $\Delta$PL in surface-excited (one-photon) PL for unannealed and annealed ZnO samples to the estimated absorption spectrum. The difference in PL intensities between the two samples is very similar in shape to the sub-band-gap absorption resonance in the green PLE spectrum, indicating that additional reabsorption is indeed occurring near the surface of the annealed ZnO sample.
Figure 6.5: (a) Time-integrated photoluminescence (TIPL) of annealed ZnO under one-photon and two-photon excitation. Time-resolved photoluminescence spectra are also shown for one-photon excitation (b) and two-photon excitation (c). The inset of (a) demonstrates the effect of reabsorption by comparing the difference ΔPL in one-photon TIPL intensities (unannealed vs. annealed) to the approximate absorption coefficient derived from photoluminescence excitation (PLE) data. In (b) and (c), the bottom three spectra in each plot are scaled by a factor of two for clarity.
When the entire volume of the annealed particle is excited via two-photon excitation, the blue side of the PL spectrum is again suppressed relative to the case of one-photon excitation due to reabsorption [Fig. 6.5(a)]. However, the annealing process appears to reduce the density of bulk nonradiative traps because the two-photon \( \eta_{UV} \) does not drop as drastically from its one-photon value (from 0.62% to 0.42%) as it did in the case of unannealed ZnO (from 1.4% to 0.16%), despite the additional presence of ultraviolet-absorbing, green-emitting defects. Thus, reabsorption of volume-excited excitons still occurs—both by bulk nonradiative traps and by green-emitting defects. In the former case, the probability of subsequent nonradiative recombination has been reduced to the extent that the annealing process has reduced the density of bulk traps (evidenced by a higher volume-excited QE). In the latter case, subsequent emission of a green photon is highly probable given the high QE of green-emitting defects (Sec. 6.3.2).

The X-2LO exciton decays for annealed ZnO are shown in Fig. 6.6 and quantified in Table 6.1. The one-photon dynamics are nearly identical to the case of unannealed ZnO—a dominant fast decay component characterized by \( \tau_f \sim 330 \) ps, followed by a slow component with \( \tau_s \sim 1.6 \) ns. On the sub-nanosecond time scale, nonradiative surface recombination still dominates because the annealing process has not significantly altered the density of surface traps. In fact, the fast decay component is somewhat faster compared to that of unannealed ZnO because additional reabsorption is occurring near the surface [inset of Fig. 6.5(a)].

The annealed ZnO decay is noticeably different for the case of two-photon excitation, where the fast component is less dominant (\( A_f \sim 0.5 \)) and the slow decay is longer (\( \tau_s > 2 \) ns). These results are consistent with the conclusions drawn from the time-integrated PL and QE data [Fig. 6.5(a)]: The annealing process has reduced the density of *bulk* nonradiative traps, so there is less competition for exciton lumi-
Figure 6.6: Time-resolved photoluminescence of annealed ZnO under one-photon and two-photon excitation. The corresponding window of spectral integration was centered at the X-2LO transition (3.177 eV±0.036 eV).

nescence under volume excitation; the slow decay time associated with the exciton’s radiative lifetime is therefore longer—closer to the value observed in high-quality single-crystal ZnO ($\tau_{\text{bulk}} \sim 3$ ns). The annealing process has also created a high density of green-emitting defects whose presence correlates with increased reabsorption of near-band-edge luminescence. For volume excitation of the annealed ZnO, the smaller value of $A_f$ suggests a reduction in nonradiative surface recombination. Of the excitons created in the bulk of the material which then propagate toward the surface, a fraction of them are absorbed by green defects before reaching the surface, where nonradiative surface recombination would have occurred (and in which case the value of $A_f$ would have been larger).

The time-resolved near-band-edge PL spectra for annealed ZnO are shown in
Fig. 6.5(b)–(c). As was the case for unannealed ZnO, the differences in one-photon and two-photon PL spectra are maintained on every time scale. The lack of time-evolving spectral distributions again suggests that the PL differences are due to reabsorption and distinct surface/bulk nonradiative trap distributions acting upon the initial spatial distributions of carriers, rather than exciton localization or surface–bulk diffusion determining the dynamics.

### 6.3.2 Defect-Related Green Luminescence

Finally, we turn our attention to the broadband, defect-related green PL band shown in Fig. 6.7(a). The spectrally integrated efficiency $\eta_{GR}$ is only slightly higher for surface excitation, suggesting that the majority of green-emitting defects are spatially concentrated in the near-surface region of the particle and are excited by one-photon excitation. The green QE drops only slightly for volume excitation because the annealing process has reduced the density of bulk nonradiative recombination centers; the excitons are now being generated throughout the volume of the material, but most of them are able to propagate to the near-surface region and be absorbed by green traps without first undergoing nonradiative recombination in the bulk. Thus, the small reduction in green QE for volume compared to surface excitation confirms that 1) the green-emitting traps are located primarily in the surface region of the particle and 2) the annealing process reduces the density of bulk nonradiative traps. Because the green-emitting defects are concentrated near the sample surface, the main recombination channel competing with green PL is nonradiative surface (rather than nonradiative bulk) recombination.

The decay of green PL integrated about the emission peak ($2.52 \pm 0.036$ eV) is shown in Fig. 6.7(b). Again the decay is biexponential in shape with a dominant
Figure 6.7: (a) Time-integrated and (b) time-resolved green photoluminescence of annealed ZnO under one-photon and two-photon excitation. In (b) the corresponding window of spectral integration was centered near the green emission peak (2.52 eV), and its width (72 meV) was chosen to be the same as that used for near-band-edge analysis.
fast component \((A_f \sim 0.7)\), but the characteristic time scales are much slower: \(\tau_f \sim 350\) ns, \(\tau_s \sim 2\) µs. The slower decay time is consistent with previously reported values of \(\tau \sim 1\) µs \([35, 140, 141]\).

Because the green radiative mechanism is not fully understood, the explanations for its biexponential shape and its slow decay times are not clear. It is of general consensus that (near-)surface states are involved in the green luminescence process \([96, 98–100]\). The body of data in this chapter likewise supports the notion that green-emitting defects are located primarily near the surface of the ZnO particles. If this is the case, then one possible explanation of the biexponential decay is that the dominant fast component corresponds to defect sites near the sample surface and characterized by one type of local environment; the weaker, slower decay component may correspond to green luminescence originating from defects in the bulk of the material, where the density of such defects is much lower (hence the small decay amplitude) and the local environment surrounding the defect is different (hence the change in decay time). However, a complex combination of experiments beyond the scope of this dissertation is needed to understand more completely the green band PL dynamics.

### 6.4 Modeling

A rigorous, quantitative model describing the results of Secs. 6.2–6.3 is well beyond the scope of this experimental investigation. Such a model must attempt to describe, among other factors, the spatial distributions of surface, bulk, and green-emitting defects. None of these distributions can be inferred with high spatial resolution from the optical data presented in this chapter. Even if these distributions were known, the convolution of these trapping effects with the geometry of the particles and the
penetration depth of the exciting laser requires a complex model considering spatial, temporal, and spectral evolutions of the luminescence signals.

However, for a qualitative understanding of how the various radiative and non-radiative recombination processes contribute to the observed quantum efficiencies, it is instructive to consider a simple, single-particle rate equation model for the exciton population. It is assumed that excitons are created and thermalized on a time scale much shorter than the luminescence decays so that processes leading to the thermalized exciton population may be neglected. This assumption is valid for the excitation fluence used to generate the data in Secs. 6.2–6.3 because it corresponds to a photogenerated carrier density in the low–intermediate regime of excitation. (The breakdown of this assumption will be discussed in Chap. 7.)

In this section a series of rate equations will be considered in order of increasing complexity. The complexity is related to the number of recombination channels competing with exciton luminescence, as inferred from the data in Secs. 6.2–6.3 for different combinations of samples (unannealed versus annealed) and excitation (one-photon/surface versus two-photon/bulk).

### 6.4.1 Two-Photon Excitation, Annealed Sample, Bulk Region

First we consider an element of volume within the bulk region of the annealed ZnO sample. The annealing process has drastically reduced the density of bulk nonradiative traps so that nonradiative recombination within this region will be ignored. In the case of two-photon excitation, carriers are photogenerated uniformly throughout the volume element. After initial generation of an exciton population from these photoexcited carriers, the only processes under consideration are depletion of excitons via radiative recombination and creation of excitons via reabsorption. The exciton
population $x$ is given by

$$\dot{x} = +g - \frac{x}{\tau_{\text{rad}}}, \quad x(t = 0) = G.$$  

The initial exciton population created by the laser is given by the initial condition $G$ (proportional to the laser fluence), and $\tau_{\text{rad}}$ is the intrinsic radiative exciton lifetime. Exciton creation via reabsorption is described by the $g$ term. We assume that the rate of exciton creation due to reabsorption is proportional to the existing exciton population according to an unknown factor $\tau_{\text{reabs}}^{-1}$:

$$\dot{x} = + \left( \frac{1}{\tau_{\text{reabs}}} \right) x - \frac{x}{\tau_{\text{rad}}} = - \left( \frac{1}{\tau_{\text{rad}}} - \frac{1}{\tau_{\text{reabs}}} \right) x = -\frac{x}{\tau_x},$$

where $\tau_x \equiv (\tau_{\text{rad}}^{-1} - \tau_{\text{reabs}}^{-1})^{-1}$ is the effective exciton lifetime that takes into account reabsorption. It is this effective lifetime that is measured by TRPL because the instantaneous UV PL intensity $I_{\text{UV}}(t)$ is proportional to the exciton population, i.e., $I_{\text{UV}}(t) \propto x(t) \propto e^{-t/\tau_x}$ [54]. We require $\tau_{\text{reabs}}^{-1} < \tau_{\text{rad}}^{-1}$ so that the exciton population asymptotically decays with time rather than increases. Therefore, reabsorption slows down the radiative decay process, but it does not change the single-exponential nature of the decay. The effective lifetime $\tau_x$ can be approximated as the slow component of the UV TRPL data because this component corresponds to exciton luminescence originating in the bulk of the material. For the case of two-photon excitation under consideration here, $\tau_x \approx 2.05$ ns (Table 6.1).

