ABSTRACT

WELLENIUS, IAN PATRICK. Rare-Earth Doped Wide Bandgap Oxide Semiconductor Materials and Devices. (Under the direction of Dr. John F. Muth).

Amorphous oxide semiconductors composed of indium gallium zinc oxide are transparent to visible light and have higher electron mobilities than conventional amorphous semiconductors, such as amorphous silicon. The advantages of higher switching speed, lack of dangling bonds leading to good electronic stability and visible spectrum transparency of amorphous oxide semiconductor devices are expected to lead to numerous applications, including transparent displays and flexible electronics.

In this thesis the integration of transparent thin film transistors with transparent electroluminescent pixels was investigated. Compared with display technologies employing organic semiconductors that degrade with exposure to moisture and ultraviolet light, the all-oxide structure of this device is expected to be environmentally robust. This is believed to be the first demonstration of an integrated active matrix pixel using amorphous oxide semiconductor materials as both the light emitter and addressing circuit elements.

The transparent active matrix pixel was designed, fabricated and characterized, that integrated amorphous indium gallium zinc oxide (IGZO) thin film transistors (TFTs) with a europium-doped IGZO thin film electroluminescent (TFEL) device. The integrated circuits were fabricated using room temperature pulsed laser deposition (PLD) of IGZO and ITO thin films onto substrates of Corning 7059 glass, sputter coated with an ITO back contact and subsequent atomic layer deposited ATO high-k dielectric. A
second ITO layer is deposited by PLD as a contact and interconnect layer. All deposition steps were carried out at room temperature.

In addition to the integration task, an important part of this thesis concerns the investigation of europium as a dopant in different oxide hosts including gallium oxide, gadolinium oxide, and amorphous IGZO. Amorphous IGZO was chosen for the integration task since it could be deposited at room temperature, however it was found that the emission intensity of Eu:IGZO thin films was strongly dependent on the oxygen pressure during deposition. It was determined that Eu\(^{3+}\) emission only occurs when the films are insulating, the result of increased oxygen pressure during deposition. Relatively low concentrations of Eu\(^{3+}\) of 1 mole percent were used for this study, with the intensity of these first generation pixels at 6 cd/m\(^2\).

Both gadolinium and gallium oxide films were investigated at higher substrate temperatures with a range of europium dopant concentrations. It was found that the both cubic and monoclinic phases of gadolinium oxide could be deposited, with the phase determined by deposition oxygen pressure. The film structure was analyzed by x-ray diffraction and transmission electron microscopy and optical spectra were obtained using time resolved photoluminescence (performed by a collaborator). These results were found to be in agreement with Stark-split energy levels calculated by another collaborator.

Using 2.5 mole percent europium-doped gallium oxide as a host, bright thin film electroluminescent devices with intensities of 221 cd/m\(^2\) observed for a TFEL device excited by a symmetric ±100 V\(_{\text{max}}\) square pulse train at 1 kHz. This compares favorably
with other red TFEL devices in the literature. Comparison with cathodoluminescence and photoluminescence data suggests that these performance metrics can be improved since the optimal concentration of europium by those experimental techniques was found to be near 10 mole percent. Time resolved photoluminescence revealed that radiative relaxation of the Eu$^{3+}$ dopant could be modeled by two exponential decay components. Comparison of the intensity versus frequency of the electroluminescent data with time resolved photoluminescence data suggests that the faster component dominates the emission of the TFEL device.
Rare-Earth Doped Wide Bandgap Oxide Semiconductor Materials and Devices

by
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Dedication

In loving memory of aunt Sara.
Biography

Ian Patrick Wellenius was born on December 4, 1981 to Bjorn and Myriam Wellenius in Potomac, MD. After graduating Washington International School in Washington, DC (1999), Patrick earned a BS (2003) and MS (2006) in Electrical Engineering from North Carolina State University, the latter under the direction of Dr. John Muth. He successfully defended his dissertation on Wednesday, September 16, 2009.
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My experience as a graduate student has been at times stressful and overwhelming, but more often than not has proven to be very rewarding, satisfying and enjoyable. This is due in no small part to the many people who have been a part of that experience over the last six years including professors, collaborators, friends and fellow students.

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Table of Contents

LIST OF FIGURES ........................................................................................................................................... ix

LIST OF TABLES ............................................................................................................................................... xi

1 INTRODUCTION ............................................................................................................................................. 1

1.1 CONTEXT ..................................................................................................................................................... 2

1.2 OVERVIEW ................................................................................................................................................ 5

2 LITERATURE REVIEW ................................................................................................................................... 9

2.1 RARE-EARTH DOPED SOLIDS ................................................................................................................. 9

2.1.1 EXCITATION MECHANISMS .................................................................................................................. 14

2.1.2 CRYSTALLINE HOSTS .......................................................................................................................... 18

2.1.3 AMORPHOUS HOSTS ........................................................................................................................... 19

2.2 WIDE BANDGAP SEMICONDUCTOR HOSTS ......................................................................................... 20

2.2.1 GALLIUM OXIDE .................................................................................................................................. 20

2.2.2 GADOLINIUM OXIDE ............................................................................................................................ 23

2.2.3 AMORPHOUS SEMICONDUCTORS ........................................................................................................... 25

2.2.3.1 Amorphous Oxide Semiconductors ............................................................................................... 28

2.2.3.2 Indium Gallium Zinc Oxide ............................................................................................................. 31

2.3 THIN FILM ELECTROLUMINESCENT DEVICES .............................................................................. 35

2.3.1 DEVICE OPERATION ............................................................................................................................. 35

2.3.2 PHOSPHOR MATERIALS ....................................................................................................................... 36

2.4 ACTIVE MATRIX PIXELS ......................................................................................................................... 38

2.4.1 PIXEL ADDRESSING .............................................................................................................................. 38

2.4.2 ACTIVE MATRIX IMPLEMENTATIONS ............................................................................................. 43

3 DEVICE FABRICATION AND TESTING ...................................................................................................... 47

3.1 THIN FILM ELECTROLUMINESCENT DEVICES .............................................................................. 47

3.1.1 FABRICATION ....................................................................................................................................... 47

3.1.2 OPTICAL CHARACTERIZATION ........................................................................................................... 49

3.1.3 SAWYER TOWER CIRCUIT ANALYSIS .............................................................................................. 49

3.2 ACTIVE MATRIX ELECTROLUMINESCENT PIXEL ............................................................................ 56

3.2.1 FABRICATION ....................................................................................................................................... 57

3.2.2 DEVICE MODULATION AND TESTING ............................................................................................. 59

4 PROPERTIES OF EUROPium DOPED GALLIUM OXIDE ................................................................. 63
# Table of Contents

11.2.2 Low-Temperature Transmission Measurements ........................................ 166
11.2.3 Swanepoel’s Method ................................................................. 168

11.3 Scanning Electron Microscopy .......................................................... 170

11.4 Photoluminescence ............................................................................ 172
  11.4.1 Continuous Wave ................................................................. 173
  11.4.2 Pulsed Excitation ................................................................. 173

11.5 X-Ray Diffraction ................................................................................ 175

11.6 Transmission Electron Microscopy ...................................................... 178

11.7 Rutherford Backscattering Spectrometry .............................................. 183

11.8 Atomic Force Microscopy ..................................................................... 185

11.9 Four-point Probe .................................................................................. 185

11.10 Van der Pauw Hall Effect ................................................................. 188

12 Appendix B: Swanepoel’s Method .......................................................... 191

13 Appendix C: MATLAB Implementation .................................................. 198
  13.1 Transmission.m .............................................................................. 198
  13.2 Envelope.m .................................................................................... 200
  13.3 Peakdet.m .................................................................................... 203
  13.4 Swanepoel1.m .............................................................................. 204
  13.5 Thickness.m ................................................................................ 205
  13.6 Cauchyfit.m ................................................................................ 206
  13.7 Modefit.m ................................................................................... 208

14 Appendix D: Eu³⁺ Level Splittings in Cubic Gd₂O₃ ...................................... 210
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Periodic Table of the Elements, with Rare Earth Elements as Indicated</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Dieke Diagram Showing Energy Levels of the Trivalent Rare Earth Ions</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Electron Configuration for Eu³⁺ in the Ground State</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Energy Level Diagram for Nd³⁺</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>A Generalized Trap-Mediated Mechanism for Indirect Excitation of RE Dopants in Semiconductor Hosts</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>Atomic Arrangement in Gallium Oxide</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>Hypothetical Atomic Structures in Crystalline and Glass Networks</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>An Illustrated Comparison of the Isotropic s-Orbitals in AOS Materials to the Anisotropic Orbitals in Covalent Semiconductors</td>
</tr>
<tr>
<td>Figure 2.9</td>
<td>Effects of Composition on Electronic Properties in Amorphous IGZO</td>
</tr>
<tr>
<td>Figure 2.10</td>
<td>XAFS Results for Amorphous and Crystalline IGZO Thin Films</td>
</tr>
<tr>
<td>Figure 2.11</td>
<td>Optical and Electronic Processes in TFEL Devices</td>
</tr>
<tr>
<td>Figure 2.12</td>
<td>Example of Passive Matrix Addressing for Liquid Crystal Displays</td>
</tr>
<tr>
<td>Figure 2.13</td>
<td>Hypothetical Luminance-Voltage Curves for Materials with Different Thresholds and Steepness Parameters</td>
</tr>
<tr>
<td>Figure 2.14</td>
<td>Circuit and Cross-Section Illustrations of an Active-Matrix Addressing Scheme for Liquid Crystal Displays</td>
</tr>
<tr>
<td>Figure 2.15</td>
<td>Active-Matrix Pixel Implementation Using Organic Semiconductor Layers</td>
</tr>
<tr>
<td>Figure 2.16</td>
<td>Active Matrix Pixel Circuit Designed for Addressing TFEL Devices</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Cross-Section of an Asymmetric TFEL Device</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Sawyer-Tower Circuit for Electronic Analysis of TFEL Devices</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Time-Varying Signal Used to Test TFEL Devices and Examples of Resulting VEL and IEL Curves</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>Idealized Charge-Voltage (Q-V) Plot for a TFEL Device</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>Illustration of Electrons Moving Through the TFEL Device Cross Section at Points A through F</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>Circuit That Was Implemented to Realize an Active Matrix Pixel Using a TFEL Light Emitting Element</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>Cross-Section Schematic of the Layout of Bottom Gated IGZO TFTs Used in the Active Matrix Pixel Circuit</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>Process Flow Diagram Illustrating the Steps Involved in Pixel Fabrication</td>
</tr>
<tr>
<td>Figure 3.9</td>
<td>Pixel TFT Testing Methods</td>
</tr>
<tr>
<td>Figure 3.10</td>
<td>TFEL Modulation Testing Method</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>PL Spectra from CWPL and TIPL Experiments on Eu:Ga₂O₃ Thin Films</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Normalized TRPL Decay for Varying Eu Concentrations</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>X-Ray Diffraction Spectra for Ga₂O₃ and (EuₓGa₁₋ₓ)₂O₃ Thin Films with Increasing Eu Mole Fraction x</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>Transmission Spectrum with Maximum and Minimum Transmission Envelopes</td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>Comparison of the Cauchy and Sellmeier Models for Refractive Index</td>
</tr>
<tr>
<td>Figure 4.6</td>
<td>Graphical Determination ofThickness Using Optical Transmission Data for a Eu:Ga₂O₃ Thin Film</td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>Absorption Coefficient and Its Square Plotted as Functions of Wavelength for a 5 Mole Percent Eu-Doped Ga₂O₃ Thin Film</td>
</tr>
<tr>
<td>Figure 4.8</td>
<td>Comparison of Simulated and Measured Transmission Spectra</td>
</tr>
<tr>
<td>Figure 5.1</td>
<td>TEM Images with Diffraction Patterns of 5 and 50 mTorr Eu:Gd₂O₃ Films</td>
</tr>
<tr>
<td>Figure 5.2</td>
<td>Radial Intensity Profiles of the Electron Diffraction Patterns for 5 and 50 mTorr Eu:Gd₂O₃ Thin Films</td>
</tr>
<tr>
<td>Figure 5.3</td>
<td>X-Ray Diffraction Results for 5 and 50 mTorr Eu:Gd₂O₃ Films</td>
</tr>
</tbody>
</table>
List of Tables

TABLE 2.1.  UNIT CELL PARAMETERS FOR MONOCLINIC GA₂O₃................................................................. 21
TABLE 2.2.  UNIT CELL PARAMETERS OF MONOCLINIC AND CUBIC GD₂O₃................................................................. 24
TABLE 2.3.  EXAMPLES OF HEAVY METAL CATIONS USED IN AMORPHOUS OXIDE SEMICONDUCTORS ............ 28
TABLE 2.4.  COMPARISON OF EL PHOSPHOR PERFORMANCE FOR SULFIDE PHOSPHORS ................................. 37
TABLE 2.5.  SUMMARY OF BIEXPONENTIAL DECAY PARAMETERS FOR EU:GA₂O₃ THIN FILMS ......................... 69
TABLE 4.1.  CAUCHY AND SELLMEIER MODEL COEFFICIENTS FOR A 10 MOLE PERCENT EU:GA₂O₃ THIN FILM .... 74
TABLE 4.2.  CAUCHY FIT COEFFICIENTS FOR DIFFERENT EU MOLE FRACTIONS ................................................ 76
TABLE 4.3.  COMPARISON OF FILM THICKNESS AS DETERMINED BY PROFILOMETRY AND EXTRACTED FROM OPTICAL TRANSMISSION .................................................................................. 77
TABLE 4.4.  COMPARISON OF MEASURED AND KNOWN INTERPLANAR DISTANCES FOR MONOCLINIC AND CUBIC EU:GD₂O₃ ........................................................................................................................................ 84
TABLE 5.1.  COMPARISON OF MEASURED AND CALIBRATED BANDGAP OF EU:GD₂O₃ FILMS .......................... 90
TABLE 5.2.  PARAMETERS OF (B)EXPONENTIAL FIT TO TIME-RESOLVED PHOTOLUMINESCENCE DECAYS ...... 93
TABLE 6.1.  FAN AND VARSHNI PARAMETERS FOR EU:IGZO THIN FILMS ...................................................... 109
TABLE 14.1.  PHOTOLUMINESCENCE PEAKS OBSERVED FROM THE 5D₀ → 7F₁ LEVELS IN EU:GD₂O₃ ............. 210
TABLE 14.2.  PHOTOLUMINESCENCE PEAKS OBSERVED FROM THE 5D₁ → 7F₁ LEVELS IN EU:GD₂O₃ ............. 211
TABLE 14.3.  PHOTOLUMINESCENCE PEAKS OBSERVED FROM 5D₁ → 7F₁ LEVELS IN EU:GD₂O₃ .................... 212
TABLE 14.4.  PHOTOLUMINESCENCE PEAKS OBSERVED FROM 5D₂ → 7F₁ LEVELS IN EU:GD₂O₃ ............. 213
TABLE 14.5.  CRYSTAL-FIELD SPLITTING OF 7F₁ AND 5D₁ MANIFOLDS IN CUBIC EU:GD₂O₃..................... 214
1 Introduction

Silicon has historically been the material of choice for semiconductor devices and integrated circuit technology; however silicon is not well-suited for optoelectronic devices due to its indirect and relatively narrow bandgap. The growing demand for a variety of optoelectronic devices has since driven the development of new semiconductor material systems whose properties may result in improved device performance. Direct bandgap semiconductors such as gallium arsenide and indium phosphide became key technologies for optical communications systems in the form of optical sources and detectors in the near-infrared spectrum. Although suitable for optical communications in the infrared, such narrow bandgap semiconductors can not be used in visible or ultraviolet light emitting devices. Such devices, which are desirable for solid-state lighting and display applications, have been extensively demonstrated using wide bandgap semiconductors, including gallium nitride and zinc oxide. In particular, GaN and its alloys have been successfully implemented in a number of visible and UV LEDs and laser diodes. As novel device applications continue to emerge, materials tailored to these applications must be developed.

Large area electronics is one example where crystalline silicon has been replaced by amorphous semiconductors, most notably amorphous silicon. In applications such as flat panel displays or solar cells, the electronic performance of crystalline semiconductors is compromised in favor of large area deposition at reduced temperatures and cost. However, amorphous silicon is not transparent to visible light due to its narrow bandgap.
Next generation displays may utilize wide bandgap materials that are transparent through the visible spectrum to realize new types of functional displays. This specific application has driven the development of amorphous, transparent organic and inorganic semiconductors and integrated circuits.

Compact, efficient light emitting devices with high color purity represent another specialized application. Such devices are desirable for display technology and also for optical biosensing applications, including pulse oxymetry. New semiconductor materials doped with rare earth elements may be of interest as phosphors or as electroluminescent devices. For these applications, the semiconductor must present a host environment that can best exploit the unique optical properties of rare earth dopants.