### 6.4.2 Two-Photon Excitation, Unannealed Sample, Bulk Region

Now we consider the bulk region of the unannealed sample, where dynamics following two-photon excitation differ from the annealed sample through the presence of bulk
nonradiative traps that introduce a parallel decay channel characterized by a trapping time $\tau_{\text{nr}}$:

$$\dot{x} = \frac{x}{\tau_x} - \frac{x}{\tau_{\text{nr}}} = -\left(\frac{1}{\tau_x} + \frac{1}{\tau_{\text{nr}}}ight)x.$$ 

Again, the single-exponential nature of the decay is not altered; the decay is simply accelerated. An estimate of $\tau_{\text{nr}}$ may be obtained by considering the slow decay component in this sample (Table 6.1) to be the effective lifetime taking both decay channels into account: $(1.50 \text{ ns})^{-1} = \tau_x^{-1} + \tau_{\text{nr}}^{-1}$ implies that $\tau_{\text{nr}} \approx 5.59 \text{ ns}$. It is worth noting that this value is within an order of magnitude of an estimated nonradiative lifetime in ZnO from the literature [56].

It is also interesting to consider the predicted UV quantum efficiency: The internal quantum efficiency $\eta_{\text{UV}}^{\text{int}}$ is given by the competition between radiative and nonradiative decay rates,

$$\eta_{\text{UV}}^{\text{int}} \equiv \frac{\tau_x^{-1}}{\tau_x^{-1} + \tau_{\text{nr}}^{-1}} \approx 0.73.$$

The experimentally accessible external quantum efficiency $\eta_{\text{UV}}^{\text{ext}}$ may be estimated by taking into account the probability $f_{\text{esc}}^{\text{refl}}$ of optical escape due to Fresnel effects [$f_{\text{esc}}^{\text{refl}}(\hbar \omega_{X-2LO} = 3.18 \text{ eV})$ in Fig. 6.2(b)]:

$$\eta_{\text{UV}}^{\text{ext}} = f_{\text{esc}}^{\text{refl}} \cdot \eta_{\text{UV}}^{\text{int}} \approx 0.18 \cdot \eta_{\text{UV}}^{\text{int}} \implies \eta_{\text{UV}}^{\text{ext}} \approx 0.13.$$ \hspace{1cm} (6.1)

This value is much larger than the UV quantum efficiencies reported in Secs. 6.2–6.3 because nonradiative surface recombination has not yet been taken into account.
6.4.3 One-Photon Excitation, Unannealed Sample, Surface Region

Now we account for the effect of nonradiative surface recombination by considering the fast decay component of the unannealed sample’s UV PL following one-photon (near-surface) excitation. Assuming the intrinsic exciton reabsorption and radiative decay processes are identical to those in the bulk region, there is now competition between the intrinsic exciton lifetime $\tau_x = 2.05$ ns and a fast nonradiative surface recombination channel characterized by a trapping time $\tau_{nrs}$:

$$\dot{x} = -\frac{x}{\tau_x} - \frac{x}{\tau_{nrs}} = -\left(\frac{1}{\tau_x} + \frac{1}{\tau_{nrs}}\right)x.$$ 

The effective lifetime near the surface for this sample and excitation condition is 0.40 ns (Table 6.1). From this measured lifetime, the nonradiative surface trapping time may be estimated: $(0.40 \text{ ns})^{-1} = \tau_x^{-1} + \tau_{nrs}^{-1}$ implies that $\tau_{nrs} \approx 0.50$ ns. Again, this value is reasonable based on the approximate quantum efficiency it predicts,

$$\eta_{\text{int}}^{\text{UV}} \approx \frac{\tau_x^{-1}}{\tau_x^{-1} + \tau_{nrs}^{-1}} \approx 0.20 \implies \eta_{\text{ext}}^{\text{UV}} \approx 0.036.$$ (6.2)

Now that nonradiative surface recombination has been considered, the estimated UV external quantum efficiency is within a factor of 3 of the experimentally measured $\eta_{\text{UV}} = 0.014$. An even more accurate estimate would result if bulk nonradiative recombination were simultaneously considered.

6.4.4 One-Photon Excitation, Annealed Sample, Surface Region

Finally, we consider the near-surface region of the annealed sample. The fast decay component under one-photon excitation is accelerated compared to the unannealed
sample because excitons are additionally able to decay through green-emitting defects in the annealed sample. The trapping of excitons at green-emitting defects, as characterized by a trapping time $\tau_{gr}$, competes with both exciton trapping at nonradiative surface traps and intrinsic radiative recombination:

$$\dot{x} = - \frac{x}{\tau_x} - \frac{x}{\tau_{nrs}} - \frac{x}{\tau_{gr}} = - \left( \frac{1}{\tau_x} + \frac{1}{\tau_{nrs}} + \frac{1}{\tau_{gr}} \right) x. \quad (6.3)$$

The values $\tau_x = 2.05 \text{ ns}$ and $\tau_{nrs} = 0.50 \text{ ns}$ may be used to estimate $\tau_{gr}$, again using the appropriate overall lifetime from Table 6.1: $(0.33 \text{ ns})^{-1} = \tau_x^{-1} + \tau_{nrs}^{-1} + \tau_{gr}^{-1}$ implies that $\tau_{gr} \approx 2.0 \text{ ns}$. The green defect trapping time is almost identical to the intrinsic exciton lifetime, which suggests that excitation of green-emitting defects occurs only during the lifetime of the excitons. This result supports the claim that the green defect excitation mechanism is strongly correlated with the presence of excitons.

Using an equation analogous to Eq. (6.2), it is readily apparent that the predicted UV quantum efficiency decreases with the addition of green-emitting defects. A decrease in the one-photon QE is indeed observed experimentally when comparing the annealed sample to the unannealed sample. Moreover, this simple rate equation model predicts the green quantum efficiency with surprising accuracy:

$$\eta_{GR}^{\text{int}} = \eta_{GR}^{\text{ext}} = \frac{\tau_{gr}^{-1}}{\tau_x^{-1} + \tau_{nrs}^{-1} + \tau_{gr}^{-1}} \approx 0.17, \quad (6.4)$$

which compares with the experimental value $\eta_{GR} = 0.14$ [Fig. 6.5(a)]. No reduction in green QE due to Fresnel reflections and reabsorption is required because there are no nonradiative traps that can absorb green emission; consequently, all of the emitted green photons eventually escape.
6.4.5 Dependence of PL Intensity on Excitation Density

For the simple rate equation model discussed in this section, only the initial condition $x(t = 0) = G \propto I_{\text{exc}}$ of the exciton population depends explicitly on excitation fluence $I_{\text{exc}}$. By neglecting the exciton formation process and beginning our analysis with a stable exciton population, we are implicitly restricting the analysis to a low-intensity regime of excitation where the other model parameters may be considered constants. Moreover, we are implicitly assuming a linear relationship between $G$ and $I_{\text{exc}}$, i.e., every quantum of excitation absorbed leads to an exciton that is part of the initial exciton population.

The dependence of the UV PL intensity $I_{\text{UV}}$ on excitation fluence is obtained by solving the rate equation for the exciton population as a function of time:

$$\dot{x} = -\frac{x}{\tau}, \quad x(t = 0) = G \implies x(t) = Ge^{-t/\tau}, \quad I_{\text{UV}} \equiv \frac{1}{\tau_x} \int_0^\infty x(t) dt = \frac{G}{\tau},$$

where $\tau$ is the overall lifetime (for example, $\tau^{-1} = \tau_x^{-1} + \tau_{\text{rs}}^{-1}$). Using the definition of UV internal quantum efficiency [Eq. (6.2)], the UV PL intensity may be re-written as follows:

$$I_{\text{UV}} = \eta_{\text{UV}}^{\text{int}} \cdot G. \quad (6.5)$$

Thus, the PL intensity is proportional to the quantum efficiency (assumed to be constant since the lifetimes are constant), and it also scales linearly with the excitation fluence.

6.5 Summary

Commercial ZnO particles in their original (unannealed, nanometer-scale) and modified (annealed, micrometer-scale) forms have been characterized optically using fem-
to second one-photon and two-photon excitation. The unannealed particles exhibit primarily near-band-edge (ultraviolet) emission with a quantum efficiency of $\eta_{UV} \lesssim 1\%$. A comparison of one-photon and two-photon QEs and (TR)PL data suggests that high densities of both surface and bulk nonradiative traps reduce the emission efficiency. The annealed particles additionally exhibit a broad, visible-wavelength band that is characteristic of ZnO:Zn phosphors. This emission band, which exhibits a relatively large quantum efficiency ($\eta_{GR} > 10\%$) and decays on a microsecond time scale, originates from defects located primarily near the surface of the particles. The annealing process also appears to reduce the density of bulk nonradiative traps, such that the primary competition for both band-edge and green emissions is nonradiative surface recombination. A simple rate equation model is used to ascertain qualitatively the effects of the various radiative and nonradiative recombination processes on the measured quantum efficiencies.
Chapter 7

Influence of Photoexcitation Density on Carrier Dynamics and Luminescence Efficiencies

The response of ZnO to various densities of photoinjected carriers provides important information about the relevant emission mechanisms and the transfer of energy between them. In particular, prior to the work presented in this dissertation, it has not been clear if the mechanism of green defect emission is mediated by trapped electrons, holes, or excitons. Femtosecond pulsed excitation generates relatively high densities of carriers owing to the short duration of time over which excitation occurs, but it provides insight into the relaxation dynamics of the subsequent quasi-thermalized carrier distributions. By studying the PL responses of excitons and green-emitting defects to various levels of pulsed excitation, we may look for correlations (or a lack thereof) between near-band-edge dynamics and green defect dynamics and thus provide insight into this energy transfer process.

On the other hand, continuous-wave excitation allows the system to reach a true equilibrium that is more indicative of potential device performance since the time scale of excitation greatly exceeds the lifetimes of the various recombination channels. Studying this regime of excitation provides realistic constraints on phosphor operation by delineating the excitation densities at which ZnO emits green/white light with acceptable efficiency.

The photoluminescence (PL) responses associated with exciton annihilation near the band edge and defect-related green emission are studied first in Sec. 7.1 for the case of varying levels of femtosecond excitation. Both time-integrated and time-
resolved PL properties are studied as a function of excitation fluence for injected carrier densities $n_{\text{exc}} \sim 10^{18} - 10^{19}$ cm$^{-3}$. A reduction in green PL quantum efficiency (QE) with increasing fluence is attributed to changes in the spatial distribution of free excitons, which in turn is due to an increase in carrier cooling time associated with the hot phonon effect. An alternative explanation involving saturation of green-emitting defects is also discussed. Both possibilities are discussed in the context of a natural extension to the rate equation model introduced in Sec. 6.4.

In Sec. 7.2 a similar analysis is performed on the excitation power dependence of steady-state PL intensities and QEs. The green QE $\eta_{\text{GR}}$ exceeds 50% in the low-irradiance limit of this regime and is the basis for consideration of ZnO as a UV-excited green/white light phosphor. The quenching of this highly efficient recombination channel for irradiances $I_{\text{exc}} > 0.2$ W cm$^{-2}$ is attributed to either thermal depopulation of the defect’s excited vibrational states by photogenerated phonon populations (hot phonon effect model), or to saturation of green-emitting defects (trap saturation model).

This study of the excitation density dependence of ZnO PL is unique in that it describes the evolution of time-integrated PL intensities and efficiencies for both emission bands under various types of excitation (pulsed and continuous). The sample under consideration is the annealed ZnO (ZnO:Zn) powder. This sample was chosen because the annealing process enhances the green emission considerably without severely suppressing near-band-edge emission (in contrast with ZnO:S samples). Being able to measure accurately the PL intensities and QEs for both emission bands simultaneously greatly facilitates the analysis of the bands’ respective excitation power dependences.
7.1 Femtosecond Pulsed Excitation

7.1.1 High Excitation Effects

Even if the output beam of the femtosecond excitation source (Appendix A) is attenuated to \( \lesssim 1 \, \mu\text{J}\,\text{cm}^{-2} \) so that it generates PL signals just above the detection limit of the PL detectors, the corresponding photoinjected carrier densities exceed \( \sim 10^{17} \, \text{cm}^{-3} \). This minimum density is already comparable to typical free electron concentrations \( n_0 \) in intrinsically \( n \)-type ZnO \( (n_0 \sim 10^{16} - 10^{18} \, \text{cm}^{-3}) \) [33, 52, 53]. By increasing the laser fluence several orders of magnitude, one can easily reach or exceed the effective density of states for both electrons \( (n_{\text{eff}}) \) and holes \( (p_{\text{eff}}) \) [142],

\[
    \rho_{\text{eff}} = 2 \left( \frac{2\pi m^* k_B T_L}{\hbar^2} \right)^{(3/2)} \rightarrow n_{\text{eff}} \approx 3 \times 10^{18} \, \text{cm}^{-3}, \quad p_{\text{eff}} \approx 2 \times 10^{19} \, \text{cm}^{-3},
\]

as well as the Mott density\(^{1}\)

\[
    3 \times 10^{17} \, \text{cm}^{-3} \leq n_M \leq 2 \times 10^{20} \, \text{cm}^{-3}.
\]

By all of these criteria, femtosecond excitation inherently corresponds to intermediate or high regimes of excitation. It is therefore important to consider so-called “hot carrier effects” which may influence carrier relaxation and subsequent recombination mechanisms. In particular, it was assumed in Chap. 6 that formation and thermalization of a stable exciton population occurred on a time scale much faster than the luminescence lifetimes. Hot carrier effects are expected to alter the carrier cooling and exciton formation processes, which in turn may affect the luminescence properties for near-band-edge and/or green band emission.

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\(^{1}\)The actual Mott density for ZnO remains a matter of debate. Klingshirn et al. [142] provide a comparison of values obtained by various calculations.
For the experimental results discussed in this section, the above-gap excitation energy was fixed at $E_{\text{exc}} = 3.86 \text{ eV}$. The portion of this energy in excess of the band gap $E_g$, $\Delta E = E_{\text{exc}} - E_g = 490 \text{ meV}$, is largely given to the electrons because their effective mass ($m_e = 0.28m_0$) is much larger than that of holes ($m_h = 0.95m_0$) [26,143]:

$$\Delta E_{e,h} = \left( \frac{m_{h,e}}{m_e + m_h} \right) (E_{\text{exc}} - E_g) \implies \Delta E_e = 380 \text{ meV}, \, \Delta E_h = 110 \text{ meV}.$$ 

As discussed in Sec. 2.1, the photoexcited carriers typically cool first by emitting LO phonons with energy $\hbar \omega_{\text{LO}} = 72 \text{ meV}$. In the present case, photoexcited holes dissipate their excess energy through emission of one LO phonon followed by acoustic phonon emission and scattering/thermalization with other holes whose excess energy is less than $\hbar \omega_{\text{LO}}$. Similarly, photoexcited electrons first dissipate energy through emission of $\leq 5$ LO phonons before further cooling by acoustic phonon emission and electron-electron scattering. The electrons dissipate $>75\%$ of the total excess energy because they are so much lighter than the holes. Therefore, it is reasonable to neglect hole dynamics and concentrate on the mechanisms by which photoexcited electrons dissipate their excess energy.

The electron-electron interaction does not affect carrier cooling times in the perturbative regime of excitation, but it can compete with or even exceed the energy dissipation rate of LO-phonon-based cooling at high carrier densities. The energy dissipation rates of electron-LO-phonon scattering and electron-electron scattering become equal at a critical density given by

$$n_c^* = \frac{8\pi(eE_0)\hbar \omega_{\text{LO}} e^2 \varepsilon_0^2}{e^4} \left[ (N_q + 1) \sinh^{-1} \left( \frac{\Delta E_e - \hbar \omega_{\text{LO}}}{\hbar \omega_{\text{LO}}} \right)^{(1/2)} - N_q \sinh^{-1} \left( \frac{\Delta E_e}{\hbar \omega_{\text{LO}}} \right)^{(1/2)} \right], \quad (7.1)$$
where \((eE_0) [\text{units eV cm}^{-1}]\) is an effective field strength characterizing the electron-phonon interaction,\(^2\) \(\epsilon\) is the average material dielectric constant, \(\varepsilon_0\) is the free-space permittivity, \(e\) is the fundamental charge, and \(N_q\) is the equilibrium LO phonon occupation number (\(\ll 1\) at room temperature for ZnO) [26,143]. Using the material parameters of ZnO yields \(n^*_c \approx 1.3 \times 10^{19} \text{ cm}^{-3}\). Thus, for injected electron-hole pair densities \(n_{\text{exc}} \ll n^*_c\), the photoexcited carriers dissipate energy primarily through LO phonon emission. For densities \(n_{\text{exc}} \gtrsim n^*_c\), carriers dissipate excess energy through hot electron-electron collisions as well.

In addition to increased competition from electron-electron scattering at high densities, the electron-LO-phonon scattering rate itself can be reduced by the so-called “hot phonon effect,” whereby the energy loss rate of photoexcited carriers is reduced due to reabsorption of nonequilibrium phonons [144]. Once the injected carrier density exceeds a threshold \(n_q\), the hot phonon effect impedes carrier cooling on a time scale given by the phonon lifetime. Calculation of \(n_q\) is not straightforward, but physically \(n_q\) corresponds to the density at which the photoinduced LO phonon population exceeds that given by a detailed-balance equilibration between carrier and phonon populations. Above this threshold, carriers begin to absorb phonons rather than emit them [145].

The results of Sun et al. provided experimental evidence for the manifestation of the hot phonon effect specifically for the case of ZnO nanostructures [65]. They studied carrier cooling and exciton formation in ZnO nanorods using ultrafast time-resolved differential transmission. For above-gap excitation of the nanorods, the above-gap probe transmission depended on the fluence of exciting light as follows: \(\text{Excitation} \lesssim 30 \mu \text{J cm}^{-2}\) (corresponding to \(n_{\text{exc}} \lesssim 5 \times 10^{18} \text{ cm}^{-3}\)) was considered to

\(^2\)The field strength \((eE_0)\) is related to the usual Fröhlich coupling constant \(\alpha = (e^2 a_p / 2\hbar \omega_{LO})(\varepsilon^{-1}_\infty - \varepsilon^{-1}_0)\) according to \((eE_0) = 2 a_p m_e \omega_{LO}^2\), where \(a_p = \sqrt{2 m_e \omega_{LO}/\hbar}\) is the polaron radius and \(\varepsilon_\infty\) and \(\varepsilon_0\) are the material high-frequency and static dielectric constants, respectively.
be in the perturbative regime because the signal consistently exhibited a fast decay component of $\sim 200$ fs and a slow decay component of $\sim 10$ ps. The fast decay was attributed to carrier cooling via the carrier-LO-phonon (Fröhlich) interaction discussed above. The slow component was attributed to the relaxation of quasithermalized carriers, primarily by means of nonradiative recombination. When the exciting fluence exceeded $\sim 50 \, \mu J \, cm^{-2}$ ($n_{exc} \gtrsim 8 \times 10^{18} \, cm^{-3}$), the time-resolved differential transmission signal exhibited an additional decay component characterized by $1.75 \pm 0.25$ ps. Sun et al. explained this delay in the carrier cooling process by the hot phonon effect because the 1.75 ps decay time they measured is identical to the $E_2$-high optical phonon lifetime previously measured by impulsive stimulated Raman scattering [146]. Thus, above a threshold $n_q \sim 5 - 8 \times 10^{18} \, cm^{-3}$, photoexcited electrons required more time to cool to the bottom of the conduction band—and therefore more time to form excitons—due to reabsorption of nonequilibrium optical phonons during the cooling process.