The work described herein is aimed towards the development of these materials and devices, ranging from display elements to sensors, using rare-earth doped oxides such as gallium oxide, gadolinium oxide and amorphous indium gallium zinc oxide. The following sections contextually place this work and outline its scope.

1.1 Context

Amorphous semiconductors, specifically amorphous silicon, have already found a successful application in large area electronics, including flat panel displays and photovoltaic devices. Regardless of display type (LCD, plasma or LED) the backplanes of large displays house transistors in an active matrix to individually address and drive several millions of pixels at moderate refresh rates (up to 240 Hz). Using crystalline silicon in such applications would be prohibitively expensive due to the large size
requirements. Amorphous silicon, being simpler and less costly to deposit over large substrates at lower temperatures than crystalline silicon, permits the fabrication of these large backplanes without the need for single-crystal growth techniques. While amorphous silicon demonstrates relatively poor carrier mobility as compared to its crystalline form, this is not often an issue for field-driven technology such as liquid crystal displays. However, the large current needed to power an OLED or LED pixel for example requires larger transistors, reducing the fill factor of the display. One alternative is to develop amorphous materials with improved electronic properties. Such a class of materials being intensely researched are amorphous oxide semiconductors (AOS), which have often demonstrated superior electronic properties to amorphous silicon and organic semiconductors. One promising AOS material is the quaternary alloy indium gallium zinc oxide (IGZO) whose mobility can be up to two orders of magnitude larger than that of amorphous silicon.

In addition to display backplanes, attention is focused on the light-emitting elements themselves. While most available commercial displays utilize LCD or plasma technologies, other technologies have been investigated in the past and present including electroluminescent devices, organic and inorganic LEDs as well as field-emission displays.

Rare-earth doped electroluminescent phosphors continue receiving attention for display applications due to their high color purity and the more recent development of high-quality wide bandgap semiconductor hosts such as GaN. Rare-earth elements such as europium, neodymium or erbium have been used in a number of applications since
their discovery in the late 1800’s. Increasingly important however, is their use in optical and optoelectronic systems. Trivalent rare-earth ions have been used in laser gain media, cathode ray tube phosphors and thin film electroluminescent devices. Their unique electronic structure gives rise to spectrally narrow optical emission features which improves color purity in display systems, as compared to broad-band light sources.

Gallium oxide and gadolinium oxide represent two wide bandgap semiconductor hosts that have demonstrated efficient rare-earth luminescence. Their wide bandgap and chemical stability makes these materials attractive options for novel electroluminescent display devices where phosphor degradation and instability has been problematic for earlier hosts based on sulfide semiconductors.

High power disk lasers are also being developed that exploit these optical properties such as Yb:Y_2O_3, Yb:Sc_2O_3 and Yb:Lu_2O_3. Sesquioxide ceramics such as yttria, scandia and lutetia are often used in high power lasers due to their excellent thermal and optical properties in polycrystalline form, eliminating the need for more costly single crystal growth techniques. In this regard, Ga_2O_3 and Gd_2O_3 are interesting materials as both have shown bright luminescence when doped by rare earth ions, though their thermal properties are not well known. Investigation of these material systems and optimization of optical and physical properties is important for future optoelectronic devices and high power lasers.
1.2 Overview

The work presented here spans from fundamental material characterization through device fabrication and testing. Pulsed laser deposited thin films of beta-phase gallium oxide ($\text{Ga}_2\text{O}_3$), gadolinium oxide ($\text{Gd}_2\text{O}_3$) and amorphous indium gallium zinc oxide (IGZO) were doped with europium to investigate their potential as novel wide bandgap materials for optoelectronic devices. Electroluminescent devices were fabricated from Eu:$\text{Ga}_2\text{O}_3$ and Eu:IGZO thin films. An active matrix pixel was also implemented using a Eu:IGZO electroluminescent device which was addressed and modulated by a series transistor, also based on IGZO technology developed at NCSU.

Chapter 2 is a survey of the relevant literature, describing the history of the material systems investigated as well as the respective state of the art. First, a brief overview of rare-earth ions and their unique properties is presented followed by a discussion of relevant properties of and technologies exploiting $\text{Ga}_2\text{O}_3$ and $\text{Gd}_2\text{O}_3$ thin films. Subsequently, the history and defining characteristics of amorphous semiconductors is discussed while focusing on the unique properties of amorphous oxide semiconductors, particularly IGZO, and device implementations. Lastly, the operation of thin film EL devices and historically important EL phosphors are discussed.

Chapter 3 illustrates device fabrication process steps and discusses characterization methods. Step by step processes are discussed for the fabrication of electroluminescent devices, thin film transistors and an integrated active matrix electroluminescent pixel. Characterization strategies are also outlined, indicating test circuitry and experimental methods where necessary.
Chapters 4 through 6 discuss experimental results from rare-earth doped thin films. In chapter 4, a study is presented on Eu-doped Ga$_2$O$_3$. The effects of dopant concentration on these thin films were observed as it is a promising material for display devices and laser gain media. The dopant concentration is an important parameter for such applications as the optimum concentration must be determined to avoid parasitic processes that reduce overall emission intensity. The films were investigated by photoluminescence, time-resolved photoluminescence, x-ray diffraction and optical transmission spectra. A method for determining the refractive index and absorption coefficient from an optical transmission spectrum is implemented using MATLAB scripts for different europium concentrations.

Chapter 5 presents results on Eu:Gd$_2$O$_3$, which was deposited in two crystalline forms: cubic and monoclinic. Understanding the differences between these two phases in terms of rare earth luminescence is another important feature as it may impact the emission spectrum and radiative decay characteristics. The films were investigated by photoluminescence, time-resolved photoluminescence, x-ray diffraction and transmission electron microscopy. Luminescence and structural results of cubic phase films were confirmed by crystal-field calculations performed by a collaborator, Dr. John Gruber.

Chapter 6 reports on amorphous Eu-doped IGZO as a novel luminescent material and this work is believed to be the first example of a rare-earth doped amorphous oxide semiconductor. The absorptive and luminescent properties of the material are characterized by temperature-dependent optical absorption and cathodoluminescence spectroscopy. The structure of the optical absorption edge is analyzed using methods
proposed by Cody and Vorlicek and compared to the commonly accepted Tauc method. The effect of oxygen pressure during deposition was investigated.

Chapter 7 discusses experimental results from novel opto-electronic devices made from Eu:Ga$_2$O$_3$ and Eu:IGZO. The optical and electronic properties of thin film electroluminescent devices based on Eu:Ga$_2$O$_3$ were characterized. Eu:IGZO devices were fabricated in varying oxygen pressures and are compared. In addition, chapter 8 reports on the properties and transient response of an active matrix electroluminescent pixel based on IGZO thin film transistors and electroluminescent devices.

Chapter 8 summarizes the results and discussion presented in chapters 5 through 8. References are listed in chapter 10. Chapter 11 contains three appendices that include: (1) an overview of Swanepoel’s method for extracting material parameters from optical transmission spectra, (2) MATLAB scripts developed to implement Swanepoel’s method and (3) tabulated results from crystal-field calculations for cubic Eu:Gd$_2$O$_3$.

Four appendices, A through D, are included. Appendix A details the key deposition, fabrication and analytical facilities used in this work. This discussion focuses on material deposition and characterization tools, including a brief history of the pulsed laser deposition technique and outlining key advances in laser technology that have enabled the technique to develop. Secondary tools providing valuable information are discussed in less detail. Appendix B outlines a method for extracting optical absorption coefficient, refractive index and the thickness of thin films from their optical absorption data. Appendix C contains MATLAB code written to implement the method described in
appendix B. Lastly, Appendix D tabulates calculated energy levels of Eu$^{3+}$ in cubic gadolinium oxide films.
2 Literature Review

2.1 Rare-Earth Doped Solids

Rare-earth doped solids have been used in a number of applications including CRT displays, solid-state lasers, radiation detection and medical applications[1]. The motivation for the use of rare-earth dopants in these applications stems from the bright, spectrally narrow emission from the dopants, largely irrespective of the host material.

Figure 2.1. Periodic table of the elements, with rare earth elements of interest as indicated.

The 17 rare-earth elements span the lanthanide series (atomic number 57 to 71) in addition to yttrium and scandium[2]. Of specific interest are the rare earth elements that
form trivalent ions with a partially filled 4f orbital, which consists of the elements between cerium and lutetium, as shown in Figure 2.1. The electronic structure of trivalent rare earth ions is such that the 4f orbital is incomplete while the 5s and 5p orbitals are filled, resulting in electron transitions within the incomplete 4f orbital. That the incomplete 4f orbital is encompassed by the 5s and 5p orbitals results in shielding of the 4f states from the electric field of the host. Thus, the 4f energy levels of a trivalent rare earth ion in a solid host are largely similar to those of the free ion.

The divalent ion exists for a number of rare earth elements, but is less common than the trivalent configuration and is most common for the rare earths with empty, half-filled (4f⁷) or completely filled (4f¹⁴) 4f orbitals. Thus, Eu²⁺ and Yb²⁺ are the most accessible divalent rare earth ions. A +4 oxidation state can also be achieved for cerium and terbium following the same criteria[3]. The importance of differentiating between the divalent and trivalent oxidation states is that radiative transitions in the trivalent state occur within the 4f orbital and demonstrate sharp spectral features while in the divalent state, transitions also involve the 5d orbital[4], resulting in broad features due to the large interaction of 5d orbitals with the crystal host.

The effect of placing a trivalent RE ion into a solid host is two-fold: (1) relaxation of selection rules for radiative transitions and (2) splitting of the 4f energy levels. Radiative transitions within the 4f orbital, often called *intra-4f* or *4f-4f* transitions, are parity forbidden in the free ion, but when a trivalent RE ion exists in a solid these selection rules may be relaxed, thus allowing intra-4f transitions to occur. The interaction of the magnetic field due to electron motion about the nucleus with the
electron spin (spin-orbit coupling) allows states of different parity to mix, which makes the intra-4f transitions possible. Due to the forbidden nature of intra-4f transitions however, the radiative lifetimes tend to be quite long compared to radiative recombination from other types of excited states[2].

In 1963, Dieke and Crosswhite[5] published their seminal paper on the observed luminescence from divalent and trivalent RE ions, resulting in the now famous “Dieke diagram” shown in Figure 2.2 for trivalent ions. While this was not the first publication outlining the energy levels of a trivalent RE ion, it has become an oft-referenced work in subsequent RE luminescence and optical absorption studies. The Dieke diagram, which plots the low-lying energy levels of the RE ions, remains a useful tool for estimating the position of these energy levels in different solid hosts.

Term symbol notation is used to describe atomic energy levels and the spectra resulting from radiative transitions within these levels. This same notation is used to discuss 4f-4f transitions within RE ions. A given state is denoted by \( ^{2S+1}L_J \), where \( S \) is the combined spin angular momentum, \( L \) is the total orbital angular momentum and \( J \) is the total angular momentum. Since each unpaired electron contributes spin one-half, one can determine \( S \) by counting the electrons with unpaired spin and multiplying by one-half. \( L \) is calculated by summing the orbital quantum numbers for the unfilled electron shell. For more than half-filled orbitals, \( J \) is the sum of \( L \) and \( S \) but if less than half-filled, \( J \) is the absolute value of the difference.
Figure 2.2. Dieke diagram showing energy levels of the trivalent rare earth ions. From [5].
In Eu\textsuperscript{3+} for example, the ground state is given by \( ^7F_0 \) and thus \( S = 3, L = 3 \) (or \( F \)) and \( J = 0 \). The 4f orbital may contain up to 14 electrons in its seven sub-orbitals and so the 4f\textsuperscript{6} electron configuration in Eu\textsuperscript{3+} results in a less than half-filled orbital, as shown in Figure 2.3. Thus, none of the six electrons are paired and the total spin is three as each electron can have spin of plus or minus one-half. Filling the orbitals in order of decreasing orbital quantum number, one can calculate \( L \) by summing the orbital quantum numbers multiplied by the number of electrons in each.

\[
L = 3 + 2 + 1 + 0 - 1 - 2 = 3
\]

Finally in this example, \( J \) is the absolute value of the difference of \( L \) and \( S \), which is zero. Determining the electron configuration of higher energy terms is more complex.

The Stark effect describes the shifting and splitting of atomic energy levels in the presence of an applied electric field. The Stark effect can be substantial for certain luminescent centers, such as transition metals, however in trivalent RE ions, shielding of the local crystal field by the outer 5s and 5p orbitals results in a fine splitting of energy levels within the 4f orbital. This splitting may be so fine that the individual levels cannot be resolved by spectral measurements. Each manifold, described by the \( 2S+1L_J \) term.
symbol, splits into 2J+1 levels due to the Stark effect. As such, manifolds with a total angular momentum of zero exhibit no Stark splitting and are useful for spectroscopic measurements. Each manifold can also be shifted due to varying crystal fields that exist at different sites in the crystal, making trivalent RE ions useful for probing the host structure.

2.1.1 Excitation Mechanisms

Rare earth dopants can be directly excited via optical absorption or impact excitation by high energy electrons. Er[6] and Nd[7] doped solid-state lasers are often optically pumped at 980 and 808 nm, respectively, due to strong absorption bands associated with the rare earth ions themselves. As shown in Figure 2.4, resonant absorption of 808 nm light results in a transition from the ground state manifold to the $^4F_{5/2}$ excited state in Nd$^{3+}$ followed non-radiative relaxation to the $^4F_{3/2}$ state. Subsequent radiative decay to the $^4I_{11/2}$ or $^4I_{9/2}$ states emits light at 1064 or 980 nm, respectively.

In thin film electroluminescent devices, impact excitation by high energy electrons is used. Similarly, cathodoluminescence is the result of high-energy electrons incident on a sample where the electron beam can directly excite or ionize the rare earth dopant.
Figure 2.4. Energy level diagram for Nd [7], illustrating the effect of resonant pumping at 808 nm.

Indirect excitation mechanisms in rare-earth doped semiconductors are numerous and can vary substantially among different host materials and preparation conditions. Generally speaking, indirect excitation involves energy transfer from ionized carriers in the host to the 4f states of the rare-earth dopant. In several reported instances, this occurs via localized defect states within the energy gap[1, 8, 9] related to the rare-earth dopant. Carriers can be ionized optically by absorbing photons of energy equal to or greater than the host material bandgap and also by electron beams as in cathodoluminescence, for example.

As illustrated in Figure 2.5, during the excitation process a free electron (hole) from the host conduction (valence) band is bound by the trap state. Through Coulombic attraction, a hole (electron) is attracted to the oppositely charged trap, forming a bound exciton which recombines some time later. Lastly, upon recombination, the exciton’s

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binding energy may be transferred to the 4f states of the rare-earth ion which may then de-excite radiatively[10]. Variants of this generalized process involving free excitons, or trapped carriers have also been discussed in the literature[11].

![Diagram](image)

**Figure 2.5.** A generalized trap-mediated mechanism for indirect excitation of RE dopants in semiconductor hosts. First, a free electron is trapped by RE-related defect state (A). The electron charge attracts a free hole (B) which then forms a trap-bound exciton (C). Recombination of the bound exciton results in energy transfer to the 4f states of the RE dopant (D).

Lozykowski[11] has investigated luminescence of the trivalent rare-earth ions in III-V semiconductors and described a kinetic model where carrier trapping occurs at isoelectronic traps within the host bandgap. Upon replacing the trivalent cations in III-V hosts (or in other semiconductors with group III ions) with trivalent rare-earth dopants, isoelectronic traps form within the bandgap of the host and in close spatial proximity to the dopant. Experimental evidence suggests that the trap state may bind an electron (hole) if the electronegativity is significantly larger (smaller) than that of the atom it replaces[12]. For rare earth ions, Pauling’s electronegativity is in the range of 1.1 to 1.2, much smaller than that of Ga (1.81) or In (1.78), suggesting that isoelectronic traps due to rare-earth doping in III-V and sesquioxide semiconductors tend to be hole traps.
Isovalent dopants have been previously exploited to modify the luminescent properties of various materials including, most famously, N:GaP.[13]

Energy transfer from bound excitons appears to be critical to the indirect excitation process as the lifetime of excitons bound to isoelectronic traps (~100-1000 ns) tends to be considerably longer than that of excitons bound to acceptor/donor-like states (~1 ns). Lozykowski describes that in Yb:InP, for example, the time constant for energy transfer from the bound exciton to the Yb 4f states is on the order of 1 ns and thus, a short-lived exciton could shunt this efficient energy transfer process[11].