A final consideration for photogeneration of high carrier densities is that of trap saturation. For a given ZnO sample, there are finite densities of nonradiative surface traps, nonradiative bulk traps, and radiative green-emitting defects (Chap. 6). Each of these recombination channels is further characterized by a distinct trapping time over which carriers are trapped and by a distinct recombination time over which the trapped carriers recombine. If the excitation conditions are such that the carrier photogeneration rate exceeds the trapping and/or recombination rates associated with a particular type of trap, then that trap level will become saturated (the full density of such traps being excited simultaneously) and the corresponding recombination efficiency reduced. Typical densities for the similar GaN material system include a radiative defect concentration $\sim 10^{16} \, cm^{-3}$ and an effective nonradiative trap concentration $\sim 10^{19} \, cm^{-3}$ [147].
Figure 7.1: Time-integrated photoluminescence spectra of annealed ZnO:Zn under low (8.3 $\mu$J cm$^{-2}$), intermediate (17 $\mu$J cm$^{-2}$), and high (110 $\mu$J cm$^{-2}$) fluence of femtosecond pulsed excitation.

7.1.2 Time-Integrated Photoluminescence and Quantum Efficiency

Representative time-integrated PL spectra for ZnO:Zn under femtosecond excitation are shown in Fig. 7.1. The chosen fluences correspond to the three regimes of excitation outlined by Sun et al. [65]. An excitation fluence of 8.3 $\mu$J cm$^{-2}$ corresponds to an approximate injected carrier density of $n_{\text{exc}} = 2 - 3 \times 10^{18}$ cm$^{-3}$ if the laser penetration depth is 50 – 70 nm (Sec. 2.1); it is considered a perturbative excitation. A fluence of 17 $\mu$J cm$^{-2}$ creates approximately $n_{\text{exc}} = 4 - 6 \times 10^{18}$ cm$^{-3}$ carriers; for these densities the hot phonon effect may begin to affect carrier cooling. Finally, the high-intensity regime, where the hot phonon effect may significantly delay carrier cooling, is represented by the spectrum for 110 $\mu$J cm$^{-2}$ excitation ($n_{\text{exc}} = 3 - 4 \times 10^{19}$ cm$^{-3}$).

It is evident from Fig. 7.1 that the shapes of the PL bands do not depend sig-
nificantly on excitation fluence. In all cases, the near-band-edge emission consists primarily of the second LO phonon replica of the free exciton (X-2LO, 3.18 eV), with a high-energy shoulder due to free exciton emission (X-0LO, 3.31 eV). The peak position does not redshift with increasing fluence, which confirms that the emission remains excitonic in origin and is not due, for example, to amplified spontaneous emission associated with band gap renormalization and electron-hole plasma formation [27, 93]. The green band related to defect emission also does not change significantly in width or peak position.

The spectrally integrated PL intensities of near-band-edge emission (UV) and green defect emission (GR) are plotted in Fig. 7.2(a) as a function of excitation fluence. When plotted in this fashion, the dependence of PL intensity $I_{PL}$ on the intensity $I_{exc}$ of exciting light is traditionally described by an equation of the form

$$I_{PL}(I_{exc}) = \eta \cdot (I_{exc})^k,$$

(7.2)

where the proportionality constant $\eta$ is the efficiency of the PL process and the exponent $k$ of the power-law dependence is indicative of the recombination mechanism [148–150]. This equation is a generalization of the PL excitation density dependence [Eq. (6.5)] derived in the context of a simple rate equation model describing exciton luminescence. In that case, the details of the exciton formation process were neglected, and it was assumed that the initial exciton population depended linearly on the excitation density, i.e., $k=1$.

The more general Eq. (7.2) allows for the fact that exciton formation is a bimolecular process; before a stable exciton population exists, free electrons and holes (the population of each being proportional to $I_{exc}$) must independently dissipate excess energy and become Coulomb-correlated. In this case the exponent associated with
Figure 7.2: Dependence of spectrally integrated near-band-edge (UV) and green (GR) photoluminescence intensities (a) and external quantum efficiencies (b) on excitation fluence. The vertical arrows in (a) correspond to carrier densities associated with high excitation effects (Sec. 7.1.1).
exciton luminescence should be \( k = 2 \). As the exciton formation process occurs in imperfect materials and competes with other carrier cooling/recombination mechanisms, the exciton formation efficiency is reduced from the ideal case, leading to an effective exponent \( k < 2 \). Indeed, slopes \( 1 < k < 2 \) are generally observed experimentally for exciton luminescence [80,148–150].

Generally it is assumed that \( \eta \) does not depend on excitation fluence, and analysis of PL emission mechanisms proceeds on the basis of slopes (\( k \)-values) derived from curves similar to Fig. 7.2(a). In the perturbative regime (< 10 \( \mu \)J cm\(^{-2} \)), both PL intensities exhibit a power-law behavior characterized by a slope of \( k_{\text{UV,GR}} \approx 1.7 \). However, a distinct change in the slopes occurs at a critical density corresponding to \( I_{\text{exc}} \approx 20 \mu \)J cm\(^{-2} \): The green dependence becomes sublinear with a slope \( k_{\text{GR}} = 0.79 \) while the band edge slope increases to \( k_{\text{UV}} = 1.87 \). The same transition is evident in the excitation fluence dependence of the respective quantum efficiencies, as illustrated in Fig. 7.2(b). In the perturbative regime, both PL bands exhibit approximately constant QEs whose magnitudes are typical for the respective emission mechanisms: \( \eta_{\text{UV}} \lesssim 1\% \) for near-band-edge PL and \( \eta_{\text{GR}} > 30\% \) for green defect emission [51,69]. Above \( I_{\text{exc}} \approx 20 \mu \)J cm\(^{-2} \), the green QE begins a steady decline while the UV QE quickly exceeds 1\% and eventually exceeds 10\%.

It is clear from Fig. 7.2(b) that \( \eta \) in Eq. (7.2) is not constant throughout this regime of excitation for either emission band; however, there is no \textit{a priori} expectation regarding the functional dependence of \( \eta \) on \( I_{\text{exc}} \). A phenomenological prediction may be derived by introducing a population dependence to the rate equation constants of the previous chapter [Eq. (6.3)]:

\[
\dot{x} = - \left[ \left( \frac{n_x}{x + n_x} \right) \left( \frac{1}{\tau_x} \right) + \left( \frac{n_{nrs}}{x + n_{nrs}} \right) \left( \frac{1}{\tau_{nrs}} \right) + \left( \frac{n_{gr}}{x + n_{gr}} \right) \left( \frac{1}{\tau_{gr}} \right) \right] x, \quad (7.3)
\]
where $x$ is the exciton population and $n_x$, $n_{nrs}$, and $n_{gr}$ are critical densities at which the corresponding recombination/capture rates undergo transitions for exciton, non-radiative surface, and green recombination channels, respectively. The transitions associated with $n_{nrs}$ and $n_{gr}$ could correspond, for example, to trap saturation (in which case the critical density is the actual trap density) or to some other physical mechanism which alters the capture rates above a certain critical density. The transition associated with the critical density $n_x$ could correspond to the Mott density (exciton dissociation and electron-hole plasma formation) or to some other mechanism which alters the effective exciton radiative lifetime.

By including these density-dependent prefactors in the corresponding definitions for estimated UV and GR external quantum efficiencies,

$$\eta_{UV} = f_{\text{esc}} \left( \frac{n_x}{x+n_x} \right) \left( \frac{1}{\tau_x} \right) + \left( \frac{n_{nrs}}{x+n_{nrs}} \right) \left( \frac{1}{\tau_{nrs}} \right) + \left( \frac{n_{gr}}{x+n_{gr}} \right) \left( \frac{1}{\tau_{gr}} \right) \quad (7.4)$$

and

$$\eta_{GR} = \left( \frac{n_x}{x+n_x} \right) \left( \frac{1}{\tau_x} \right) + \left( \frac{n_{nrs}}{x+n_{nrs}} \right) \left( \frac{1}{\tau_{nrs}} \right) + \left( \frac{n_{gr}}{x+n_{gr}} \right) \left( \frac{1}{\tau_{gr}} \right) \quad (7.5)$$

the predicted excitation density dependence of the efficiencies may be compared to the experimental data. The best-fit results are superimposed on the experimental QE data in Fig. 7.2(b). The UV and GR data sets were fit simultaneously with fixed values for $n_x$ and $\tau_x$, and adjustable values for the remaining parameters ($n_{nrs}$, $\tau_{nrs}$, $n_{gr}$, $\tau_{gr}$, and $f_{\text{esc}}$). Any fixed value of $n_x \gg n_{nrs}, n_{gr}$ in conjunction with a fixed

---

3 The dominant nonradiative recombination channel is that of surface traps rather than bulk traps since the one-photon, above-gap excitation primarily creates carriers/excitons near the surface of the sample.

4 As in Eq. (6.1), the UV efficiency contains a prefactor $f_{\text{esc}}$ that accounts for the probability of internal reflection and subsequent nonradiative recombination; such a factor is not necessary for green efficiency because reabsorption is negligible.
$\tau_x = 2$ ns (Sec. 6.4) led to the same set of best-fit critical densities: $n_{\text{hrs}} \sim 2 \times 10^{19}$ cm$^{-3}$ and $n_{\text{gr}} \sim 4 \times 10^{18}$ cm$^{-3}$.

The fact that the model converged to the same set of fit parameters for any $n_x \gg n_{\text{hrs}}, n_{\text{gr}}$ indicates that, to the extent the model accurately represents the data, the effective exciton radiative lifetime is independent of excitation fluence. When considering only the three recombination channels of exciton luminescence, exciton nonradiative recombination, and exciton capture at green defects, there is evidently no “critical density” at which the effective exciton radiative lifetime changes.