The effects of defect states have also been observed in the radiative decay of RE ions using time-resolved photoluminescence (TRPL). Several reports exist where the radiative decay is modeled by the sum of two decaying exponentials with unique time constants[9, 14]. Observation of such a phenomenon is not uncommon but does complicate analysis somewhat, requiring further investigation to determine intrinsic radiative decay rates. In one such report for Eu:GaN[9], the temperature-dependent biexponential decay of the 4f states in Eu$^{3+}$ was successfully modeled. One exponential was assigned to the radiative decay of the RE dopant while the other represented energy transfer with a defect level acting as a reservoir that could replenish the excited 4f state in Eu$^{3+}$. Similar non-radiative energy transfer mechanisms may manifest themselves by altering the observed radiative decay characteristics.
2.1.2 Crystalline Hosts

Several examples of RE-doped crystalline materials exist in both thin film and bulk form. One historically important example is Nd:YAG which has since become an important tool for spectroscopy and laser processing of materials. Another important example are Er-based light emitters because their emission coincides with one of the low-absorption loss windows (~1450-1600 nm) in optical fibers[1]. Erbium doped Si (Er:Si) has been widely investigated[6] in hopes that optoelectronic components could be monolithically integrated with Si electronics for telecommunications applications.

A variety of semiconductors, many with bandgaps larger than that of silicon, have been doped with RE ions including GaN[15-17], GaAs[18, 19], ZnO[20], ZnS[21, 22] and CaS[21]. The motivation for exploring wide bandgap semiconductor hosts is manifold. Temperature-related luminescence quenching effects, previously observed in narrow bandgap hosts, is inversely proportional to the bandgap of the host. Additionally, excitation of RE ions in wide bandgap hosts may be more efficient due to the higher binding energy of excitons involved in energy transfer[1]. Of particular importance is that the host should be transparent to the luminescence emitted by the RE dopant. By definition, a wide bandgap semiconductor is transparent through at least part of the visible spectrum and into the UV, allowing higher energy transitions from RE ions to be observed. This is of particular interest for full-color display applications requiring red, green and blue sub-pixels to realize a larger color gamut.
2.1.3 Amorphous Hosts

Amorphous solids including glasses, semiconductors and polymers represent interesting hosts for rare earth dopants. The interest in amorphous semiconductor hosts is the ability to produce them in larger quantities and without the expense or complexity associated with crystalline forms.

High quality glass hosts, including chalcogenides, can be formed in large quantities from the melt. Er-doped optical fiber amplifiers (EDFA) are an important technology for telecommunications, due to the low-absorption window in silicate fibers that coincides with Er emission\[6\]. Other rare earth ions such as Nd[7] and Yb[23] are often used in laser gain media. The low maximum phonon energies observed in these glasses minimizes parasitic non-radiative processes[24], but also often requires direct optical excitation of the rare-earth dopant. As such, production of large quantities of the material enables useful optical devices with long optical path lengths, leading to gain such as in fiber amplifiers.

Amorphous inorganic semiconductors, such as a-Si:H, a-SiC and a-SiNx, can be deposited over large areas at low temperatures, making them compatible with flexible polymer substrates. Such materials have been investigated for electronically excited devices such as novel LED[25-27] and TFEL[28] devices. Narrow bandgap hosts such as a-Si:H or a-Ge have often been doped with Er ions resulting in near-IR optical sources[19, 29], also potentially useful for optical communications systems. One advantage of a-Si:H over crystalline Si is a higher solubility limit for rare-earth dopants[1]. In addition, co-doping has been reported as an effective mechanism for
enhancing luminescent efficiency[1]. Amorphous semiconductors with larger bandgaps such as a-AlN doped with Er[30] have also been investigated for visible spectrum applications.

2.2 Wide Bandgap Semiconductor Hosts

2.2.1 Gallium Oxide

Beta-phase Ga$_2$O$_3$ is a wide bandgap semiconductor with a direct gap of ~4.9 eV. Though often an insulator, conductive Sn:Ga$_2$O$_3$ has been reported with a bandgap of 4.9 eV, resulting in a transparent conducting oxide (TCO) with the widest bandgap to date[31]. This makes Sn:Ga$_2$O$_3$ a viable material for deep UV ($\lambda < 300$ nm) optoelectronic devices and transparent contacts. Ga$_2$O$_3$ thin films are also often used as high-temperature oxygen[32] and other gas[33] sensors. Additionally, nanostructured films can be fabricated leading to unique optical and electronic properties[34, 35].

A broad blue luminescence is often observed in PL and CL experiments and has been previously attributed to emission from a self-trapped exciton[14, 36, 37]. The literature provides examples of Eu:Ga$_2$O$_3$[14] as well as Ga$_2$O$_3$ doped with other rare earth and transition elements which all demonstrate photoluminescence, and in several cases electroluminescence[38].

Previous studies at NCSU measured the radiative lifetime of Eu:Ga$_2$O$_3$ at 1.4 ms and can be modeled as a bi-exponential decay with fast (0.2 ms) and slow (1.4 ms) time constants[14]. Temperature-dependent time-resolved photoluminescence (TRPL)
showed that the actual time constants did not vary with temperature, but that the relative strength of each did. At low temperatures, it was found that the fast mechanism dominated the overall decay, indicating that the slow mechanism was primarily responsible for the observed luminescence. The Auger processes responsible for energy transfer from the host to the Eu dopant are quenched at low temperature, causing decreased luminescent intensity.

Beta-phase Ga$_2$O$_3$ takes the monoclinic structure, illustrated in Figure 2.6, whose unit cell parameters are given in Table 2.1[39] and is the most stable of the Ga$_2$O$_3$ phases, forming readily at high temperatures. In this structure, there are two unique gallium sites (tetrahedral and octahedral) and three unique oxygen sites. The two cation sites are of interest in this discussion because trivalent rare earth dopants would preferentially substitute for trivalent gallium ions. As will be discussed later, this results in splitting and shifting of sensitive radiative transitions, such as the $^5$D$_0$ to $^7$F$_2$ transition in Eu$^{3+}$ due to the Stark effect[40].

| Table 2.1. Unit cell parameters for monoclinic Ga$_2$O$_3$, adapted from [39]. |
|-------------------------------|----------------|
| **Parameter** | **Value** |
| A | 12.23 Å |
| b | 3.04 Å |
| c | 5.80 Å |
| $\alpha$, $\gamma$ | 90° |
| $\beta$ | 103.7° |
Figure 2.6. Atomic arrangement in gallium oxide. Illustration (top) of the arrangement of oxygen octahedra and tetrahedra in Ga$_2$O$_3$. Plan view (bottom) of the monoclinic structure of Ga$_2$O$_3$ in the ac plane. The dashed lines indicate the unit cell which contains four molecules. From [39].

The oxygen octahedra and tetrahedra, as shown in Figure 2.6, are arranged such that the polyhedra only share corners, not edges or faces, resulting in an increased minimum cation-cation distance (3.05 angstroms) compared to edge- or face-sharing.

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arrangements[39]. This may play an important role in the performance of films highly
doped with rare earths. Parasitic quenching mechanisms may occur when rare-earth
dopants exist with sufficiently high atomic percentages such that they are in close spatial
proximity. Increasing the distance between nearest cation neighbors in the host
subsequently maintains an increased distance between nearest rare-earth dopants and for
a given percentage of cation sites that are substitutionally occupied by the dopant.

2.2.2 Gadolinium Oxide

Gadolinium oxide is a wide bandgap insulator (values reported up to 6.2 eV) that
can assume cubic, monoclinic or hexagonal crystalline structures. The optical absorption
edge has components that vary linearly with the square and square-root of the photon
energy, indicative of both direct and indirect band alignments[41]. This may suggest the
existence of direct and indirect energy gaps of comparable width.

Gd$_2$O$_3$ thin films have attracted attention as dielectric layers for GaAs-based field
effect transistors[42] because of the high quality interface between GaAs and the
dielectric. Gd$_2$O$_3$ has also been investigated as a host for rare earth dopants in either thin
film or powdered form[43-48]. There continues to be interest in rare-earth doped
materials as a laser medium for high power disk lasers because of the long-lived excited
states[45] of rare-earth ions in Gd$_2$O$_3$ and the excellent thermal properties of sesquioxide
hosts[49]. An interesting aspect of this application is that since Gd is itself a rare-earth
element, substitutional doping of Gd cations by other rare-earth ions with similar ionic
radii may result in reduced deformation of the host lattice. This could enable greater dopant concentrations to be achieved before optical and thermal properties degrade.

In the case of high-power solid state laser media, thermal effects can be problematic, such as in thermal lensing. Thermal conductivity is often reduced by the inclusion of dopant species[50], but if the dopant has a similar ionic radius to the host cation, then deformation of the host lattice is reduced and thermal effects may be mitigated. Gd₂O₃ may be of interest in this regard because of the similarity between the ionic radii of the dopant ion and the Gd ion it replaces.

Table 2.2. Unit cell parameters of monoclinic and cubic Gd₂O₃.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Monoclinic[53]</th>
<th>Cubic[42]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>10.06 Å</td>
<td>10.81 Å</td>
</tr>
<tr>
<td>b</td>
<td>3.57 Å</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>8.76 Å</td>
<td>-</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>β</td>
<td>100°</td>
<td>-</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
<td>-</td>
</tr>
</tbody>
</table>

When deposited at high temperatures, Gd₂O₃ typically forms in the monoclinic phase, although it can, under certain growth conditions, form the cubic phase[48]. Unit cell parameters for the monoclinic and cubic phases are listed in Table 2.2. The cubic phase is typically preferred for dielectric layers due to high-quality epitaxial growth on and passivation of GaAs device layers[42]. However, no clear phase preference for optical applications has emerged. Past research has demonstrated that the phase of deposited films can be controlled via oxygen pressure during deposition[51], and the
effect of local structure on optical emission from rare earth dopants has been discussed in the literature[52].

2.2.3 Amorphous Semiconductors

Amorphous semiconductors are of interest for applications where the reduced electronic performance compared to crystalline material is less critical than the ability to inexpensively and uniformly deposit material over larger areas. Examples of large area electronics include flat-panel displays and solar cells and more recently in solid state lighting. Amorphous silicon (a-Si) has been the material of choice for large displays and photovoltaics for several years though novel amorphous semiconductors may offer certain advantages. Organic semiconductors such as pentacene are viable alternatives to a-Si in similar applications, but also pose unique difficulties.

Amorphous materials, in general, are characterized by a lack of long-range order. More specifically, amorphous solids lack the translational symmetry demonstrated by their crystalline counterparts, as illustrated in Figure 2.7. However the interatomic bond lengths tend to be similar for a given composition, thus amorphous solids are not composed of randomly positioned atoms, but rather tend to form an aperiodic network of atoms, albeit one lacking translational symmetry. As a result, coordination numbers and short-range order are approximately preserved between the crystalline and amorphous phases of a given composition[54].
Historically, amorphous semiconductors have been divided into two major groups: tetrahedrally-coordinated semiconductors and chalcogenide glasses. Amorphous silicon (a-Si), arguably the most thoroughly investigated amorphous semiconductor to date, belongs in the former as do several group IV amorphous compounds (a-Ge, a-SiC)[55]. Compounds of elements from group VI of the periodic table (chalcogens) such as sulfur, selenium or tellurium are commonly called chalcogenides.

Recently there has been increased interest in amorphous materials that do not fall into either of these two categories. The literature reports several amorphous semiconductors made from III-V and II-VI compounds[56] as well as organic materials[57] such as pentacene[58-60]. Of recent interest is the growing field of

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amorphous oxide semiconductors (AOS) which demonstrate high carrier mobility despite their amorphous nature.

Efficient band conduction typical of crystalline semiconductors is not observed in either the group IV amorphous semiconductors or in glasses because disorder gives rise to localized states[61, 62]. The work of Anderson describes how disorder in a solid causes localization of states in the band tails and the extent of the localization.

The Bloch theorem cannot be applied to amorphous semiconductors due to the lack of translational symmetry and thus, electron states are not described by well-defined $k$-values[63]. However, forbidden and allowed electron states still exist in these materials as the densities of these states are largely determined by the local chemical bonds. In an amorphous solid, where substantial disorder exists, localized states dominate carrier transport resulting in “hopping” mechanisms where carriers tunnel from one localized state to the next. This mechanism, called variable range hopping (VRH) is characterized by a dependence of the logarithm of conductivity on $T^{-1/4}$[64-66]. The VRH model suggests that at low temperatures carriers will hop among states near the Fermi level, even if that results in hopping to a state that is spatially more distant than another that may be further from the Fermi level. At higher temperatures, carriers tend to hop to states that are closer in space[62].
2.2.3.1 Amorphous Oxide Semiconductors

AOS compounds represent an interesting class of materials for amorphous electronic devices due to their high carrier mobility and the ability to control conductivity over a large range. Also important is that a number of AOS compounds have a bandgap near or larger than 3 eV, making them viable candidates for transparent electronic devices and circuits. It should also be noted that AOS materials demonstrate better environmental stability than organic semiconductors which often require encapsulation[67]. Transparent amorphous electronics are highly desirable for display backplanes as well as light emitting devices that luminesce throughout the visible spectrum.

Table 2.3. Examples of heavy metal cations with electron configuration \((n-1)\)d\(^{10}\)ns\(^{0}\) where \(n\) is at least four.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation State</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>+1</td>
<td>[Ar](3d^{10})4s(^{0})</td>
</tr>
<tr>
<td>Ag</td>
<td>+1</td>
<td>[Kr](4d^{10})5s(^{0})</td>
</tr>
<tr>
<td>Au</td>
<td>+1</td>
<td>[Xe] 4f(^{14})5d(^{10})6s(^{0})</td>
</tr>
<tr>
<td>Zn</td>
<td>+2</td>
<td>[Ar](3d^{10})4s(^{0})</td>
</tr>
<tr>
<td>Cd</td>
<td>+2</td>
<td>[Kr](4d^{10})5s(^{0})</td>
</tr>
<tr>
<td>Hg</td>
<td>+2</td>
<td>[Xe] 4f(^{14})5d(^{10})6s(^{0})</td>
</tr>
<tr>
<td>Ga</td>
<td>+3</td>
<td>[Ar](3d^{10})4s(^{0})</td>
</tr>
<tr>
<td>In</td>
<td>+3</td>
<td>[Kr](4d^{10})5s(^{0})</td>
</tr>
<tr>
<td>Tl</td>
<td>+3</td>
<td>[Xe] 4f(^{14})5d(^{10})6s(^{0})</td>
</tr>
<tr>
<td>Ge</td>
<td>+4</td>
<td>[Ar](3d^{10})4s(^{0})</td>
</tr>
<tr>
<td>Sn</td>
<td>+4</td>
<td>[Kr](4d^{10})5s(^{0})</td>
</tr>
<tr>
<td>Pb</td>
<td>+4</td>
<td>[Xe] 4f(^{14})5d(^{10})6s(^{0})</td>
</tr>
</tbody>
</table>

AOS materials are characterized by heavy metal cation constituents with \((n-1)\)d\(^{10}\)ns\(^{0}\) electronic configurations where \(n\) is greater than or equal to four to ensure
sufficient orbital overlap despite structural disorder. As is discussed in the following paragraph, the overlap of isotropic conduction band orbitals is responsible for the high carrier mobility in these materials. Examples of suitable cations are listed in Table 2.3. A wide variety of AOS materials have been reported including AgSbO₃[68], Cd₂GeO₄[69], Cd₂PbO₄[70], indium oxide[71], zinc indium oxide[72], zinc tin oxide[73] and zinc rhodium oxide[74] though indium gallium zinc oxide (IGZO) may be the most successful and widely investigated AOS material to date.

The earliest report of amorphous IGZO based devices came in 2004[75] which demonstrated enhancement-mode transparent thin film transistors (TFTs) with channel mobility on the order of 10 cm²/V-sec. Mobilities observed in crystalline semiconductors can be orders of magnitude larger, but for an amorphous semiconductor, this mobility is quite high.

The high mobility of n-type AOS materials is owed to the large, overlapping s-orbitals of the constituent heavy metal cations that constitute the conduction band. The isotropic nature of the s-orbital allows a large degree of disorder to exist in the solid without substantially degrading carrier mobility as shown in Figure 2.8. More importantly, relative orientation of adjacent orbitals is not required to maintain a continuous chain of orbitals, as would be necessary with highly anisotropic p, d or f orbitals. Since the relative positions between neighboring atoms are preserved to some extent by the interatomic bonds in an amorphous solid, orientational order is a determining factor for carrier mobility in amorphous semiconductors. The isotropic orbital shape in AOS materials thus reduces the overall impact of order on the carrier
mobility. The criterion that $n$ is greater than or equal to four ensures that the $s$ orbitals of the metal cations are large enough, thus increasing orbital overlap among neighboring cations.

Figure 2.8. An illustrated comparison of the isotropic $s$-orbitals in AOS materials (right) to the anisotropic orbitals in covalent semiconductors (left). The crystalline scenario is shown at top for silicon and for an oxide semiconductor while the amorphous scenario is shown at bottom. The isotropic $s$-orbitals allow greater flexibility in the relative orientations of adjacent cations. From [75].

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2.2.3.2 Indium Gallium Zinc Oxide

Since the first report of amorphous IGZO TFTs in 2004[75], several groups have published on material properties[76-79], IGZO devices [80, 81] and integrated circuits [82]. IGZO is a viable n-type material for a number of large area electronics because of its high carrier mobility (10-40 cm²/V-sec), wide bandgap (~3 eV) and the ability to control conductivity over a range of values. Beyond basic TFTs, the literature reports on memory and optoelectronic devices as well as integrated circuits such as ring oscillators and active matrix backplanes. The level of performance and variety of applications of IGZO devices are evidence of the potential for this material system in large area electronics.

Aside from the high carrier mobility, an important property of IGZO is the ability to control the n-type carrier concentration over several orders of magnitude by controlling conditions during film deposition[76] or by post-growth treatments[83]. The excess carriers are the result of point defects in the film, either oxygen vacancies or metal interstitials, both of which are n-type defects. This is an important property that was difficult to obtain in the case of a-Si, where formation of dangling covalent bonds prohibited effective doping of thin films. The solution was to passivate the dangling bonds by adding hydrogen to the films, resulting in amorphous hydrogenated silicon (a-Si:H). Once the dangling bonds were passivated, dopants could be introduced to alter the conductivity of the films.
Like other ternary and quarternary compounds, the properties of IGZO thin films can be tailored for specific applications by varying the composition, according to Figure 2.9[79]. A number of compositions have been reported in the literature. For example, Hideo Hosono’s group commonly uses a composition with atomic ratio of 1.1:1.1:0.9 of In:Ga:Zn[75]. Other groups have reported amorphous IGZO films and devices with atomic ratios (In:Ga:Zn) of 2.2:2.2:1[84] and 1:1:1[83]. The IGZO thin films presented here were deposited with a ratio of 1:1:5[81] and is indicative of the wide range of IGZO compositions that can be implemented. High quality amorphous IGZO films are

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commonly deposited by sputtering[75, 83, 84] or PLD[81]. Studies at NCSU have indicated that films with a metal cation ratio of 1:1:1 increased carrier mobility to above 30 cm²/V-sec. This increase in mobility is due to the fact that the In 5s orbital forms the low-energy portion of the conduction band.

The amorphous phase of IGZO demonstrates substantial short range order that is similar to the crystalline phase. Nomura, et al investigated the local coordination structure of a-IGZO thin films by x-ray absorption fine structure (XAFS) studies[78]. The results of the study indicate that the running coordination numbers for the amorphous and crystalline phases of IGZO are similar to about 4 angstroms, which is on the order of a small unit cell parameter for some crystalline semiconductors. These results reiterate the discussion in 2.2.3 regarding short-range order in amorphous solids. Consequently, a-IGZO may be a suitable amorphous host for rare earth dopants where this short-range order can positively influence emission characteristics.
Figure 2.10. XAFS results for amorphous (labeled a) and crystalline (labeled sc) IGZO thin films. The measured Fourier transformed XAFS spectra are shown for the K-edge of In (a), Zn (b) and Ga (c). The running coordination numbers are shown as a function of radial distance (d-f). For all cations, the local structure is similar between the amorphous and crystalline phases.\textsuperscript{1} From [78].

2.3 Thin Film Electroluminescent Devices

2.3.1 Device Operation

Electroluminescence is a light emitting process whereby a material is excited by an applied voltage. Low DC voltages are used to excite devices such as LEDs and high AC voltages excite devices such as the ones described here. In a thin film electroluminescent device (TFEL) a phosphor layer is located between two insulating layers. Contact layers are deposited on the two insulators. For alternating applied electric fields, electrons (or holes) are accelerated in alternating directions through the phosphor layer. If the field is large enough, the carriers will have sufficient kinetic energy to impact excite luminescent centers in the phosphor, which then relax radiatively.

Wager and Keir[85, 86] described TFEL operation in terms of the six processes illustrated in Figure 2.11. These processes are: (1) electron injection, (2) transport, (3) impact excitation, (4) radiative recombination, (5) trapping, and (6) optical outcoupling. The application of a large electric field results in electron injection into the phosphor layer by tunnel emission from interfacial traps states. The injected carriers are energetically transported through the conduction band (or valence band for p-type devices) and those with sufficient kinetic energy can impact excite the luminescent centers in the phosphor. A fraction of the electrons can tunnel through the opposite dielectric and recombine at the electrode, but many will be trapped at interface states between the phosphor and dielectric layers. Meanwhile, after impact excitation, the excited luminescent centers may decay radiatively, resulting in the observed
electroluminescence. Non-radiative decay occurs as well, resulting in phonon emission to the host lattice.

![Diagram of optical and electronic processes in TFEL devices]

Figure 2.11. Optical and electronic processes in TFEL devices¹. From [85].

2.3.2 Phosphor Materials

Alternating field thin film electroluminescent (TFEL) devices have attracted interest for many years for their potential in producing relatively low cost color displays or for applications requiring low-intensity lighting such as dashboard displays for automobiles. Historically, interest has been focused on sulfides such as ZnS[87] and

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CaS[88], with the most attention focused on ZnS:Mn phosphors due to the efficient emission resulting from $^4T_1$ to $^6A_1$ transition in Mn$^{2+}$. Performance metrics are listed in Table 2.4 for a number of sulfide phosphors[89]. More recently, wide band gap nitrides and oxides have attracted interest with GaN and Ga$_2$O$_3$ and a number of ternary[90] and quaternary[91, 92] material systems investigated. Materials with an increased bandgap potentially have several advantages with respect to thermal quenching, excitation and emission spectra. In addition, the environmental stability of III-N and oxide semiconductors is often superior to the sulfides.

It has been relatively difficult to obtain bright, red emission from sulfide phosphors, although ZnS codoped with Sm and Cl as well as filtered ZnS:Mn[88] devices have been used to make red pixels with reduced efficiency. GaN[93-95] and Ga$_2$O$_3$[14, 38] have been shown to be good hosts for transition metals and rare earth elements. The use of the Eu$^{3+}$ ion for red emission is attractive since it is efficient and has good color purity, which led to its use in cathode ray tubes. Good EL results have been obtained with both Eu:GaN[96, 97] and Eu:Ga$_2$O$_3$[36].

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Color</th>
<th>$x$</th>
<th>$y$</th>
<th>L (cd/m²)</th>
<th>Efficiency (lm/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS:Mn</td>
<td>Yellow</td>
<td>0.5</td>
<td>0.5</td>
<td>300</td>
<td>3-6</td>
</tr>
<tr>
<td>CaS:Eu</td>
<td>Red</td>
<td>0.68</td>
<td>0.31</td>
<td>12</td>
<td>0.2</td>
</tr>
<tr>
<td>ZnS:Mn$^2$</td>
<td>Red</td>
<td>0.65</td>
<td>0.35</td>
<td>65</td>
<td>0.8</td>
</tr>
<tr>
<td>ZnS:Tb</td>
<td>Green</td>
<td>0.3</td>
<td>0.6</td>
<td>100</td>
<td>0.6-1.3</td>
</tr>
<tr>
<td>SrS:Ce</td>
<td>Blue/green</td>
<td>0.3</td>
<td>0.5</td>
<td>100</td>
<td>0.8-1.6</td>
</tr>
<tr>
<td>SrGa$_2$S$_4$:Ce</td>
<td>Blue</td>
<td>0.15</td>
<td>0.1</td>
<td>5</td>
<td>0.02</td>
</tr>
<tr>
<td>CaGa$_2$S$_4$:Ce</td>
<td>Blue</td>
<td>0.15</td>
<td>0.19</td>
<td>10</td>
<td>0.03</td>
</tr>
<tr>
<td>ZnS:Mn/SrS:Ce</td>
<td>White</td>
<td>0.44</td>
<td>0.48</td>
<td>470</td>
<td>1.5</td>
</tr>
</tbody>
</table>

1Luminance values were reported for 60 Hz excitation.
2Emission from ZnS:Mn phosphors was filtered to pass only red light.
The choice of TFEL phosphor material and dopant are strongly linked by the nature of the dopant. Wager, et al[86] summarized the effects of isovalent, acceptor and donor impurities on the electroluminescent and electronic properties of TFEL devices for the cases of Mn:ZnS (isovalent), Cu:SrS (acceptor) and Ce:SrS (donor). The effects of acceptor or donor impurities tend to manifest themselves in the generation of dynamic space charge in the phosphor layer which has secondary effects, such as trailing edge emission. The study concluded that isovalent impurities are thus the preferred dopant type for TFEL devices because they result in near-ideal device operation.

As such, to exploit the unique optical properties of trivalent RE ions, a phosphor host should be selected where the RE ions substitute for a trivalent cation. Examples of this include III-V semiconductors such as GaN or AlN and sesquioxides such as Ga$_2$O$_3$ and Y$_2$O$_3$.

2.4 Active Matrix Pixels

2.4.1 Pixel Addressing

Flat panel displays of all types require that pixels be addressed individually. This has typically been achieved using one of three addressing schemes: direct, passive matrix (PM) and active matrix (AM). Simple displays requiring low-resolution and small size can implement direct addressing, where each pixel is individually connected to driving circuitry. For a display with $N$ rows and $M$ columns the total number of connections
required is $N \times M$. Even for displays of moderate resolution, the number of connections rapidly becomes impractical. Examples of this include small segmented LED displays with approximately 50 pixels or less[98].

For larger displays, a matrix is used to power individual pixels, reducing the number of required connections. Two addressing schemes exploit this matrix implementation: passive and active addressing. In passive-matrix schemes, as used in some liquid crystal displays, one substrate will have row electrodes and the other will have column electrodes such that the optical element in between the substrates can be activated by the intersection of a given row and column with an applied voltage. This functionality is illustrated in Figure 2.12. As such, the required connections are reduced from $N \times M$ for direct addressing, to $N + M$ for matrix addressing.

However, the performance of passive-matrix techniques is limited. Only one row can be selected at any given time while the column electrodes are simultaneously selected. In order to refresh an entire image, the rows are selected in sequence, while a voltage is briefly applied to each element. The result is that a pixel is activated when the time-averaged voltage is above the threshold for the desired behavior. Another consequence of passive-matrix schemes is that voltages are present on rows that have not been selected and in order to preserve the desired functionality of the display, this voltage must remain below the material’s threshold voltage. This influences the choice of materials for passive-matrix displays by requiring a suitable threshold voltage such that the optical elements are not inadvertently activated while keeping operating voltages and hence power consumption to a minimum.
Figure 2.12. Example of passive matrix addressing for liquid crystal displays. From [98].

Equation (2.1) quantifies the relationship between the achievable resolution in a display as a function of threshold voltage ($V_{th}$) and “steepness” of the response ($\Delta$) of the element[99]. Here $N_{Max}$ denotes the maximum number of rows or columns that can be implemented using a material with parameters $V_{th}$ and $\Delta$. Figure 2.13 illustrates how these material properties may be defined. According to equation (2.1), the maximum achievable resolution may be increased by choosing a material or device with a very steep response (small $\Delta$) and a high threshold voltage although the latter comes at the expense of increased power consumption. As a rule of thumb, passive-matrix displays do not exceed ~400 rows (or columns).
Active-matrix addressing does not suffer from material-limited resolution because a transistor is integrated with each pixel. Here, the non-linear behavior of a transistor can isolate each pixel from deleterious voltages present on the address lines during its “off” state, improving achievable resolution and contrast simultaneously. A circuit illustration in Figure 2.14 demonstrates the integration of a transistor with a capacitive optical device, such as a liquid crystal cell. The cross-section in the same figure also
demonstrates the substantial complexity involved in fabricating such a pixel which is the major disadvantage of active-matrix addressing.

Figure 2.14. Circuit (left) and cross-section (right) illustrations of an active-matrix addressing scheme for liquid crystal displays. Active-matrix addressing can be implemented for other display technologies as well, including LEDs/OLEDs and TFEL devices. From [98].

While work on active-matrix schemes dates to the early 1970’s, it was not until 1979 that a-Si was thought to be useful in this application. Fabrication of high quality a-Si TFTs has allowed active-matrix displays to evolve; reducing fabrication costs and improving fill factor. High-quality a-Si:H TFTs can be fabricated at low temperatures, allowing the use of less expensive glass substrates for large displays, rather than more expensive quartz. As TFT technology matured, carrier mobility increased and devices could be reduced in size, increasing pixel fill factor.

However, the narrow bandgap of a-Si:H poses a major limitation. The a-Si:H TFTs must be optically shielded from the display due to their sensitivity to visible light emitted by the display. With such a narrow bandgap, light of varying wavelengths can,
for example, ionize carriers in the devices, impairing control of the display elements themselves. The use of amorphous wide-bandgap materials for active-matrix backplanes could eliminate the need for optical shielding. A benefit of removing optical shields and using wide-bandgap semiconductors is that the entire pixel becomes optically transparent in the visible spectrum, which improves the fill-factor of the display. In addition, as amorphous wide-bandgap materials continue to be developed, it may be possible to monolithically integrate the backplane of the display with the row and column driver circuitry onto a single substrate, further reducing display complexity and improving reliability and yield.

2.4.2 Active Matrix Implementations

Active-matrix backplanes have been researched since the 1970’s. Early active-matrix liquid crystal displays were achieved using CdSe TFTs[100] as a switching element, but by 1981 practical displays made with a-Si based TFTs could operate at voltages as low as 15 V[101]. These displays implemented backplane structures similar to those shown in Figure 2.14. By the 1990’s, the emergence of high-quality TFTs based on organic semiconductors created interest in active-matrix displays based on these materials for their ease of deposition and reduced cost compared to inorganic alternatives. In addition, organic semiconductors could be integrated monolithically and inexpensively with organic light emitting materials, such as MEH-PPV, as shown in Figure 2.15[102, 103].
The class of materials known as amorphous oxide semiconductors is a relatively recent development, but reports have been published on their applicability to active-matrix displays. Examples are limited but include zinc-tin-oxide (ZTO)[104] as well as IGZO[82, 105] backplanes with OLED light emitting elements.

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Active-matrix backplanes can be used to address a variety of opto-electronic devices for LCD, LED/OLED, plasma, field-emission or electroluminescent displays but the circuitry required for each may be different. This is true and relevant in the case of electroluminescent displays where the TFEL device operating voltages are necessarily much larger than the operating voltages of the switching devices.

In order to drive a TFEL device, large ac voltages are required which are not readily supported by amorphous TFTs. In addition, negative voltages applied to the drain of a TFT may result in substantial leakage current. As such, the bipolar operation of a TFEL device necessitates revised backplane circuitry. A common pixel circuit for TFEL display backplanes is shown in Figure 2.16[106].

![Active matrix pixel circuit designed for addressing TFEL devices.][106] © 2000 IEEE
Here, the high ac driving voltages applied to the TFEL are decoupled from the switching elements in the pixel by placing TFT2 between the TFEL device and ground. When a voltage is applied to the gate line and the signal line, effectively addressing the pixel, the signal line voltage is applied to TFT2. Since minimal current should flow through the TFT gate, almost no voltage drop is observed across the channel of TFT1. The capacitor $C_s$ allows the TFEL device to remain in the “on” state without a voltage applied to the gate or signal lines. When a voltage is applied to the gate and signal lines the TFEL device luminesces and the capacitor charges. The TFEL remains “on” until the gate line is high and the signal line is grounded, providing a path for the capacitor to discharge. The remaining combinations of gate and signal inputs have no effect on the TFEL luminescence.
3 Device Fabrication and Testing

3.1 Thin Film Electroluminescent Devices

3.1.1 Fabrication

Thin film electroluminescent devices were fabricated using PLD and either a shadow mask or lift-off step to define mesas. Substrates were commercially obtained Corning 7059 glass with a sputtered indium-tin-oxide (ITO) conductive layer and an atomic layer deposited aluminum-oxide/titanium-oxide (ATO) high-k dielectric layer on top. Use of these substrates facilitates the fabrication of TFEL devices, leaving only two subsequent depositions.