The green critical density $n_{\text{gr}} \sim 4 \times 10^{18}$ cm$^{-3}$ is very similar to the hot phonon critical density $n_q \sim 5 - 8 \times 10^{18}$ cm$^{-3}$ reported by Sun et al., and could suggest that the green luminescence QE decreases above this threshold because of the hot phonon effect. The nonradiative critical density $n_{\text{hrs}} \sim 2 \times 10^{19}$ cm$^{-3}$ is very similar to the density $n_c^* \sim 1 \times 10^{19}$ cm$^{-3}$ at which the electron-electron energy dissipation rate becomes comparable to the electron-LO-phonon energy dissipation rate [Eq. (7.1)]. Above this density the GR QE continues to decrease while the UV QE increases by another order of magnitude. Thus, the best-fit critical densities suggest that hot phonon and hot electron effects combine to enhance UV luminescence at the expense of GR luminescence. The increase in carrier cooling time resulting from these hot phonon/electron effects evidently favors exciton formation and luminescence over green defect excitation and luminescence.

These results can alternatively be explained in a trap saturation model as follows: When the excitation fluence exceeds 13 $\mu$J cm$^{-2}$ (corresponding to $n_{\text{gr}} \sim 4 \times 10^{18}$ cm$^{-3}$), the green-emitting defects are saturated on the time scale of the exciton lifetime, so more of the excitons recombine nonradiatively or generate UV luminescence rather than transferring their energy to green-emitting defects. As the excitation fluence is further increased beyond 70 $\mu$J cm$^{-2}$ (corresponding to $n_{\text{hrs}} \sim 2 \times 10^{19}$ cm$^{-3}$), nonra-
diative surface traps also become saturated during the exciton lifetime, and the QE of the remaining recombination channel (UV luminescence) is again enhanced.

Regardless of the physical interpretation of the parameters $n_{nrs}$ and $n_{gr}$, the rate equation model presented in Chap. 6—and extended here to allow for excitation density dependence of the recombination/capture rates—provides a qualitative understanding of the quantum efficiencies in ZnO. In the perturbative regime, a photo-generated exciton population may decay through the three channels of radiative recombination, nonradiative recombination, and energy transfer to green-emitting defects. The respective quantum efficiencies of the recombination channels are given by the relative strengths of the corresponding intrinsic recombination/capture rates. These rates—and therefore the corresponding quantum efficiencies—are modified at higher densities of excitation in a way that is captured by Eqs. (7.4)–(7.5).

Considering next the exponent $k$ [Eq. (7.2)], which is sensitive to changes in the recombination mechanisms rather than their efficiencies, we plot in Fig. 7.3 the power-law behavior of the PL intensity normalized to the density-dependent quantum efficiency:

$$I_{PL}(I_{exc}) = \eta(I_{exc}) \cdot (I_{exc})^k \Rightarrow \log(I_{PL}/\eta) = k \log(I_{exc}).$$

(7.6)

This normalization procedure decouples the implicit excitation density dependence of the quantum efficiency $\eta$ from the explicit power-law dependence on $I_{exc}$. Whereas $\eta$ gives the probability of exciton recombination through a particular channel, the power law relating emitted photons to absorbed photons provides information about the overall photoexcited exciton population. As discussed above, the exponent $k$ effectively describes the efficiency of the exciton formation process and therefore is an indication of the relative size of the overall exciton population prior to recombination.
Figure 7.3: Pulsed excitation power-law behavior of the ratio of spectrally integrated photoluminescence intensity to the corresponding quantum efficiency for near-band-edge (UV) and green (GR) emissions.

through various channels.

Because the UV and GR QEs were approximately constant in the perturbative regime, the slopes for $I_{\text{exc}} \lesssim 10 \mu J \text{ cm}^{-2}$ in Fig. 7.3 remain approximately the same after normalization. The transition at $I_{\text{exc}} \sim 20 \mu J \text{ cm}^{-2}$ remains clearly evident, as indicated by the distinct change in slope from $k \approx 1.75$ to $k = 1.15$ at this fluence. What is perhaps surprising is that the UV and GR power dependences are now identical both below and above the critical density. In other words, the GR PL emission mechanism exhibits a power dependence identical to that of exciton-related UV PL for all values of excitation fluence. This result clearly indicates a common underlying mechanism for both PL bands and supports the hypothesis discussed in Chaps. 5–6 that excitation of green-emitting defects occurs by transfer of energy from excitons.
A decrease in $k$ above the critical density suggests that the efficiency of the exciton formation process has been reduced. If the transition is due to hot phonon and/or hot electron effects, the corresponding increase in carrier cooling and diffusion times provides more time (and therefore increased probability) for free carriers to recombine nonradiatively prior to exciton formation. Moreover, both the LO phonon energy (72 meV) and the initial kinetic energy of electrons (380 meV) exceed the exciton binding energy (60 meV). If either of these entities collides inelastically with an exciton, then exciton dissociation may occur and effectively reduce the exciton formation efficiency.

If the reduction in exciton formation efficiency above $n_{gr} = 4 \times 10^{18}$ cm$^{-3}$ is instead considered in the context of a trap saturation model, then the dependence of the efficiency on the number of populated green traps suggests that excitons are more likely to form in the vicinity of green defects—or perhaps that either the electron or hole comprising the exciton is localized on the green defect itself. In this case, a saturation of green-emitting defects would correspond to a saturation in the lattice sites favorable for exciton formation; with continued increase of photoexcitation density above this saturation density, the efficiency of exciton formation would be reduced and would lead to a reduced $k$-value.

### 7.1.3 Time-Resolved Photoluminescence

Figure 7.4 shows the near-band-edge PL decays for the three representative excitation fluences discussed in connection with Fig. 7.1. As in Chap. 6, the decay traces were generated by spectrally integrating the PL in the vicinity of the X-2LO transition (3.177 eV ± 0.036 eV) because this transition strength is proportional to the overall exciton population [69, 75]. It is clear from Fig. 7.4 that the overall decay of the
Figure 7.4: Time-resolved photoluminescence decays of ZnO:Zn near-band-edge emission under low (8.3 $\mu$J cm$^{-2}$), intermediate (17 $\mu$J cm$^{-2}$), and high (110 $\mu$J cm$^{-2}$) fluence of femtosecond pulsed excitation. The corresponding window of spectral integration was centered at the X-2LO transition (3.177 eV $\pm$ 0.036 eV).

UV PL slows with increasing excitation fluence. The increase in lifetime from the low to intermediate excitation regimes is not drastic because hot phonon and/or trap saturation effects are only beginning to affect carrier cooling/capture times; however, the high-intensity trace for $I_{\text{exc}} = 110$ $\mu$J cm$^{-2}$ clearly reflects an increase in exciton lifetime.

The experimentally accessible “exciton lifetime” $\tau$ given by the PL decay in Fig. 7.4 is an effective lifetime which results from the competing processes of intrinsic exciton luminescence, nonradiative surface recombination, and energy transfer to green-emitting defects [Eq. (7.3)]:

$$\left(\frac{1}{\tau}\right) = \left[\left(\frac{n_x}{x + n_x}\right) \left(\frac{1}{\tau_x}\right) + \left(\frac{n_{nrs}}{x + n_{nrs}}\right) \left(\frac{1}{\tau_{nrs}}\right) + \left(\frac{n_{gr}}{x + n_{gr}}\right) \left(\frac{1}{\tau_{gr}}\right)\right].$$
Therefore, the slowing of PL decay with increasing fluence is not indicative of a change in the intrinsic exciton radiative lifetime $\tau_x$, which by definition is constant for a given sample. Instead, the change in PL lifetime indicates a change in the relative efficiencies of the various capture/recombination processes, as given by the respective (exciton-density-dependent) capture rates in Eq. (7.3).

The effect of increasing fluence on this effective exciton lifetime is quantified in Fig. 7.5, where the best-fit biexponential decay parameters are shown. We recall from Chap. 6 the interpretation that the fast decay component corresponds to exciton luminescence originating near the surface of the sample, where nonradiative surface recombination competes heavily with radiative exciton annihilation; the slow decay component corresponds to exciton luminescence originating from deeper within the particle, where a lower density of bulk nonradiative traps competes with exciton luminescence. The data in Fig. 7.5(a) indicate that both decay times increase with increasing fluence at the same rate for $I_{\text{exc}} < 200 \, \mu\text{J cm}^{-2}$. That both decay components increase at the same rate is further confirmation of both decay components’ having the same origin (exciton annihilation).

Although beyond the scope of the current discussion, the acceleration of PL decay at the highest measured fluence ($230 \, \mu\text{J cm}^{-2}$) is real and is due to the onset of amplified spontaneous emission. This fluence corresponds to an estimated injected carrier density of $n_{\text{exc}} = 5.3 - 7.5 \times 10^{19} \, \text{cm}^{-3}$, or an average exciton separation of $n_{\text{exc}}^{-1/3} = 2.4 - 2.7 \, \text{nm}$. Under this condition, the average exciton separation is approaching the exciton Bohr radius of $\sim 1.8 \, \text{nm}$ [64,142,151,152], and the screening of the Coulomb potential gives rise to electron-hole plasma (EHP) formation. EHP luminescence is generally “stimulated” in nature, meaning that its intensity grows superlinearly with excitation fluence and its lifetime is very short ($< 10 \, \text{ps}$) [27,93].

As illustrated in Fig. 7.5(b), the strength of the fast decay component steadily
Figure 7.5: Dependence of near-band-edge photoluminescence decay parameters on excitation fluence.
decreases with increasing fluence.\textsuperscript{5} This reduction is consistent with the hot phonon theory because the increased carrier cooling time allows electrons and holes more time to diffuse away from the surface and into the bulk before their excess kinetic energy is dissipated via interaction with phonons. Consequently, excitons that would have formed near the surface when the sample was photoexcited in the perturbative regime are now formed, on average, farther away from the surface due to phonon-enhanced carrier diffusion prior to exciton formation. Thus, the initial exciton population is less concentrated near the surface of the sample, and the relative strength of the fast, near-surface PL decreases. Because the green-emitting defects are located primarily near the surface of the sample (Chap. 6), the reduced near-surface population of excitons leads to a reduction in green PL intensity and efficiency (Fig. 7.2). Thus, the time-resolved characteristics of UV emission in the vicinity of the hot phonon transition provide insight into why the GR PL efficiency decreases with increasing fluence: a reduced energy transfer efficiency from excitons to green-emitting defects due to a change in the exciton population from being concentrated near the surface (where most GR defects reside) to being distributed more uniformly throughout the sample.