On these substrates, the phosphor layer (either Eu:Ga2O3 or Eu:IGZO) was deposited followed by an ITO or IGZO top contact layer. A cross-section of the device is illustrated in Figure 3.1. The devices are driven by applying an ac voltage across the top and bottom contact layers as shown. Both were deposited by PLD. Eu:Ga2O3 phosphors were deposited at a substrate temperature of 850 °C for 20,000 pulses (~200 nm thick) with a laser energy of 250 mJ per pulse in 5 mTorr oxygen ambient. Eu:IGZO phosphors were deposited at room temperature for 20,000 pulses (~200 nm) with a laser energy of 150 mJ per pulse in 100 mTorr oxygen ambient. The ITO top contact layers were deposited at room temperature with laser energy 150 mJ per pulse in 10 mTorr oxygen ambient.
To define the ITO top contact layer, one of two methods was used: lift-off lithography or a shadow mask. Since the deposition was carried out at room temperature, developed photo-resist could be present on the substrate. After the film is deposited, soaking the sample in acetone for a few minutes dissolves the resist, removing unwanted portions of the film. Alternatively, a silicon shadow mask can be fabricated and placed over the substrate during deposition to prevent deposition of material in unwanted areas. This method is possible only for devices where layer to layer alignment is not critical as mask placement is crude.

Silicon shadow masks were fabricated using an anisotropic potassium hydroxide (KOH) chemical etch using a silicon nitride (SiNₓ) etch mask. (100) Si wafers were coated on both sides with SiNₓ. Patterns were lithographically defined on one side and
the SiNx film was plasma etched to open vias to the wafer underneath. The wafer was then wet-etched using highly selective 40% KOH etch at 80 °C for four to five hours to etch through the silicon wafer. The SiNx membrane remaining on the backside of the mask can be chemically stripped or blown away with compressed air[107].

### 3.1.2 Optical Characterization

TFEL devices were driven using a homemade inverting amplifier using an Apex PA97 operational amplifier, with open circuit voltage gain between 8 and 90 to amplify the output of an Agilent 20 MHz arbitrary waveform generator. EL emission was captured using one of three detectors: a CCD spectrometer, PMT or large area Si photodiode. To capture EL spectra, an Ocean Optics USB4000 fiber coupled CCD spectrometer was used. For low-light photon counting, a PMT was used and for luminance measurements, a calibrated photodiode was used. Additionally, time-resolved EL experiments were carried out using a PMT connected to a Tektronix DPO4104 4-channel 1 GHz oscilloscope through an EG&G Model 181 current preamplifier.

### 3.1.3 Sawyer Tower Circuit Analysis

The Sawyer-Tower circuit, as outlined by Wager and Keir[85], is used for electronic characterization of TFEL or other capacitive devices. In this technique, the TFEL device is placed in series with a resistor and capacitor as shown in Figure 3.2. For these experiments, a 10 kΩ resistor and 0.1 μF sense capacitor were used. The resistance and
capacitance are both smaller than that of the TFEL device under test and so should not substantially reduce the power dissipated by the device.

![Figure 3.2. Sawyer-Tower circuit for electronic analysis of TFEL devices [85] 1.](image)

In this technique, a waveform similar to that shown in Figure 3.3 is amplified and used to excite the TFEL device. Note the labeling of the critical points of the waveform as described by Wager and Keir. All points except B and G are self-explanatory. These two points however denote the onset of conduction current through the device and can be determined from a plot of current versus time. This notation will be used in discussing the technique as well as experimental results.

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During operation of the device, three voltages are measured in the circuit to give an instantaneous measure of the voltage across, current through and charge accumulated in the TFEL device. Equations (3.1) to (3.3) are used to derive a number of other properties of TFEL devices. Examples of $V_{EL}(t)$ and $I_{EL}(t)$ are shown in Figure 3.3.

$$I_{EL} = \frac{V_1 - V_2}{R} \quad (3.1)$$

$$V_{EL} = V_2 - V_3 \quad (3.2)$$

$$Q_s = C_s V_3 \quad (3.3)$$

---

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$I_{EL}$ is the current through the TFEL device, $R$ is the value of the series resistor, $V_{EL}$ is the voltage across the device, $Q_s$ is the charge in the sense capacitor and $C_s$ is the value of the sense capacitor. It should be noted that since all the measured voltages are time-varying, so are the derived quantities and thus can be plotted as functions of time.

A Q-V plot, similar to the example shown in Figure 3.4, is a popular analytical tool for examining the behavior of TFEL devices. It is important to note that the charge $Q$ is the instantaneous charge detected by the sense capacitor given by equation (3.2) and not the internal charge while the voltage $V$ is the instantaneous voltage across the EL device given by equation (3.3) and not the true field inside the EL phosphor.

The labeling scheme in the Q-V plot is the same as for the original waveform, thus the figure is interpreted in a counter-clockwise fashion. Several effects can be observed using this type of analysis including polarization charge, leakage charge, relaxation charge and conduction charge. Polarization ($Q_{pol}$) charge is the charge stored at the EL phosphor/dielectric interface immediately prior to applying the subsequent voltage pulse. Leakage ($Q_{leak}$) charge is the charge stored at this same interface which is lost during the zero-voltage portion of the waveform, caused by the release of carriers from shallow interface states. Conduction ($Q_{cond}$) charge is the charge transported across the phosphor layer during the application of the high-voltage pulse and accepted as responsible for impact excitation and thus, EL emission. Lastly, relaxation ($Q_{relax}$) charge is the charge that flows across the phosphor layer during the non-zero steady-state portion of the applied waveform.
Figure 3.4. Idealized charge-voltage (Q-V) plot for a TFEL device[85].

The + and – superscripts correspond to the polarity of the applied waveform. The ‘e’ superscript denotes that this type of charge is an external charge flowing through the sense capacitor and is equal in magnitude to the internal charge through the EL device, which is denoted by the absence of this superscript. However, external charges are useful qualitative analytical tools that mimic internal charges flowing through the TFEL device.

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Comparing the idealized Q-V curve in Figure 3.4 to an idealized plot of the internal charge versus the phosphor field (Q-Fp) is instructive. The unidentified charge differences from Figure 3.4 are fluctuations in charge moving through the circuit only, and not internal to the TFEL device. Specifically, measurable variations in charge are observed between points D and E and also I and J, though in Q-Fp analysis the measured charge is constant from D to E and I to J.

The motion of electrons in a TFEL stack is illustrated in Figure 3.5 to clarify the operation of a device using Wager and Keir’s analytical method. At A, electrons are already trapped at interface states as a result of the previous negative voltage pulse. At C, the positive voltage pulse has been applied and the constant voltage portion of the cycle begins. The majority of charge has already been transported across the phosphor, but some transport continues between C and D. This is the relaxation charge described previously. At D, immediately before the voltage is re-set to zero, the transported charge reaches a maximum. Between E and F, during the zero portion of the waveform, a portion of the charge is released from shallow interface traps and recombines. At F, the charge circled in the figure is stored at the opposite interface from point A. Points G through J are similar in principle to this illustration, but with opposite polarity.
Figure 3.5. Illustration of electrons moving through the TFEL device cross section at points A through F. For a symmetric device structure with similar interfaces, behavior at points G through J are similar to A through F, though the polarity is the opposite. Interface trapped charge at points A and F are circled for clarity.
3.2 **Active Matrix Electroluminescent Pixel**

A major motivation for the development of AOS materials is their application in novel display devices. A practical extension of TFEL device research is the realization of an active matrix pixel utilizing AOS materials for the TFT channels as well as the light emitting element. The circuit diagramed in Figure 3.6 was designed for this purpose.

![Diagram of active matrix pixel](image)

Figure 3.6. Circuit that was implemented to realize an active matrix pixel using a TFEL light emitting element. The TFTs, labeled T1 and T2, are based on IGZO channel material.

The TFTs, T1 and T2, are both a bottom-gated design using an IGZO channel, as shown in Figure 3.7. Multiple T2 TFTs were designed with varying geometries to explore the effects of channel length (200, 400 or 800 microns) on the luminescence intensity from the TFEL device. Channel widths were fixed at 200 microns for T1 and
T2 TFTs. The channel width of T1 was fixed at 200 microns since the only current draw on the device would be the gate leakage of T2.

![Cross-section schematic of the layout of bottom gated IGZO TFTs used in the active matrix pixel circuit.](image)

3.2.1 Fabrication

Fabrication of the active matrix electroluminescent pixel involves six mask levels and a number of process steps as illustrated in Figure 3.8. Commercial substrates consisting of 1 mm thick Corning 7059 glass, coated with a 250 nm sputtered indium tin oxide (ITO) conductive layer and a subsequent atomic layer deposited 220 nm aluminum oxide-titanium oxide (ATO) high-k dielectric were obtained from Planar Systems. The first two process steps consist of plasma etching of the ITO and ATO layer to allow fabrication of interconnected bottom-gated TFTs. The ITO layer is significantly thinned
during plasma etching to reduce the step height and off-state leakage current through the TFT. The ATO dielectric is only used for the TFEL device where a high breakdown voltage and high-k dielectric is critical to device performance. To plasma etch the ATO and ITO layers, a BCl₃ chemistry is used with a forward power of 100 W. Etch rates of 9 and 10 nm/min were observed for ATO and ITO layers, respectively.

Figure 3.8. Process flow diagram illustrating the steps involved in pixel fabrication. Starting with the (A) initial ATO/ITO/Glass substrates, ATO and ITO layers were etched (B) to allow TFEL and TFT integration. Subsequently, the SiN₃ dielectric is deposited (C) followed by (D) IGZO channel, (E) Eu:IGZO phosphor and (F) ITO top contact depositions. Pulsed laser deposited layers were defined using standard lift-off techniques.
After substrate etching, a 200 nm thick SiN\textsubscript{x} dielectric layer is deposited by plasma enhanced chemical vapor deposition (PECVD) at 300 °C. This conformal layer acts as the gate dielectric for the bottom gated TFTs. The SiN\textsubscript{x} layer is lithographically defined and plasma etched using standard techniques. The 50 nm IGZO channel layer, 200 nm Eu:IGZO phosphor layer and 200 nm thick ITO contact layers were pulsed laser deposited in oxygen ambient at room temperature. Pulsed laser deposited (PLD) layers were individually patterned using standard lift-off lithography techniques.

The light emitting area of the TFEL device is 2 mm x 2 mm. Three different channel lengths for TFT T2 i.e., 100, 200 and 400 µm, were fabricated to investigate the effect of channel size on the transient characteristics of the TFT as well as the ability to modulate the TFEL device. The channel width for all TFTs was 800 µm and a single geometry was used for T1 (W/L = 800/200).

3.2.2 Device Modulation and Testing

The pixel was characterized in stages: (1) dc TFT characteristics, (2) transient TFT response, (3) interconnected TFT transient response, (4) TFEL characteristics and (5) TFEL modulation by a single series TFT.

Standard dc TFT characteristics were obtained using an HP 4155 parameter analyzer. These characteristics included the $I_{ds}=V_{gs}$ family of curves and $I_{ds}=V_{ds}$ transfer curves. From these measurements, relevant TFT parameters could be extracted, including channel mobility, turn-on voltage and subthreshold swing. These are important metrics against which alternative amorphous TFT devices are measured and compared.
The transient response of TFTs is more difficult to quantify as device geometry dominates over material properties. However, the motivation of these experiments was to demonstrate the capability of an AOS pixel and hence it should be capable of operating at relevant display frequencies. In this pixel circuit, the TFTs should be capable of responding quickly to changes in drain and gate bias as this is how the individual pixels are addressed. To test this response, a 20 MHz Agilent arbitrary waveform generator was used to apply a square pulse train at the gate and then the drain of a TFT while the drain and then gate were held at constant bias, as shown in Figure 3.9A and B. The drain current was monitored as a function of time using an EG&G PARC model 181 current preamplifier connected to a Tektronix DPO4104 four channel 1 GHz oscilloscope.

Just as important is the propagation of that pulsed signal to the second TFT. Here, two interconnected TFTs were measured as shown in Figure 3.9C and D. using instrumentation as discussed above. The output of the unmodulated TFEL device was characterized according to the method in section 3.1.2.
To demonstrate proper functionality, the TFEL device was modulated using TFT T2 as shown in Figure 3.10. An ac bias was applied to the top contact of the TFEL while the bottom contact was interconnected to the TFT drain and the source grounded. A positive gate bias was applied to modulate the current through the TFT channel. The optical intensity was monitored using a large area silicon photodiode as in section 3.1.2 as a function of TFT gate bias.

Figure 3.9. Pixel TFT testing methods.
Figure 3.10. TFEL modulation testing method.
4 Properties of Europium Doped Gallium Oxide

The objective of this Eu:Ga$_2$O$_3$ study is to evaluate the effects of high dopant concentrations (up to 20 mole percent) in this host material with regard to rare-earth luminescence, host structure and optical properties such as absorption and refractive index. The results presented here indicate structural changes occur in the host due to the presence of large amounts of the Eu dopant. Undoped films were polycrystalline with multiple orientations and the addition of Eu results in polycrystalline films where the crystallites tend to the (004) orientation. All films demonstrated characteristic Eu$^{3+}$ luminescence though luminescence intensity is highest for films doped with 10 mole percent europium doping. Time-resolved measurements indicate that the optimal Eu concentration is between 5 and 10 mole percent doping as increased Eu content results in luminescence quenching.

Beta phase gallium oxide ($\beta$-Ga$_2$O$_3$) has received considerable attention in recent years as a material for wide bandgap, self-assembled nano-structures[108, 109] and as an efficient luminescent host material for a number of trivalent rare earth ions.[38] In the case of europium doped gallium oxide, the radiative lifetimes can be quite long (1.4 ms)[14], indicating it may be a viable gain medium for optically pumped lasers.

Trivalent rare earth ions are commonly used in laser gain media, cathode ray tube (CRT) phosphors, fluorescent lighting and thin film electroluminescent (TFEL) devices. Their optical properties stem from a unique electronic structure: electrons in the outer 5$s$ and 5$p$ orbitals substantially screen electrons in the incomplete 4$f$ orbital from the local
electric field of the host. This screening reduces the effect of the host on the emissive and absorptive properties of the rare earth dopant, resulting in spectrally narrow emission and absorption bands from radiative transitions within the free ion-like $4f$ states.

It has been historically difficult to achieve bright red electroluminescent (EL) phosphors from traditional sulfide phosphors such as ZnS and SrS. The most efficient red EL devices were fabricated using filtered Mn:ZnS, which has a broad yellow emission band owing to the $^4T_1$ to $^6A_1$ transition in the Mn$^{2+}$ dopant[110]. However, filtered TFEL devices are non-ideal due to reduced efficiency. More recently, bright red TFEL devices have made from Eu:Ga$_2$O$_3$[38, 111] owing to the $^5D_0$ to $^7F_J$ transitions in Eu$^{3+}$. Other successful red EL phosphors include Eu:CaS[89], but it has been reported that non-ideal device characteristics are observed for donor or acceptor impurities and that isovalent impurities are preferred[86]. Thus, to best exploit the unique luminescent properties of trivalent rare earth dopants, it would be preferable to implement a TFEL device using a phosphor with a group III cation. Examples of such phosphors would include III-V semiconductors such as GaN[93, 94] and sesquioxides such as Ga$_2$O$_3$[38, 111] or Y$_2$O$_3$[112].

Rare-earth doped semiconductor materials and devices are typically fabricated with dopant concentrations on the order of a few atomic percent[9, 14, 113, 114]. Increasing dopant concentration typically results in increased optical intensity from thin films or devices, but beyond a critical concentration the luminescence intensity and radiative lifetimes abruptly decrease. This observed quenching may arise from the formation of non-radiative defect states, reduced efficiency of traps at dopant sites, and
the rapid non-radiative energy transfer from the rare earth ion’s excited state to neighboring ions or defect states.

It is important to investigate the optimal dopant concentrations in TFEL device phosphors so that new bright, efficient devices can be realized throughout the visible spectrum, resulting in improved full-color displays. Active-matrix pixels have been demonstrated for organic LED (OLED) light emitting elements utilizing novel amorphous materials for the TFT backplanes[82, 104]. More recently, these amorphous TFTs were integrated with an amorphous TFEL device structure, resulting in a visible-transparent pixel. Integration of these backplanes with bright, transparent TFEL devices could be technologically important for certain applications such as heads-up displays (HUDs) for automotive or military applications.

In this study, the effects of high europium doping on optical and structural properties of Eu:Ga$_2$O$_3$ thin film samples were studied by photoluminescence and x-ray diffraction. In order to ascertain optimal doping conditions for TFEL device applications, we quantify how the luminescence intensity and radiative lifetimes depend on structural changes in Eu:Ga$_2$O$_3$ as the Eu$^{3+}$ mole fraction increases over the range of 2.4 to 20%.

### 4.1 Photoluminescence

Films were optically pumped during CWPL experiments using a 1 mW, 280 nm LED from Sensor Electronic Technology, Inc. For time-integrated and time-resolved photoluminescence (TIPL and TRPL) spectroscopy, the samples were excited using the frequency-tripled output from a 1kHz Ti:sapphire laser (266 nm), with pulse widths near
100 fs. TIPL data were taken for laser intensities of $68 \pm 12 \mu J/cm^2$, while TRPL data was taken with an intensity of $\sim 100 \mu J/cm^2$. The spectral resolution of the spectrometer used in TIPL experiments was 0.3 nm. For TRPL, the luminescence was dispersed by a 0.75 m Spex monochromator, coupled to a photomultiplier tube whose output was monitored by a 1 GHz oscilloscope to capture the luminescence decay with 0.5 nm and 2 µs resolution.

Figure 4.1. PL spectra from CWPL (left) and TIPL (right) experiments. Results from both are largely in agreement regarding emitted intensity from the Eu$^{3+}$ dopant. The inset shows the peak CWPL intensity as a function of Eu mole fraction in Ga$_2$O$_3$ films.

CWPL and TIPL spectra in Figure 4.1 demonstrate characteristic europium ion emission with the strongest peak at 611 nm caused by the $^5D_0 \rightarrow ^7F_2$ transition. Because the films were much thicker than the absorption depth of the excitation laser, variations in the emission intensity arise from the varying efficiency of the emission. Although the
fine structure in the PL spectra is unresolved at room temperature, higher dopant concentrations do not substantially broaden spectral features. Due to the large change in the angular orbital quantum number, the $^5D_0 \rightarrow ^7F_2$ transition is highly sensitive to local fields and demonstrates significant Stark splitting[40]. The asymmetric shape of the emission peak, with a slight shoulder at longer wavelengths, corroborates previously observed Stark splitting of the $^5D_0 \rightarrow ^7F_2$ transition in Ga$_2$O$_3$[115].

The intensity of the 611 nm peak was used to gauge overall emission intensity as a function of europium concentration (inset in Figure 4.1). Whereas CWPL measures emission following the establishment of a new, photo-induced equilibrium carrier distribution, TIPL measures emission as a consequence of relaxation back to equilibrium following impulsive photoexcitation. Consequently, CWPL spectra provide more insight into device performance, while TIPL spectra provide more insight into intrinsic properties of the emitter. The CWPL and TIPL spectra agree: emission intensity grows with dopant concentration up to 10%, and then falls off with higher europium concentration. This agreement between CWPL and TIPL indicates that the increase is an intrinsic effect directly attributable to increasing the Eu concentration, minimally influenced by photoexcitation conditions and excitation-dependent carrier equilibration.

However, the CWPL and TIPL disagree about which sample was the weakest emitter: the 2.4% Eu sample under CW excitation but the 20% sample for pulsed excitation. To understand the connection between emission strength and excitation conditions, the radiative decay of the samples was measured (Figure 4.2). TRPL spectra exhibited a biexponential decay, representing two distinguishable processes depopulating
the $^5D_0$ state in the Eu$^{3+}$ dopant. This TRPL decay is parameterized by the repeating biexponential relation shown in Equation (4.1), where the sum of the relative strengths ($A_s$ and $A_f$) is normalized to unity. The repeating exponential is required when either decay constant ($\tau_f$ or $\tau_s$) is longer than the $t_0 = 1$ ms pulse repetition rate of the laser. The parameters found from this fitting procedure are summarized in Table 4.1.

$$I_{PL} = \sum_{n=0}^{2} \left( A_s e^{-\frac{(t+nt_0)}{\tau_s}} + A_f e^{-\frac{(t+nt_0)}{\tau_f}} \right)$$

The biexponential decay observed in these highly doped films agrees with previously published results on lower doped films. There, the fast and slow components of the decay were analyzed at room temperature and at 86 K and were correlated to the TIPL signal[14]. In that study, it was observed that the individual time constants for the two components were unchanged at 86 K, but the relative strengths differed with the slow component becoming weaker. As the relative strength of the slow component decreased at low temperatures, so did the intensity of the TIPL signal, indicating the slow decay component was primarily responsible for the observed Eu$^{3+}$ emission. The faster decay component was not investigated further, but may be due to energy transfer to and from a defect level as has been reported for Eu:GaN[9, 113].
Figure 4.2. Normalized TRPL decay for varying Eu concentrations. These results show that the onset of quenching is observed for values of $x$ between 0.05 and 0.1, although the overall intensity is highest for $x = 0.1$.

Table 4.1. Summary of biexponential decay parameters for Eu:Ga$_2$O$_3$ thin films.

<table>
<thead>
<tr>
<th>Eu mole fraction $x$</th>
<th>$A_f$</th>
<th>$\tau_f$ (ms)</th>
<th>$A_s$</th>
<th>$\tau_s$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.024</td>
<td>0.402 (5)</td>
<td>0.160 (4)</td>
<td>0.598 (9)</td>
<td>0.930 (10)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.410 (10)</td>
<td>0.250 (10)</td>
<td>0.590 (20)</td>
<td>1.130 (30)</td>
</tr>
<tr>
<td>0.10</td>
<td>0.256 (4)</td>
<td>0.148 (4)</td>
<td>0.743 (6)</td>
<td>0.736 (4)</td>
</tr>
<tr>
<td>0.20</td>
<td>0.308 (6)</td>
<td>0.0316 (8)</td>
<td>0.692 (8)</td>
<td>0.0885 (4)</td>
</tr>
</tbody>
</table>

The decay constants of the 2.4% and 5% samples ($\tau_f \approx 0.2$ ms, $\tau_s \approx 1$ ms) agree with previous reports of lower concentration (0.2% and 0.4%) Eu-doped Ga$_2$O$_3$ thin films ($\tau_f \approx 0.2$ ms, $\tau_s \approx 1.4$ ms), indicating relaxation is still dominated by radiative decay from $^5D_0$ to the $^7F_j$ family of states. The rate constants begin speeding up for the 10% sample
because the increased Eu concentration introduces competing, non-radiative quenching mechanisms that sap excitation from the \( ^5D_0 \) state, suggesting that the optimal Eu mole fraction is \( 0.05 \leq x \leq 0.10 \). Both time constants accelerate sharply for the 20% Eu doped film (\( \tau < 90 \mu s \)), clearly indicating that the TIPL emission from the 20% sample is being quenched. The fact that this sample has a brighter CWPL spectrum than the 2.4% sample suggests that luminescence quenching is somewhat compensated during cw excitation by the photoexcited carrier distribution.

Although Eu ion or Eu\(_2\)O\(_3\) clustering has been observed at high concentrations in other hosts\([116-119]\), formation of Eu\(_2\)O\(_3\) clusters is not believed to be responsible for luminescence quenching observed here. Characteristic Eu\(^{3+}\) luminescence from bulk monoclinic Eu\(_2\)O\(_3\) has been reported\([120, 121]\) with emission features that do not agree with the spectra presented.

Rather, the accelerated decay observed for the 20% sample is attributed to the effects of lossy, non-radiative energy transfer among nearby Eu ions or to defect centers. As the concentration of Eu ions is increased, the average ion-ion distance decreases, subsequently increasing the likelihood of parasitic energy transfer. Energy may eventually migrate from the initial excited Eu ion to a quenching center, representing a net energy loss mechanism\([1, 122]\). Similar energy transfer mechanisms have been observed in Eu:GaN\([113]\) where site-selective spectroscopy revealed that one of the sites luminesced only under CW and not pulsed excitation. There, equilibrium conditions established under CWPL enabled the Eu site to be excited via energy migration. That energy migration does not substantially affect the observed radiative decay until
relatively large Eu concentrations are obtained in the film can be attributed in part to the long minimum cation-cation distance (3.05 angstroms) in monoclinic Ga$_2$O$_3$. The equilibrium conditions established under CWPL enabled the Eu site to be excited via a similar energy migration mechanism. However, given the experimental data presented here, it cannot be determined whether luminescence is quenched due to lossy ion-ion energy transfer or if energy is transferred to non-radiative defect centers. Both mechanisms may become dominant with increasing Eu fraction given the reduced ion-ion distance or potentially increased defect density.

4.2 Structural Characterization

To correlate these optical effects with structural changes, X-ray diffraction data was acquired using a Rigaku D/Max III diffractometer with Cu K$_\alpha$ radiation in the $\theta$-2$\theta$ configuration. XRD results, shown in Figure 4.3, indicate the undoped Ga$_2$O$_3$ films are indeed monoclinic and polycrystalline, as grown. The monoclinic phase is identified by comparing measured diffraction data with known diffraction peaks listed in the International Center for Diffraction Data (ICDD) catalog. Films were observed to be polycrystalline: the numerous diffraction peaks correspond to multiple crystal orientations. The undoped film produces diffraction peaks corresponding to the (-102), (004), (-104) and (-113) planes as shown in Figure 3 with the labels A, C, D and E, respectively. The broad feature, labeled B, is an instrument artifact observed with all Ga$_2$O$_3$ films in this study, as well as with a Si calibration standard. Also, diffraction from
the (0006) plane of the sapphire substrate is observed near 42° and serves to monitor the calibration of the diffractometer between subsequent scans.

![X-ray diffraction spectra](image)

**Figure 4.3.** X-ray diffraction spectra for Ga$_2$O$_3$ and (Eu$_x$Ga$_{1-x}$)$_2$O$_3$ thin films with increasing Eu mole fraction $x$. The Ga$_2$O$_3$ film is polycrystalline and demonstrates characteristic monoclinic diffraction peaks. The peaks labeled A, C, D and E have been assigned to the (-102), (004), (-104) and (-113) planes in monoclinic Ga$_2$O$_3$, while the B peak is an instrument artifact.

The crystalline properties of the films evolve as the europium fraction increases. With 2.4% europium fraction the diffraction peaks from the (004) and the (-104) planes become much weaker, while the (-113) peak is more intense and appears to have a small shift towards a larger plane spacing. This shift indicates strain in the film due to the significant difference in ionic radii between europium and gallium, an additional
indicator that Eu$^{3+}$ is substitutionally incorporated into the host lattice. With further increases in europium fraction, a diffraction peak at 29.25° (two-theta) is observed and is assigned to the (004) plane in Ga$_2$O$_3$.

### 4.3 Refractive Index

Optical transmission data for Eu:Ga$_2$O$_3$ thin films were analyzed using the method outlined by Swanepoel[123] to determine the refractive index, thickness and optical absorption coefficient. Using the MATLAB scripts included in section 13, envelope functions were generated from optical transmission spectra only, as shown in Figure 4.4 for a 2.4 mole percent Eu-doped film. From these envelope functions, the refractive index and absorbance were independently determined as functions of wavelength. The transmission envelopes were formed by interpolating up to the local extremum value with the second longest wavelength. In this way, no portion of the envelope functions is extrapolated outside of known extrema values.

Refractive index data extracted from the transmission spectrum is plotted in Figure 4.5 along with values extrapolated according to Cauchy and Sellmeier models given in Table 4.2. Both models are in good agreement and adequately describe the calculated refractive index values over the measured range. The Sellmeier and Cauchy models begin to diverge substantially in the UV region, beyond approximately 300 nm. Comparison of optical parameters for different materials show a similar deviation in the UV spectral region, where the Sellmeier model predicts a somewhat higher refractive index than the Cauchy model. The fit coefficients for a 10 mole percent doped film are
given in Table 4.2 with a 95% confidence interval. R-squared values are included as indicators of quality of fit.

Figure 4.4. Transmission spectrum with maximum and minimum transmission envelopes. Open symbols denote local maxima and minima values.

Table 4.2. Cauchy and Sellmeier model coefficients for a 10 mole percent Eu:Ga$_2$O$_3$ thin film.

<table>
<thead>
<tr>
<th></th>
<th>Cauchy</th>
<th>Sellmeier</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$1.858 \pm 0.001$</td>
<td>$B_1$ $2.464 \pm 0.001$</td>
</tr>
<tr>
<td>$B \times 10^{-2}$</td>
<td>$1.062 \pm 0.005$</td>
<td>$C_1 \times 10^{-2}$ $1.421 \pm 0.007$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9992</td>
<td>$R^2$ $0.9982$</td>
</tr>
</tbody>
</table>
Figure 4.5. Comparison of the Cauchy and Sellmeier models for refractive index. The calculated index values from a 10% Eu:Ga$_2$O$_3$ thin film are shown with open circles. Intermediate data points are omitted for visual clarity. For comparison, the refractive index as measured by prism coupling has been included at 633 nm. The bandgap is indicated on the figure by the vertical dotted line.

Refractive index values for the remaining Eu:Ga$_2$O$_3$ thin films were fit using the Cauchy model. The coefficients are listed in Table 4.3 with a 95% confidence interval and R-squared values. The refractive index of undoped Ga$_2$O$_3$ at 633 nm has been measured at 1.931 by the prism-coupling method. This method was used to verify the experimental results of Swanepoel’s analytical method. In Table 4.3, the measured index values ($n_p$) are compared with calculated values from Swanepoel’s method ($n_c$) and agree to better than 1%, which indicates the success of both the method as well as the MATLAB implementation used to obtain these results.
Table 4.3. Cauchy fit coefficients for different Eu mole fractions.

<table>
<thead>
<tr>
<th>Eu fraction</th>
<th>A</th>
<th>B (x10⁻²)</th>
<th>n_p</th>
<th>n_c</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 %</td>
<td>1.884 ± &lt;0.001</td>
<td>1.240 ± 0.005</td>
<td>-</td>
<td>1.915 ± .001</td>
<td>0.9990</td>
</tr>
<tr>
<td>5 %</td>
<td>1.851 ± 0.001</td>
<td>1.363 ± 0.021</td>
<td>1.892</td>
<td>1.885 ± .002</td>
<td>0.9831</td>
</tr>
<tr>
<td>10 %</td>
<td>1.858 ± &lt;0.001</td>
<td>1.062 ± 0.004</td>
<td>1.902</td>
<td>1.885 ± .001</td>
<td>0.9992</td>
</tr>
<tr>
<td>20 %</td>
<td>1.890 ± &lt;0.001</td>
<td>1.422 ± 0.007</td>
<td>1.930</td>
<td>1.925 ± .001</td>
<td>0.9986</td>
</tr>
</tbody>
</table>

Figure 4.6. Graphical determination of thickness using optical transmission data for a Eu:Ga₂O₃ thin film.

The thickness was determined according the method outlined in section 11.2.3, with the results shown in Figure 4.6 for a 5 mole percent doped film. Extracted thickness values were comparable to those measured with a stylus profilometer as listed in Table
4.4. The intervals given for the extracted values represent a 95% confidence interval for the true thickness of the film, as determined by the linear least-squares fit used. Again, calculated and measured values are in good agreement. Swanepoel suggests that the accuracy of the determined thickness is on the order of 1% or better, but the confidence interval shown here is noticeably larger than that. Non-uniformity in the thickness of the thin film sample could influence the results of the method, yielding an average thickness with a larger confidence interval. However, the obtained linear fit shown in Figure 4.6 is in support of the accuracy of these results.

<table>
<thead>
<tr>
<th>Eu Mole Fraction</th>
<th>Extracted Thickness (nm)</th>
<th>Measured Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 %</td>
<td>621 ± 14</td>
<td>610</td>
</tr>
<tr>
<td>5 %</td>
<td>753 ± 10</td>
<td>700</td>
</tr>
<tr>
<td>10 %</td>
<td>622 ± 15</td>
<td>660</td>
</tr>
<tr>
<td>20 %</td>
<td>583 ± 10</td>
<td>600</td>
</tr>
</tbody>
</table>

Prism coupling offers simultaneous determination of the refractive index and thickness of a thin film on a substrate, provided the film layer is thick enough to guide multiple modes. In this section, the results of prism coupling experiments were obtained with films thicker than those analyzed by Swanepoel’s method.

Once the film thickness is calculated, the absorption and extinction coefficients can be calculated from the film absorbance which was determined independently of other film properties. Subsequently, the bandgap of each film was determined from the respective absorption data. The bandgap of the Eu:Ga$_2$O$_3$ films seems to trend with
structural data where there is substantial change in observed properties between the 2.4% film and the 5% film. From 5 to 20% the change in bandgap, like the change in structure, seems more gradual.

![Figure 4.7. Absorption coefficient, \( \alpha \), (left) and its square, \( \alpha^2 \), (right) plotted as functions of wavelength for a 5 mole percent Eu-doped Ga_2O_3. The latter plot is used to determine the bandgap of the film by extrapolating the linear portion of the curve to the energy axis.](image)

Table 4.5. Bandgap of Eu:Ga_2O_3 thin films determined from optical absorption measurements.