The evolution of near-band-edge decay parameters with increasing fluence can also be understood in the context of a trap saturation model. For $I_{\text{exc}} \sim 10 \mu\text{J cm}^{-2}$ the green-emitting defects become saturated. The quenching of this recombination channel forces excitons to recombine radiatively or to be trapped at nonradiative traps (primarily nonradiative surface traps for one-photon excitation). However, with increasing $I_{\text{exc}} > 70 \mu\text{J cm}^{-2}$, the nonradiative surface traps soon begin to saturate as well, leaving exciton luminescence as the primary recombination channel. The\textsuperscript{5}\textsuperscript{5}As for the decay times, the 230 $\mu\text{J cm}^{-2}$ data point for decay amplitude deviates from the overall trend because the onset of stimulated EHP emission occurs on a fast time scale and effectively enhances the strength of the fast decay component.
Figure 7.6: Representative time-resolved photoluminescence decays of ZnO:Zn green emission under low (8.3 $\mu$J cm$^{-2}$), intermediate (17 $\mu$J cm$^{-2}$), and high (110 $\mu$J cm$^{-2}$) fluence of femtosecond pulsed excitation. The corresponding window of spectral integration was centered at the emission peak (2.445 eV), and its width (72 meV) was chosen to be the same as that used for near-band-edge analysis.

effective exciton lifetime is thus increased. Moreover, because the green-emitting defects and the nonradiative traps are both concentrated near the surface of the sample, their saturation suggests an overall saturation of near-surface states. The measured luminescence therefore originates more from the bulk of the material as the excitation fluence increases. The fast decay amplitude associated with exciton annihilation near the surface thus decreases and the slow decay associated with bulk luminescence becomes more prominent.

Representative green PL decays are shown in Fig. 7.6 for low, intermediate, and high excitations relative to the 20 $\mu$J cm$^{-2}$ transition. The decay of defect-related green PL shows the opposite trend—a slightly accelerated decay—with increasing
excitation fluence. Moreover, the biexponential fit parameters shown in Fig. 7.7 indicate that the green PL undergoes more of a discrete change in decay behavior at the critical density. Whereas the UV decay parameters varied smoothly with increasing fluence, the GR decay parameters appear approximately constant both in the perturbative and high excitation regimes, but with a change of 10-20% in their values.

It is not surprising that the changes in green PL decay properties are small given that the lifetime of the PL is determined mostly by the slow, intra-defect thermalization process rather than the fast carrier thermalization and exciton formation processes. In the context of a simple configuration coordinate model of defect emission (Sec. 2.3), the accelerated green band decay can possibly be explained as follows: Green emission originates from transitions between the defect’s lowest vibrational level of the excited electronic state and various vibrational levels of the ground electronic state. Electrons in higher-lying vibrational levels of the excited state nonradiatively cascade down to the lowest vibrational level and “backfill” that state as radiative recombination is occurring. However, when the excitation fluence is high enough to generate a non-equilibrium distribution of hot phonons and to reduce the carrier cooling rate, electrons in the defect’s higher-lying vibrational states can be ejected from the defect’s excited electronic state by interaction with hot phonons and/or electrons. When the electron populations are reduced in the defect’s excited vibrational states, the back-filling into the lowest vibrational state is reduced, and the effective PL lifetime decreases.
Figure 7.7: Dependence of defect-related green photoluminescence decay parameters on excitation fluence.
7.2 Continuous-Wave Excitation

Continuous-wave excitation of the same ZnO:Zn sample was achieved using the 325 nm (3.82 eV) line of a HeCd laser. The excitation energy—and therefore the initial excess energy imparted to the photoexcited carriers—was very similar to that used in the previous section for femtosecond pulsed excitation. Representative steady-state PL spectra are shown in Fig. 7.8 for low (∼0.1 W cm⁻²), intermediate (∼1 W cm⁻²), and high (∼10 W cm⁻²) levels of irradiance. The spectra are generally similar to the time-integrated PL spectra under pulsed excitation (Fig. 7.1): Defect-related green luminescence dominates the spectrum, and the weaker near-band-edge emission consists primarily of X-2LO transitions, with a high-energy shoulder attributed to X-0LO emission.
The irradiance dependence of near-band-edge (UV) and defect-related green (GR) PL intensities and quantum efficiencies are shown in Fig. 7.9(a) and (b), respectively. The results are qualitatively similar to the case of pulsed excitation: In the limit of low excitation, both PL bands exhibit a power-law behavior characterized by a slope \( k \gtrsim 1 \); the green QE is at its highest and depends only slightly on irradiance, while the UV QE is approximately constant at its lowest value. Above a certain threshold (in this case, \( I_{\text{exc}} \sim 0.2 \text{ W cm}^{-2} \)), the green PL slope becomes sublinear while the UV slope increases slightly. At the same time, the GR QE begins to fall off very quickly with increasing \( I_{\text{exc}} \) but the UV QE steadily increases.

Quantitatively, though, there are several differences between continuous-wave and pulsed excitations. Most notable are the increase in maximum GR QE by almost a factor of 2 (58% compared to 34%) and a reduction in maximum UV QE by a factor of 4 (0.1% compared to 0.4%) for continuous excitation. Such changes in efficiencies can be attributed to changes in the relative recombination/capture times \( \tau_i \) for the competing recombination channels of energy transfer to green-emitting defects (\( \tau_{\text{gr}} \)) and nonradiative surface recombination (\( \tau_{\text{nrs}} \)). To elucidate the differences between pulsed and continuous-wave excitations, the QEs in Fig. 7.9(b) were also fit simultaneously using density-dependent QE predictions given by Eqs. (7.4)–(7.5). The results are summarized in Table 7.1.

In the low-density limit of excitation (\( n_{\text{exc}} \ll n_x, n_{\text{gr}}, n_{\text{nrs}} \)), the model QEs are determined essentially by the intrinsic recombination/capture times \( \tau_i \). These lifetimes are “intrinsic” in the sense that they are approximately constant (independent of excitation density) in the perturbative regime of excitation, as evidenced by the constant UV and GR QEs. However, it is clear from Table 7.1 that the low-density values of \( \tau_{\text{gr}} \) and \( \tau_{\text{nrs}} \) are different for pulsed and continuous-wave excitations. The differences in measured UV and GR QEs are consistent with the differences in these best-fit,
Figure 7.9: Dependence of spectrally integrated near-band-edge (UV) and green (GR) photoluminescence intensities (a) and external quantum efficiencies (b) on excitation irradiance.
Table 7.1: Comparison of model recombination/capture times and critical densities [Eqs. (7.4)–(7.5)]. Values denoted by an asterisk (*) were held fixed during the fitting procedure.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pulsed</th>
<th>Continuous</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_x/n_{nrs}$</td>
<td>1500</td>
<td>2.6</td>
</tr>
<tr>
<td>$n_{nrs}/n_{gr}$</td>
<td>5.1</td>
<td>12</td>
</tr>
<tr>
<td>$\tau_x [\text{ns}]$</td>
<td>2.0*</td>
<td>2.0*</td>
</tr>
<tr>
<td>$\tau_{gr} [\text{ns}]$</td>
<td>0.13</td>
<td>0.0082</td>
</tr>
<tr>
<td>$\tau_{nrs} [\text{ns}]$</td>
<td>0.078</td>
<td>0.013</td>
</tr>
<tr>
<td>$f_{\text{refl}}$</td>
<td>0.46</td>
<td>0.46*</td>
</tr>
</tbody>
</table>

Intrinsic values of $\tau_{gr}$ and $\tau_{nrs}$: The green capture time is faster than the nonradiative capture time in the continuous case, so green emission becomes the dominant decay channel. Moreover, the fits to Eqs. (7.4)–(7.5) indicate that both capture times are faster compared to the fixed exciton lifetime for continuous excitation, so the UV QE is reduced from the pulsed case.

As was the case for pulsed excitation, the primary change in continuous-wave PL/QE slopes corresponds to the critical density associated with exciton transfer to green-emitting defects; the value of $n_{gr} = 0.3 \text{ W cm}^{-2}$ (in units of irradiance) extracted from a fit to the phenomenological model is close to the value of 0.2 W cm$^{-2}$ observed experimentally. Relative to the green defect critical density, the critical density associated with nonradiative capture is more than twice as large in the continuous-wave case (Table 7.1). Once the irradiance has exceeded the green defect critical density, the UV QE begins to increase. However, it does not increase as quickly and to the extent that it did in the pulsed case because now the nonradiative recombination channel remains viable for higher relative values of excitation; i.e., the excitation density must be increased significantly more beyond the green defect critical density.
Figure 7.10: Continuous-wave power-law behavior of the ratio of spectrally integrated photoluminescence intensity to the corresponding quantum efficiency for near-band-edge (UV) and green (GR) emissions.

before the nonradiative recombination channel also becomes quenched (and therefore allows near-band-edge luminescence to become the dominant recombination channel).

Regarding the power-law slopes in the regime of low excitation, the values $k_{UV} = 1.25$ and $k_{GR} = 1.08$ in Fig. 7.9 are distinct; however, as discussed in Sec. 7.1.2, the differences in power-law slopes of PL intensities are most properly considered once the PL intensity has been normalized to the QE. The result of this procedure is shown in Fig. 7.10 for continuous-wave excitation. In both the low ($< 0.2 \text{ W cm}^{-2}$) and high ($> 0.2 \text{ W cm}^{-2}$) regimes of excitation, the UV and GR slopes are identical to each other. The change in slope that occurs at $I_{exc} \sim 0.2 \text{ W cm}^{-2}$ corresponds to the irradiance at which the GR QE begins its sharp decline and the UV QE begins to increase.