<table>
<thead>
<tr>
<th>Eu Fraction</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>4.94</td>
</tr>
<tr>
<td>5</td>
<td>4.83</td>
</tr>
<tr>
<td>10</td>
<td>4.90</td>
</tr>
<tr>
<td>20</td>
<td>5.00</td>
</tr>
</tbody>
</table>

Lastly, to verify the self-consistency of Swanepoel’s method, a transmission spectrum was simulated using the obtained results for a 5 mole percent Eu:Ga_2O_3 thin film and then compared to an experimentally obtained transmission spectrum. Initial simulations were approximately correct, although the positions of the fringe maxima and
minima deviated from the measured spectrum. This was corrected by adjusting the film thickness used in the simulation until a satisfactory fit was obtained. The initial estimate of the thickness was $753 \pm 10$ nm and the value resulting in the improved fit shown in Figure 4.8 was 735 nm. The latter value is closer to the measured thickness of the film (700 nm) and is within an acceptable margin error of the profilometer tool. The refractive index of the film likely also requires adjustment as both the film index and thickness influence the positions of interference fringes. The index values determined by Swanepoel’s method deviate little from experimentally obtained index values, however, and may be close to the true values already.

Figure 4.8. Comparison of simulated (dotted line) and measured (solid line) transmission spectra. The figure at right presents greater detail of the transparent region where interference fringes are observed, allowing better comparison of the quality of simulation.
5 Properties of Europium Doped Gadolinium Oxide

The objective of this Eu:Gd$_2$O$_3$ study is to compare two different crystalline phases of Gd$_2$O$_3$ – monoclinic and cubic – in order to determine if one is better suited to optical or optoelectronic devices. Either of the two phases could be obtained by modifying the oxygen pressure during pulsed laser deposition with most conditions favoring monoclinic phase formation while cubic films were obtained at 50 mTorr oxygen pressure. The luminescence from the two phases differed both in positions of emission peaks and in the radiative decay properties of those peaks. Crystal-field splittings calculated by our collaborator, Dr. John Gruber, are in good agreement with the observed Eu$^{3+}$ emission from the cubic phase which bares a striking similarity to the crystal-field splittings determined for cubic Eu:Y$_2$O$_3$[124]. Other studies have indicated an ability to modify the host structure by co-doping, but here we report the ability to choose the crystal phase of Eu:Gd$_2$O$_3$ thin films by control of deposition conditions only. Specifically, a transition from monoclinic Gd$_2$O$_3$ to the cubic phase has been observed by adjusting the oxygen pressure during pulsed laser deposition. The structural properties have been analyzed by transmission electron microscopy (TEM) and x-ray diffraction (XRD). The different phases observed by TEM and XRD are accompanied by changes in photoluminescence emission from the $^5$D$_0$ to $^7$F$_J$ family of transitions associated with the Eu$^{3+}$ ion.

Eu:Gd$_2$O$_3$ thin films were deposed onto double side polished c-axis sapphire substrates using a KrF excimer laser (248 nm) with 250 mJ energy per pulse. Films were deposited for 36,000 pulses under low (5 mTorr) and high (50 mTorr) oxygen pressures.
from a 1.6 mole percent Eu:Gd$_2$O$_3$ target. The sapphire substrates were heated to 600 °C during deposition and rotated to improve film uniformity. The PLD target was rastered and rotated to avoid pitting the target surface. The resultant films were approximately 400 nm thick.

The target was prepared in-house by mixing Eu$_2$O$_3$ and Gd$_2$O$_3$ powders (Alfa Aesar) in the desired molar ratio – here 1.6 mole percent Eu$_2$O$_3$. The mixture was suspended in ethanol and shaken for several hours as the ethanol dried to ensure homogeneity. The dried mixture was subsequently ground with a mortar and pestle, and cold-pressed into a 1” diameter disk at 5000 psi using a hydraulic press. The pressed disk is then sintered in air using an alumina crucible at 1600 °C for 6 hours in a tube furnace.

5.1 Structure
High-resolution images and electron diffraction patterns were obtained using a Hitachi HF2000 transmission electron microscope with an electron energy of 200 keV. To obtain samples for TEM analysis, 50 nm thick films of Eu:Gd$_2$O$_3$ were directly deposited by PLD onto 50 nm thick amorphous SiN$_x$ membranes supported by a 3 mm diameter silicon ring. Owing to their amorphous nature, these TEM substrates (DuraSiN from Protochips, Inc.) contribute no observable diffraction or contrast during imaging or analysis, facilitating sample preparation. Additionally, the substrates are physically robust and withstood high temperature deposition of Eu:Gd$_2$O$_3$ films.
$\theta$-20 phase analysis measurements were performed by x-ray diffractometry using a Philip’s X’pert PRO MRD diffractometer with a Cu K$_{al}$ source. These scans were performed with 0.05° step size with an integration time of one second per reading.

![TEM images with diffraction patterns of 5 (left) and 50 mTorr (right) films. Images show polycrystalline structure with fine grain size. Inset SAED patterns confirm polycrystalline structure and are used to calculate the interplanar distances.](image)

TEM images and selected area electron diffraction (SAED) patterns are presented in Figure 5.1 for both 5 and 50 mTorr deposited Eu:Gd$_2$O$_3$ films. The ring-like nature of the SAED patterns is evidence that both films have a small grain size, since patterns from single crystal samples have discrete spots, rather than rings. Inspection of the high-resolution TEM images reveals nanoscale crystalline grains, as evidenced by the observed lattice in some places, which agrees with the ring features of the SAED patterns.
A radial intensity profile was calculated from the diffraction pattern for the 5 and 50 mTorr films, as shown in Figure 5.2 and the observed peaks were compared to known interplanar distances reported in the International Center for Diffraction Data (ICDD) database. The $d$ values obtained by electron diffraction measurements are in satisfactory agreement with values listed in the ICDD database. Furthermore, assignments made using this data consistently indicate the 5 and 50 mTorr films are monoclinic and cubic phase, respectively. Due to the similar ionic radii of Eu$^{3+}$ and Gd$^{3+}$, it was assumed that the presence of substitutional europium in these films does not itself substantially alter the unit cell in either the cubic or monoclinic phase. The results of electron diffraction experiments indicate this assumption is appropriate.

Figure 5.2. Radial intensity profiles of the electron diffraction patterns for Gd$_2$O$_3$ thin films.
### Table 5.1. Comparison of measured and known interplanar distances for monoclinic and cubic Gd₂O₃.

<table>
<thead>
<tr>
<th>Plane</th>
<th>5 mTorr</th>
<th></th>
<th></th>
<th>50 mTorr</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d₁</td>
<td>d₂</td>
<td>Plane</td>
<td></td>
<td>d₁</td>
<td>d₂</td>
</tr>
<tr>
<td>(111)</td>
<td>3.153</td>
<td>3.155</td>
<td>(111)</td>
<td></td>
<td>3.115</td>
<td>3.122</td>
</tr>
<tr>
<td>(003)</td>
<td>2.858</td>
<td>2.868</td>
<td>(003)</td>
<td></td>
<td>1.960</td>
<td>1.974</td>
</tr>
<tr>
<td>(-511)</td>
<td>2.189</td>
<td>2.195</td>
<td>(-511)</td>
<td></td>
<td>1.679</td>
<td>1.669</td>
</tr>
<tr>
<td>(-313)</td>
<td>2.127</td>
<td>2.131</td>
<td>(-313)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(313)</td>
<td>1.922</td>
<td>1.915</td>
<td>(313)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(020)</td>
<td>1.802</td>
<td>1.784</td>
<td>(020)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(404)</td>
<td>1.704</td>
<td>1.700</td>
<td>(404)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(421)</td>
<td>1.551</td>
<td>1.539</td>
<td>(421)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Known interplanar distances from ICDD database entries, in angstroms.
b Planes for the 5 and 50 mTorr deposited films were assigned based on the ICDD database entries for monoclinic and cubic phase material, respectively.

XRD results are in good agreement with SAED and TEM data. The observed multiple peaks in each XRD pattern, presented in Figure 2, are indicative of a polycrystalline sample. The diffraction peaks from the 5 mTorr sample could be assigned to known monoclinic Gd₂O₃ planes, albeit with some contribution from the cubic phase. The most intense diffraction was observed for the monoclinic (003), (-405) and (-514) planes with non-trivial contributions from the monoclinic (111) and (600) planes. The diffraction peaks from the 50 mTorr sample were assigned to known cubic planes, though some monoclinic domains were observed as well. This may be indicative of an incomplete phase transformation from the monoclinic phase to the cubic phase or vice versa. The major cubic plane observed was the (400) with some diffraction observed from the (222) and (411) cubic planes. No hexagonal phases were observed for any samples grown, as expected; this phase is less common than either cubic or monoclinic phase but may form under high pressures or when deposited on (0001) GaN[125, 126].
Both x-ray and electron diffraction results indicate the 5 and 50 mTorr Eu:Gd₂O₃ films were monoclinic and cubic, respectively, but do not show identical diffracting planes. This is because the two techniques differ substantially in how the samples are probed. In addition, the samples analyzed by TEM may have somewhat differing structure than those analyzed by XRD. The former are much thinner films (50 nm) and were deposited on amorphous SiNx support membranes while the latter (400 nm) were deposited on sapphire substrates. The different substrate may encourage material growth with different phase and orientation. This precise scenario was observed for the case of Gd₂O₃ on GaN where the hexagonal surface of GaN encouraged growth of the hexagonal
phase of Gd$_2$O$_3$ for thin layers. However, that both analytical techniques independently indicate the same phase for the respective films confirms the influence of deposition atmosphere on Gd$_2$O$_3$ film growth.

5.2 Photoluminescence

To observe the effect of different crystalline phase on the emission from the Eu$^{3+}$ dopants, time-integrated and time-resolved photoluminescence (TIPL and TRPL) spectra were obtained. TRPL data was obtained for the 550-650 nm (1.90-2.25 eV) region encompassing the $^5D_0 \rightarrow {}^7F_0$, $^7F_1$, $^7F_2$, and $^7F_3$ transitions while TIPL spectra were obtained over the a larger spectral region. TIPL and TRPL spectra were obtained by exciting samples, mounted in a liquid nitrogen-cooled cryostat at 90 K, with a 1 kHz, frequency-tripled (266 nm, 4.66 eV), regeneratively amplified Ti:sapphire laser with ~10 µJ pulses of ~100 fs duration focused to a 1 mm diameter spot size. The photoluminescence was imaged into a 0.75 m grating spectrometer with a resolution of 0.5 nm (1.5 meV) measured by a PMT located at the exit slit to the spectrometer. Standard methods of lock-in detection were used for TIPL, while TRPL traces were collected by a digital oscilloscope with < 10 µs temporal resolution limited by the instrument response. Each TRPL trace was taken for a 3 meV energy window centered on the measured TIPL features.

It was observed that both the 5 and 50 mTorr samples had the same narrow features typical of other Eu-doped wide bandgap semiconductors as shown in Figure 5.4[113, 127]. However the locations, the strengths, and the amount of resolvable fine
structure of the peaks differed. For example, the region around the strongest transition,
$^5D_0 \rightarrow ^7F_2$ between 605-635 nm (1.95-2.05 eV), plotted in Figure 5.4, shows how
dramatically different the spectra are. Notice that the spectra are not simply shifted, as
might occur from differing strain, but are fundamentally different: the location of the
peaks and the splittings between the numerous components cannot be mapped from one
spectrum to the other.

Figure 5.4. Luminescence spectra of 5 and 50 mTorr Eu:Gd$_2$O$_3$ thin films. Spectra at right show
detail from 605 to 635 nm in spectra at left.

These differences arise from the different local environments encountered by the
Eu$^{3+}$ ions for the predominantly monoclinic (5 mT) and cubic (50 mT) phases favored
under the different growth conditions. The different crystal environments manifest
themselves in the spectra through patterns of Stark splitting and shifts due to Eu$^{3+}$ ions
occupying different sites in the crystal lattice. The peak locations and intensities of the $^5D_0 \rightarrow ^7F_2$ multiplet are clearly not the same in the two samples. Additionally, the 5 mT sample had a higher intensity luminescence. Both spectra were compared with the analysis of Daly, Schmitt, and Gruber for monoclinic Eu:Gd$_2$O$_3$[45]. That analysis, which found the Eu$^{3+}$ dopants located at three sites in the monoclinic lattice, reproduced the spectral features observed in the 5 mT (monoclinic) sample to within 10 meV as shown in Figure 5.5. However, almost none of the features from the 50 mT sample could be correlated with any of the features from the analysis of Daly et al., indicating that the optical spectra do not arise from Eu$^{3+}$ dopants in a monoclinic host.

The local host environment of the Eu$^{3+}$ dopant also affects the radiative lifetime of the excited states, in this case the $^5D_0$ state. TRPL spectra were obtained centered about a wavelength that roughly coincided with a photoluminescence peak. The data (not shown) were fit to a bi-exponential model where $|A_f| + |A_s| = 1$, as in equation (4.1). The fit parameters, summarized in Table 5.2, indicate how the properties of the decay differ between samples. The decay of two representative spectral features from the monoclinic sample could be characterized by a single decay constant of 0.4 ms, typical for radiative decay of rare earth dopants. Representative features of the cubic sample exhibit biexponential decay, where slow radiative decay (> 600 µsec) competes with a substantial contribution from a faster component (20-70 µsec) likely associated with a parasitic non-radiative decay channel. It is interesting to compare the decay of the overlapping features at 1.987 eV. The differing decay characteristics suggest that they do not arise from constituent crystallites of the same phase in the different samples; rather,
the TRPL data suggest they represent an accidental coincidence of emission features from the respective monoclinic and cubic phases.

Figure 5.5. Photoluminescence spectra of Gd₂O₃ grown under 5 mTorr oxygen pressure. The spectral region corresponds to the $^5D_0 \rightarrow ^7F_2$ transition, and the multiplicity of lines results from Stark splitting induced by the crystal field and emission from Eu$^{3+}$ ions in different sites in the unit cell. Vertical grey lines denote emission from three monoclinic crystal sites assigned in [45]: site A, solid; site B, dotted; site C, dashed.
Table 5.2. Parameters of (bi)exponential fit to time-resolved photoluminescence decays.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>5 mT O₂</th>
<th>50 mT O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>T (μs)</td>
</tr>
<tr>
<td>1.987</td>
<td>1</td>
<td>411(2)</td>
</tr>
<tr>
<td>2.008</td>
<td>1</td>
<td>414(5)</td>
</tr>
<tr>
<td>2.029</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

5.3 Calculated Emission from Cubic Phase

The PL spectra and radiative decay results from cubic Eu:Gd₂O₃ in section 5.2 are corroborated by new theoretical results by Dr. John Gruber. The calculated and measured emission peaks are shown in Figure 5.6 and given in Table 5.3. Using the calculated energy levels, emission peaks over the range of 605 to 635 nm, have been assigned to the ⁵D₀ to ⁷F₂ and the ⁵D₁ to ⁷F₄ transitions in trivalent europium. When compared to the measured emission peaks, the calculated values are in good agreement. This is in strong support of earlier conclusions that the cubic phase of Gd₂O₃ could be obtained by careful control of the oxygen pressure during pulsed laser deposition.

Two unique cation sites exist in cubic Gd₂O₃ having C₃i and C₂ symmetry. The inversion symmetry of the C₃i site limits observable Eu³⁺ emission to magnetic dipole transitions with ΔJ = 0 or 1. Thus, the majority of observed emission lines are owed to Eu³⁺ ions on sites with C₂ symmetry where the electric dipole transitions are allowed between all levels. Two magnetic dipole transitions from Eu³⁺ ions on C₃i sites are tentatively identified: ⁵D₀ to ⁷F₀ (574 nm) and ⁵D₁ to ⁷F₀ (525.9 nm). Due to these
restrictions, the analysis presented here is limited to luminescence from Eu\(^{3+}\) ions on
cation sites with the C\(_2\) symmetry.

The assumption that the incorporation of Eu ions into the Gd\(_2\)O\(_3\) host does not
substantially deform the host structure is validated by the absence of several emission
lines from Eu ions on this C\(_{3i}\) site. In contrast, studies on Eu:GaN have reported
symmetry-forbidden emission from Eu-occupied sites, indicative of structural
deformation owing to the incorporation of the Eu dopant[113].

All Stark-split levels of the \(^7F_J\) multiplet manifold, for values of \(J\) from 0 to 4,
have been identified by analyzing PL emission from the \(^5D_0\) level at 17219 cm\(^{-1}\). Broad
emission peaks that could not be resolved were deconvoluted to obtain data presented
here. Two of the three \(^5D_1\) energy levels could be identified at 18945 and 18992 cm\(^{-1}\)
from experimental data while the third level could only be identified from unresolved
data at 18937 cm\(^{-1}\). Only the two well resolved \(^5D_1\) levels were used in the analysis of
the \(^7F_J\) levels. Of the five possible \(^5D_2\) energy levels, two well resolved peaks were used
to analyze the \(^7F_J\) levels. Analyses of the \(^7F_J\) levels based on the aforementioned \(^5D_0\), \(^5D_1\)
and \(^5D_2\) levels are in good agreement with each other.
Figure 5.6. Photoluminescence spectrum from 50 mTorr Eu:Gd$_2$O$_3$ with calculated emission peaks indicated by solid and dotted lines. The solid and dotted lines represent radiative transitions from the $^5D_0$ to $^7F_2$ and $^5D_1$ to $^7F_4$ energy levels, respectively.