The equivalence of $k_{UV}$ and $k_{GR}$ in both regimes of continuous-wave excitation
again confirms that the green emission mechanism depends directly on the formation of excitons. However, the slope $k \sim 1.1$ is much lower than it was in the case of pulsed excitation ($k \sim 1.7$) for excitation below the critical density. Evidently exciton formation is not very efficient for continuous-wave excitation, even in the low-intensity limit. This fact is reflected in the faster values of the intrinsic $\tau_{gr}$ and $\tau_{nr}$ relative to a fixed value of $\tau_x$ (Table 7.1). The actual numerical values of the $\tau_i$ are perhaps of limited physical value because the rate equation model as a whole is phenomenological in nature. But the relative changes in the recombination/capture times are described by Eqs. (7.3)–(7.5) for pulsed versus continuous-wave excitation. These changes in the $\tau_i$ are consistent with the observed changes in low-density QEs and $k$-values.

Figure 7.10 suggests that the exciton formation efficiency decreases above the critical density 0.2 W cm$^{-2}$ and is approaching the theoretical minimum $k = 1$ [149]. This reduction in exciton formation efficiency corresponds to a reduction in green QE and could imply that the decreasing green QE is due to a decreasing initial population of excitons available to excite the defects. Alternatively, the initial exciton population could be increasing with irradiance, but a carrier-density-dependent mechanism with threshold 0.2 W cm$^{-2}$ could be dissociating the excitons (thus reducing the effective efficiency of exciton formation) before they are able to transfer their energy to green-emitting defects.

In the case of femtosecond excitation, the experimental critical density of photoinjected carriers was $n_c^{inj} \sim 5 \times 10^{18}$ cm$^{-3}$. An estimate of the experimental steady-state photoinjected carrier density can be obtained from Eq. (2.4). The characteristic time scale in this case is taken to be the lifetime of the dominant recombination channel, i.e., the fast component of the green decay ($\tau_{GR}^{fast} \sim 220$ ns, Fig. 7.7). The resulting estimated equilibrium photoexcited carrier density corresponding to $I_{exc} = 0.2$ W cm$^{-2}$ is $n_c^{cw} \leq 1 \times 10^{16}$ cm$^{-3}$. 

132
Because this density is so much less than the critical density for femtosecond excitation, it is unlikely that the phonon populations are large enough to delay carrier cooling, enhance carrier diffusion, and thus separate spatially the excitons from the green defects. Indeed, the low QE of near-band-edge emission throughout both regimes of continuous excitation suggests that excitons remain concentrated near the surface where both nonradiative surface recombination and energy transfer to green defects are the dominant decay channels. Yet it remains plausible that the reduction in green QE above $I_{\text{exc}} \sim 0.2 \text{ W cm}^{-2}$ is due to thermal depopulation of the defect’s excited vibrational levels through interaction with the equilibrium, photoinduced phonon populations.

On the other hand, in the context of a trap saturation model, a best-fit critical irradiance $n_{\text{gr}} = 0.3 \text{ W cm}^{-2}$ corresponds to a critical density $n_{\text{gr}} \sim 2 \times 10^{16} \text{ cm}^{-3}$ green-emitting defects and is very comparable to the estimated density of radiative defects in the GaN material system [147]. For the analogous yellow band emission in the latter material, the corresponding room-temperature QE is $\sim 10\%$. The QE is perhaps not as high as for green band emission in ZnO because the estimated nonradiative trap density is significantly higher ($n_{\text{nrs}}/n_{\text{yellow}} \sim 1000$ versus $n_{\text{nrs}}/n_{\text{gr}} \sim 12$), yielding a higher probability for nonradiative recombination in GaN. The phenomenological model used to fit the irradiance dependence of ZnO’s two emission bands thus predicts values for green-emitting defect and nonradiative trap densities that are reasonably self-consistent with our data and with similar results from another material system. The simultaneous reduction in GR QE and enhancement in UV QE for $I_{\text{exc}} > 0.2 \text{ W cm}^{-2}$ may be explained by a saturation of green-emitting defects.
7.3 Summary and Discussion

The relative PL intensities and corresponding quantum efficiencies of near-band-edge (UV) emission and defect-related green (GR) emission are found to depend sensitively on photoexcitation density. For both femtosecond pulsed and continuous-wave excitations, the power-law exponents of QE-normalized green PL intensities are identical to those of near-band-edge exciton-related PL. This result independently confirms the previous assertion (Chaps. 5–6) that the most efficient excitation mechanism for green emission is the creation of excitons spatially located near the green-emitting defects. The power-law exponents also indicate that exciton formation efficiency is highest in the low-intensity limit of pulsed excitation and is significantly reduced in both regimes of continuous-wave excitation.

The rate equation model of Chap. 6 has been expanded to account phenomenologically for the excitation density dependence of the UV and GR quantum efficiencies. Density-dependent prefactors, each characterized by a distinct critical density, modify the low-density recombination/capture rates for exciton luminescence, nonradiative surface recombination, and energy transfer to green-emitting defects. Using theoretical quantum efficiencies derived from these density-dependent rates, the excitation-density-dependence of UV and GR QEs were simultaneously fit. The fits provided physically reasonable critical densities that could be interpreted self-consistently in the context of two potential explanations of the data: the hot phonon effect and the trap saturation model.

For femtosecond pulsed excitation, the hot phonon effect can potentially explain the reduction of green QE and the enhancement of exciton-related QE above a critical photogenerated density of \( n_{\text{exc}} \sim 5 \times 10^{18} \text{ cm}^{-3} \). Time-resolved characterization of near-band-edge emission suggests that the increased carrier cooling time afforded by the
hot phonon effect allows carriers to diffuse farther from the surface (and therefore farther from green defects) before forming excitons. This cooling delay leads to a decrease in the excitation efficiency of green defects and to an enhancement in exciton lifetime. Time-resolved characterization of the green band PL suggests that green QE is further reduced in the hot phonon regime due to thermal depopulation of the vibrational levels in the defect’s excited electronic state.

The pulsed excitation data can alternatively be explained by a trap saturation model. With increasing fluence, green-emitting defects are first saturated, followed by nonradiative surface traps. Because both of these recombination channels are associated with near-surface states, exciton-related luminescence—primarily within the bulk of the material—becomes the dominant recombination channel at high fluences. The increase in UV efficiency, the enhanced exciton lifetime, and the reduction in the fast decay amplitude of exciton luminescence are consistent with this interpretation.

The green QE was found to be maximum in the low-density limit of continuous-wave excitation. In the hot phonon model, the drastic reduction in green QE for $I_{\text{exc}} > 0.2 \text{ W cm}^{-2}$ can be explained by thermal depopulation of the defect’s excited state vibrational levels. On the other hand, a simple phenomenological model describes the irradiance dependence of both emission bands by predicting values for green-emitting defect and nonradiative trap saturation densities that are consistent with reported values for the similar GaN material system.

Thus, the body of data described in this chapter is self-consistent in the context of at least two theories—the hot phonon effect and a trap saturation model. It should be noted, though, that the critical density associated with green QE quenching is very different for femtosecond pulsed excitation ($n_{gr}^{fs} \sim 4 \times 10^{18} \text{ cm}^{-3}$) and continuous-wave excitation ($n_{gr}^{cw} \sim 2 \times 10^{16} \text{ cm}^{-3}$). This discrepancy could point to a deficiency in the rate equation model to describe the behavior of PL efficiencies in two drastically
different regimes of excitation, or it could suggest that different density-dependent mechanisms are relevant for pulsed and continuous-wave excitations. To discern which theory (or set of theories) is correct, the experiments in this chapter should be repeated for several above-gap excitation energies. The hot phonon effect in particular depends on the initial excess energy imparted to the photogenerated carriers [144]. As the excitation energy is increased, the electrons and holes must dissipate more energy via LO phonon emission before cooling to the bottom/top of their respective bands. One would then expect that, for increasing excitation energy, the exciton lifetime would increase and/or the critical density for the onset of the hot phonon effect would decrease. On the other hand, trap saturation effects should largely be independent of excitation energy because trapping and energy transfer occur after carriers have cooled—and possibly even after they have formed excitons.

Apart from the dependence of PL intensities and QEs on photoexcitation density within the regime of femtosecond pulsed or continuous-wave excitation, the most striking aspect of the data is the difference in low-density QEs between these two regimes. Continuous-wave excitation clearly enhances green band PL ($\eta_{GR}^{cw} = 58\%$ vs. $\eta_{GR}^{fs} = 34\%$) but reduces the efficiency of exciton luminescence ($\eta_{UV}^{fs} = 0.4\%$ vs. $\eta_{UV}^{cw} = 0.1\%$). The efficiency of exciton formation is characterized by $k_{UV,GR}^{fs} = 1.74$ and $k_{UV,GR}^{cw} = 1.09$ in these same regimes of excitation, suggesting that a reduction in exciton formation efficiency corresponds to reduced $\eta_{UV}$ and enhanced $\eta_{GR}$.

A reduction in $\eta_{UV}$ is certainly intuitive if exciton formation efficiency decreases; however, a simultaneous enhancement in $\eta_{GR}$ is perhaps surprising in light of our repeated demonstration that excitation of green PL occurs most efficiently by energy transfer from excitons. But the model fits to the QE data (Table 7.1) indicate that for continuous excitation, the capture times into green-emitting defects and nonradiative surface traps become much faster relative to the exciton’s radiative lifetime. Thus,
even if the starting population of excitons is reduced because of reduced formation efficiency (lower $k$-value), a larger fraction of the excitons subsequently transfer their energy to defects/traps (primarily green defects since $\tau_{\text{gr}}^{\text{cw}} < \tau_{\text{nrs}}^{\text{cw}}$) rather than produce UV luminescence.

The relative efficiencies of exciton and green PL are thus affected by two aspects of the relaxation process: first, by the efficiency of exciton formation to establish an exciton population; and second, by the relative (density-dependent) recombination/capture rates of excitons from that population into UV luminescence, green-emitting defects, and nonradiative traps.
Chapter 8

Conclusion

From a device perspective, it is important to consider ways to overcome the reduction in green quantum efficiency ($\eta_{GR}$) with increasing excitation density—or at least to increase the starting (low-intensity) value of $\eta_{GR}$—so that higher excitation densities can be used. As discussed in Chap. 4, sulfur doping is a promising technique to enhance green emission. Figure 8.1 compares the irradiance dependence of the annealed ZnO sample to the ZnO:S sample obtained by adding 0.5% by weight of sulfur to the ZnO powder prior to annealing [51]. The maximum total efficiency $\eta = \eta_{UV} + \eta_{GR} \approx \eta_{GR}$ for this particular ZnO:S sample is slightly less than that of the annealed sample, but the efficiency appears to fall off more slowly with increasing irradiance. Depending on the interpretation of the physics, this slowdown could be due to a reduction in the equilibrium phonon population available to scatter electrons out of the defect’s excited state, or to an increase in the green defect saturation density. In any case, for phosphor applications sulfur doping might allow the ZnO to be pumped harder (thus producing more light) for a given quantum efficiency.

Figure 8.2 shows preliminary results for the sulfur concentration dependence of total efficiency $\eta \approx \eta_{GR}$ for powders prepared by the technique described in Sec. 4.1. The excitation conditions were comparable to those of $I_{exc} \sim 1 \text{ W cm}^{-2}$ in Fig. 8.1.\footnote{\label{fn:aging}The aging effect discussed in Chap. 4 is evident when comparing the 0.5\% S data point of Fig. 8.2 ($\eta \sim 65\%$) to the 1 W cm$^{-2}$ data point for ZnO:S in Fig. 8.1 ($\eta \sim 35\%$). The data in Fig. 8.2 were acquired with freshly prepared samples which exhibited maximum efficiency for a given sulfur concentration, whereas the data in Fig. 8.1 were acquired after the 0.5\% S sample had been exposed to air for $\sim 11$ months.}

Even at this intermediate excitation density, there is a clear trend of increasing $\eta_{GR}$.
with increasing sulfur concentration. The improvement appears to saturate for doping concentrations \( \gtrsim 1.0\% \) and indicates a maximum achievable efficiency of \( \sim 75\% \) for this particular combination of starting materials and annealing conditions. It is striking that simply changing the concentration of sulfur in the starting materials has more than doubled the quantum efficiency of the resulting phosphor powder. This result illustrates the significant control over optical properties that is easily obtained by simple adjustments to the material processing procedure. One would expect similar results to hold for the case of ZnO nanowire growth described in Sec. 4.1.

The quantum efficiency of YAG:Ce phosphors in commercial white light-emitting diodes (LEDs) is \( \sim 75\% \) [153]. The data in Figs. 8.1–8.2 indicate that similar efficiencies are attainable for highly S-doped ZnO powders if the excitation density...
Figure 8.2: Dependence of spectrally integrated quantum efficiency on the concentration (by weight) of sulfur present during the annealing process. Continuous-wave HeCd irradiance was $\sim 1 \text{ W cm}^{-2}$.

is $\lesssim 1 \text{ W cm}^{-2}$. Currently available low-power UV LEDs, which could be used as an excitation source for these ZnO powders, emit $\sim 2 \text{ mW}$ over an active area of $\sim 0.01 \text{ cm}^2$, yielding an excitation power density of $\sim 0.2 \text{ W cm}^{-2}$ [154]. By physically locating the ZnO phosphor in the dome of the LED and further reducing the excitation power density, the powder would emit with maximum efficiency (Fig. 8.1). High-power UV LEDs, on the other hand, currently exhibit output powers $\sim 250 \text{ mW}$ ($\sim 25 \text{ W cm}^{-2}$) [154]. Even with the power density reduction achieved by spatial separation of the emitting die and the phosphor, this excitation would exceed $0.2 \text{ W cm}^{-2}$.

It is clear from Fig. 8.1 that the efficiency of annealed/doped ZnO powders is much lower at such high irradiances.

Further optimization of the sulfur doping process may reduce the severity of $\eta_{GR}$ reduction with increasing irradiance, thus allowing higher-power operating conditions.
for ZnO-based phosphors. The growth and/or processing parameters for ZnO nano-
and micro-structures may be tuned more intelligently using the experimental and
modeling insights provided in this dissertation. The optical studies described in
Chaps. 5–7 consistently describe a physical picture in which a stable and low-energy
exciton population is vital to the efficient transfer of energy to green-emitting defects.
These defects reside primarily near the surface of the material, where nonradiative
surface traps provide a competing recombination channel. The rate equation model
introduced in Chap. 6 to quantify the capture rates into these competing channels
was extended in Chap. 7 to account for the excitation density dependence of these
capture rates. This extended model allowed us to quantify the critical densities
at which exciton capture at green defects and nonradiative surface traps begin to
quench.

A natural extension of these results is to perform similar measurements and analy-
ses for sulfur-doped ZnO powders of varying sulfur concentration. Systematic trends
such as the quantum efficiency versus sulfur concentration (Fig. 8.2) can likely be
quantified by a rate equation model that additionally takes into account the sul-
fur concentration dependence of the capture rates into green-emitting defects and
nonradiative surface states. The maximum $\eta_{GR}$ will be obtained when the capture
rate into green defects is maximized while the capture rate into nonradiative sur-
face traps is simultaneously minimized. It is clear from the comparison of S-doped
nanowires to undoped and S-doped powders (Chap. 4) that growth/processing tech-
niques provide many degrees of freedom to achieve this goal even with a relatively
simple and inexpensive vapor deposition system. Based on the comprehensive and
self-consistent physical picture they have outlined, the experimental methods and
theoretical analyses presented in this dissertation provide meaningful constraints on
these growth/processing degrees of freedom.
Appendix A

Femtosecond Laser System

This appendix provides a brief description of the laser system used to generate femtosecond one-photon and two-photon excitation beams for the experiments described in Chaps. 4–7.

A continuous-wave, frequency-doubled Nd:YVO₄ laser (Spectra-Physics Millennia Xs) operating at ~5 W average power serves as the pump for a Kerr-lens mode-locked, Ti:sapphire femtosecond oscillator (Spectra-Physics Tsunami). Tsunami outputs ~7.5 nJ pulses at a repetition rate of ~80 MHz (corresponding to 600 mW average output power). The pulses are approximately Gaussian in the spectral domain (full width at half-maximum ~7–8 nm) and in the time domain (pulse width ~120 fs), as determined experimentally using second-harmonic-generation frequency-resolved optical gating [155,156]. The center wavelength of Tsunami is fixed at 780 nm.

Half of the output from Tsunami seeds a two-stage Ti:sapphire amplifier (Quantronix Titan DP). The amplifier is pumped by a Q-switched, frequency-doubled Nd:YLF laser (Quantronix Falcon) generating 12 mJ per pulse at a repetition rate of 1 kHz (12 W average power). Inside the amplifier, 40% of the pump beam is used to amplify the stretched seed beam inside a regenerative amplifier cavity. Once the seed beam has been amplified from approximately 3 nJ to 0.7 mJ, it is ejected from the cavity and enters a double-pass amplifier stage pumped by the remainder of the Falcom pump beam. The fully amplified seed beam (2.7 mJ) is then recompressed with 65% efficiency and emerges from the amplifier with energy 1.8 mJ. The center wavelength, bandwidth, and pulse width of the amplified Ti:sapphire pulses are
approximately the same as those of the input seed pulses from Tsunami.

Half of the output from Titan pumps an optical parametric amplifier (Light Conversion Ltd. TOPAS) at a wavelength of 780 nm ($\hbar \omega_p = 1.59$ eV). For the measurements performed in this dissertation, the angle of the TOPAS down-converting nonlinear crystal was chosen to generate a signal energy $\hbar \omega_s = 0.960$ eV. The idler energy was therefore $\hbar \omega_i = \hbar \omega_p - \hbar \omega_s = 0.630$ eV. After TOPAS has amplified the signal to $E_s = 380$ µJ per pulse, the second harmonic of the signal ($\hbar \omega_{2s} = 1.92$ eV, $E_{2s} = 75$ µJ) is generated by an external, frequency-doubling beta barium borate (BBO) crystal. This second harmonic of the signal is used for two-photon excitation: $2 \cdot \hbar \omega_{2s} = 3.84$ eV $> E_g$, where $E_g \sim 3.4$ eV is the band gap of ZnO. A second external BBO crystal is used to generate the fourth harmonic of the signal ($\hbar \omega_{4s} = 3.84$ eV, $E_{4s} = 15$ µJ) by frequency-doubling the second harmonic of the signal. The fourth harmonic of the signal is used for one-photon excitation.

For either source of femtosecond excitation, the beam is focused to a spot of diameter $\sim 0.5$ mm on the sample. The incident fluence is adjusted by inserting metallic neutral density filters into the beam path prior to sample illumination. The sample’s response to photoexcitation is then characterized using the techniques described in Chap. 3.
Bibliography


Biography

John Vincent Foreman was born and raised in Winchester, TN. After graduating from nearby Tullahoma High School (Tullahoma, TN) in June 1998, he attended Berry College near Rome, GA. There he double-majored in Physics and Mathematics, and graduated summa cum laude in May 2002. While at Berry he conducted an honors thesis project (“Confirmed Identification of the BL Lac Object 3EGJ0433+2908”) under the direction of Dr. Paul Wallace, and he served as a research assistant for Dr. Todd Timberlake. He received the Lawrence E. McAllister Award for outstanding work in physics during the 1999–2000 academic year and the Writing Across the Curriculum Award for his work in mathematics in 2001–2002.

After graduating from Berry, John enrolled in the Ph.D. program of Duke University’s Department of Physics. For the performance of his teaching assistant duties in the year 2002–2003 he received the Teaching Assistant of the Year Award. In the following summer, he joined the experimental group of Dr. Henry Everitt and began research in the field of ultrafast semiconductor spectroscopy. John was the recipient of the Fritz London Graduate Fellowship in 2006–2007 for excellent work in the fields of atomic, molecular, and optical physics. In May 2005 he earned his A.M. in Physics, and in April 2009 he successfully defended his Physics Ph.D. dissertation, “Photoexcited Emission Efficiencies of Zinc Oxide.”

In the summer of 2003, John married Berry College alumna Sara Emily Lewis of Nashville, TN. They currently reside in Huntsville, AL, and have one child, Andrew.
Publications