The radiative decay measurements obtained at 1.987 eV in Table 5.2 resulted in a single exponential and biexponential decay for the monoclinic and cubic phases, respectively with differing time constants. This change in decay kinematics is also supported by the calculated emission spectrum, which assigns a cubic phase emission
peak that coincides with a monoclinic phase emission peak from the other film within the spectral bandwidth (3 meV) of TRPL measurements.

Table 5.3. Measured and calculated Eu\(^{3+}\) emission lines in cubic Eu:Gd\(_2\)O\(_3\) films.

<table>
<thead>
<tr>
<th>(2S+1L_J^a)</th>
<th>(5D_0 (17219 \text{ cm}^{-1}))</th>
<th>(5D_1 (18945 \text{ cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_m (\text{nm}))</td>
<td>(\lambda_c (\text{nm}))</td>
</tr>
<tr>
<td>(7F_0)</td>
<td>580.6</td>
<td>580.7</td>
</tr>
<tr>
<td>(7F_1)</td>
<td>587.8</td>
<td>587.5</td>
</tr>
<tr>
<td></td>
<td>592.6</td>
<td>592.8</td>
</tr>
<tr>
<td></td>
<td>599.4</td>
<td>600.1</td>
</tr>
<tr>
<td>(7F_2)</td>
<td>611.0</td>
<td>611.8</td>
</tr>
<tr>
<td></td>
<td>613.0</td>
<td>613.1</td>
</tr>
<tr>
<td></td>
<td>613.9</td>
<td>614.0</td>
</tr>
<tr>
<td></td>
<td>625.0</td>
<td>625.3</td>
</tr>
<tr>
<td>(7F_3)</td>
<td>629.8</td>
<td>631.2</td>
</tr>
<tr>
<td></td>
<td>650.6</td>
<td>650.9</td>
</tr>
<tr>
<td></td>
<td>651.5</td>
<td>651.5</td>
</tr>
<tr>
<td></td>
<td>652.6</td>
<td>653.3</td>
</tr>
<tr>
<td></td>
<td>655.0</td>
<td>654.8</td>
</tr>
<tr>
<td></td>
<td>656.9</td>
<td>657.9</td>
</tr>
<tr>
<td></td>
<td>669.0</td>
<td>662.7</td>
</tr>
<tr>
<td>(7F_4)</td>
<td>662.1</td>
<td>663.7</td>
</tr>
<tr>
<td></td>
<td>686.7</td>
<td>687.3</td>
</tr>
<tr>
<td></td>
<td>693.3</td>
<td>693.4</td>
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<td>695.6</td>
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<td></td>
<td>706.3</td>
<td>706.6</td>
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<td></td>
<td>707.9</td>
<td>709.1</td>
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<td>710.8</td>
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<td>712.6</td>
</tr>
<tr>
<td></td>
<td>712.6</td>
<td>713.2</td>
</tr>
</tbody>
</table>

\(^a\)Terminal manifold for listed transition originating from \(5D_0\) and \(5D_1\) manifolds.

\(^b\)Photoluminescence feature not observed.

The calculated level splittings are remarkably similar to that of cubic Eu:Y\(_2\)O\(_3\)[124] which has similar unit cell and symmetry to that of cubic Gd\(_2\)O\(_3\). The unit
cell parameter of cubic Gd₂O₃ is 10.81 angstroms while that of cubic Y₂O₃ is 10.60 angstroms[128]. Calculated levels and splittings for cubic films are included in Appendix D: Eu³⁺ Level Splittings in Cubic Gd₂O₃. Splittings calculated for cubic Eu:Y₂O₃ are also included for comparison.
6 Optical Properties and Doping of Amorphous IGZO

Amorphous europium doped IGZO thin films were characterized by cathodoluminescence and it was shown that the luminescence depends strongly on oxygen pressure during deposition. For high oxygen pressure conditions, characteristic Eu$^{3+}$ emission is observed and increases in intensity for increasing pressure. In addition, at low oxygen pressures emission from Eu$^{2+}$ was observed in the UV spectrum. Optical properties of Eu:IGZO and undoped IGZO films are presented and luminescence results are correlated to defect state densities in the films.

6.1 Undoped IGZO Films

Pulsed laser deposited undoped a-IGZO thin films have a wide bandgap and high electron mobility (~10 cm$^2$/V-s), which makes a-IGZO a viable material for novel large-area electronics applications. IGZO thin films were deposited at 0.5, 5, 10, 20, 40 and 80 mTorr oxygen pressure for 36,000 pulses with ~150 mJ energy per pulse.

Optical transmission data shown in Figure 6.1 reveal optical transparency greater than 80% throughout the visible spectrum for films deposited in varying oxygen pressures. The optical absorption edge, near 345 nm for a 20 mTorr deposited film, is relatively sharp and is blue-shifted compared to that of ZnO thin films, indicating a broader bandgap. The dependence of near-IR transmission with oxygen pressure suggests large changes in free carrier concentration. For increasing oxygen pressure, optical absorption in the near-IR decreases, presumably due to reduced carrier density. The film deposited
at 0.5 mTorr is highly non-stoichiometric due to the absence of oxygen and demonstrates poor optical qualities compared to the other films. It is likely semi-metallic according to the substantial near-IR absorption, again caused by free carriers.

![Optical transmission spectrum](image)

**Figure 6.1. Optical transmission spectrum for IGZO films deposited in 0.5, 5, 10, 20, 40 and 80 mTorr oxygen pressures**

The dependence of carrier density on oxygen pressure is confirmed by four-point probe and Hall effect measurements as shown in Figure 6.2. The conductivity and carrier concentration can both be controlled over several orders of magnitude via changes in the oxygen pressure during deposition. Hall measurements confirmed n-type conductivity for semiconducting films, in agreement with previous reports in the literature[69, 70].

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Films deposited at higher than 20 mTorr pressure could not be characterized by Hall effect due to their low conductivity. The carrier mobility was observed to decrease from 16 to about 12 cm$^2$/V-s upon increasing the oxygen pressure form 5 to 20 mTorr. The n-type conductivity in IGZO thin films has been attributed to the presence of point defects, such as either metal interstitials or oxygen vacancies. The dependence on oxygen pressure observed here corroborates this theory as the addition of more oxygen during deposition may somewhat modify the stoichiometry within the film.

![Figure 6.2. Effects of deposition oxygen pressure on the electronic properties of IGZO thin films. The conductivity (left) and carrier concentration (right) decrease exponentially with oxygen pressure. The carrier mobility (right) decreases somewhat with increasing pressure.](image)

Hall effect measurements on amorphous semiconductors often results in a sign reversal of the Hall coefficient, which would indicate the incorrect carrier type. This is often called the anomalous Hall effect and occurs in amorphous semiconductors where conduction is dominated by a variable-range hopping mechanism. That the anomalous

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Hall effect was not observed in these experiments would indicate that VRH is not a
dominant conduction mechanism in IGZO thin films, giving way to more efficient band
conduction.

TFTs were fabricated using undoped a-IGZO thin films as the channel layer with
an ITO source and drain contact. The results presented below indicate the high quality of
device that can be fabricated from this material system.

Figure 6.3. Optical transmission spectra for the (A) glass substrates and (B) TFT stack with IGZO
and ITO layers. Pictures of IGZO TFTs with (C) metal and (D) ITO source and drain contacts. The
complete device stack is highly transparent through the visible region

Optical transmission spectra of the device stack indicate high transparency is
maintained throughout the visible spectrum. The glass/ITO/ATO substrates are highly
transparent throughout the visible and into the UV spectrum as indicated by Figure 6.3.

1 Reprinted with permission from A. Suresh, P. Wellenius, A. Dhawan and J. Muth, "Room temperature
pulsed laser deposited indium gallium zinc oxide channel based transparent thin film transistors," Appl.
UV transmission is reduced due to the room-temperature deposition of the 200 nm thick ITO contact layers. Higher temperature deposition would result in improved optical properties of the ITO layer, but a room-temperature process was desired.

Figure 6.4. Characteristic curves for n-type TFTs. $I_{DS-VD}$ (left) and $I_{DS-VGS}$ curves (right) indicate high-quality devices with low gate-leakage current. At right, the absolute value of the gate leakage is plotted and denoted by $I_G$ on the figure. The two $I_{DS-VGS}$ curves are for 50 (solid circles) and 75 nm (open circles) thick channel layers where the 50 nm channel results in enhancement-mode devices and the 75 nm channel in depletion-mode devices.

The TFT characteristics shown in Figure 6.4 indicate high-quality devices with near-ideal behavior. The $I_{DS-VDS}$ family of curves demonstrate that devices, with a 50 nm thick channel deposited in 25 mTorr oxygen pressure, are enhancement-mode, n-type TFTs that reach hard saturation. The transfer curves at right show a dependence on

---

channel layer thickness where a 50 nm channel results in enhancement mode devices while a 75 nm channel results in depletion mode devices. For the 50 nm channel, the entire layer is depleted of free carriers at zero gate bias, resulting in an insulating off-state. For the thicker channel, a large number of free carriers remain in the channel, allowing for off-state conduction. For the 50 nm channel TFT, a on/off drain current ratio of $5 \times 10^7$ was observed, due in part to the low off-state drain leakage of about 10 pA. The subthreshold swing of the device is given by the maximum slope of the transfer curve and was calculated at 200 mV/decade. The saturation mobility of the device was measured at 11 cm$^2$/V-s which agrees well with the measured Hall mobility for thin films.

The effect of deposition conditions and gate dielectric were also investigated with the results shown in Figure 6.5. The transfer curves for a (a) 25 mTorr and (b) 40 mTorr deposited IGZO channel layer are shown along with the reverse-sweep for two dielectrics: ATO and SiN$_x$. Since the conductive channel in these devices forms near the channel/dielectric interface, the dielectric must be chosen so as to optimize the quality of this interface. Interfacial trapping sites can be deleterious to field-effect mobility, threshold voltage and subthreshold swing and should be minimized. By probing the transfer curves in both the forward and reverse directions one can observe the presence of interface states that can trap charge, thus shifting device threshold. In Figure 6.5(a), the forward and reverse sweeps of the TFT using an ATO dielectric overlap very well, indicating a low number of interface states. However, in (b) the SiN$_x$ sweeps do not overlap near threshold, suggesting a larger number of interface states.
Figure 6.5. $I_{DS}$-$V_{GS}$ transfer curves for devices fabricated with two dielectrics and channel layer deposition conditions. In (a), a 25 mTorr IGZO channel was deposited on ATO and SiN, with a reverse-direction sweep on the ATO dielectric showing limited hysteresis. In (b), a 40 mTorr IGZO channel was deposited on the same dielectric layers and indicates a larger hysteresis for the SiN, dielectric. Note the effect of the deposition conditions on device threshold between (a) and (b)\(^1\).

The 25 mTorr channel devices in Figure 6.5(a) show a lower threshold voltage than the 40 mTorr channel devices in (b). This difference could be the result of interface trapped carriers. Since the 40 mTorr channel has fewer free carriers than the 25 mTorr channel, it is possible that a greater gate voltage is required to generate more free carriers before these traps are filled and the conductive channel can be formed. Since the subthreshold swing remains largely unchanged between the two channel layers, the number of interfacial trap states is likely similar. Another observation of Figure 6.5 is that the off-state and saturation drain current for the 40 mTorr channel are both lower than the 25 mTorr channel. This can be attributed to the reduction in conductivity and mobility of the 40 mTorr film shown earlier.

6.2 Europium Doped IGZO Films

6.2.1 Electronic Properties

The measured conductivity of Eu:IGZO films is higher than what was measured for the undoped films. This can be the result of unintentional defect formation due to Eu doping or could also be attributed to the substitution of Zn cations by Eu. The difference in valence between Zn$^{2+}$ and Eu$^{3+}$ would result in increased background n-type carrier concentration.

A TFT device was fabricated using a 40 mTorr Eu:IGZO channel to determine the mobility of the channel layer. Here, the measured mobility was on the order of 3.5 cm$^2$/V-s, compared to 10 cm$^2$/V-s for the undoped films. This decrease in mobility can be ascribed to the presence of the large Eu$^{3+}$ ions which can cause increased impurity scattering in the channel layer.

6.2.2 Temperature Dependent Optical Absorption

Europium-doped IGZO thin films are transparent throughout the visible spectrum, as shown in Figure 6.6. The transparency and absorption edge remain comparable to the undoped films though, at this low level of doping, it is not expected to observe substantial changes in the bandgap or the overall absorptive properties of the films.
Figure 6.6. Optical transmission spectra of Eu:IGZO thin films deposited at 10, 20, 40 and 80 mTorr. All films were approximately 80% transparent in the visible region. Increasing oxygen pressure appears to cause a blue-shift in the absorption edge, similar to results for undoped IGZO films. The direction of the arrow indicates increasing oxygen pressure.

The optical gap of amorphous thin films has typically been characterized using Tauc’s method described by Equation (11.4). The absorption coefficient $\alpha$ and the Tauc curve are both plotted against energy in Figure 6.7 for a 100 mTorr Eu:IGZO film. The linear portion of the Tauc curve is extrapolated to the energy axis where the intercept gives the width of the bandgap which is 3.14 eV in this case. Absorption below the bandgap can be observed which is often attributed to the existence of Urbach tail states. By plotting the absorption coefficient on a semilog scale, as in Figure 6.7, one can more easily observe the effects of fundamental and tail state absorption. Here, a variant of the Tauc curve ($\alpha = A*(E-E_g)^2/E$) has been superimposed over the absorption data and the intersection of this curve with the energy axis again denotes the bandgap, which is in
good agreement with the value determined by linear extrapolation. Absorption due to an Urbach tail follows an exponential dependence on energy which, on a semilog plot, appears linear.

Figure 6.7. Tauc analysis of measured optical absorption coefficients. The absorption coefficient and corresponding Tauc curve (left) are plotted as functions of energy and the linear portion of the Tauc curve is extrapolated to determine the bandgap of a 100 mTorr Eu:IGZO film. A semilog plot of the absorption coefficient (right) serves to illustrate optical absorption due to tail states. Absorption data is decomposed into that due to fundamental absorption (Tauc curve) and tail states (Urbach tail).

Alternatives to Tauc’s expression have been derived separately by Cody[129] and Vorlcek[130], described by Equations (11.5) and (11.6), respectively. These methods are compared in Figure 6.8 near the absorption edge of an 80 mTorr deposited Eu:IGZO thin film. The major argument against Tauc’s method is a thickness dependence of the determined optical gap as the Tauc plot is linear only over a small range of values of the dependent variable, here \((\alpha E)^{1/2}\). As such, the thickness of the film may affect which portion of the absorption edge is extrapolated to determine the optical gap.
Figure 6.8. Comparison of Tauc, Cody and Vorlicek methods for determining the optical gap of amorphous semiconductors near the absorption edge of an 80 mTorr deposited Eu:IGZO thin film.

In Figure 6.8, normalized values of Tauc’s \((\alpha E)^{1/2}\), Cody’s \((\alpha/E)^{1/2}\) and Vorlicek’s \((\alpha E)^{1/3}\) methods are plotted against energy. The linear portion of each curve is extrapolated (indicated by the dotted lines) to the energy axis, where the intercept denotes the optical gap. The optical gaps determined by each method differ by as much as 250 meV, but there is some merit to the arguments of Cody and Vorlicek. Cody’s method results in a curve that is linear over about 40-50% of the absorption edge, compared to 25-30% for Tauc’s method, which could arguably yield a more accurate optical gap determination. Vorlicek’s method, in this instance, produces results comparable to Tauc’s method in terms of the range of linearity.

Despite the arguments of Cody and Vorlicek, Tauc’s method remains the most commonly used approach in the literature. Optical gaps of Eu:IGZO films were determined using Tauc’s method and measured as a function of temperature to better
understand the optical and electronic characteristics of IGZO based thin films. By placing the samples in a low-temperature cryostat, the temperature could be varied from room temperature (292 K) down to 77 K using liquid nitrogen.

![Absorption spectra for 20 and 100 mTorr Eu:IGZO films. Spectra were obtained at room temperature (dotted lines) and 80 K (solid lines). The substantial difference in sub-bandgap absorption between the two films is attributed to shallow defect states which are more prevalent in films deposited at lower oxygen pressures.](image)

Temperature-dependent absorption measurements revealed key differences between conductive and insulating Eu:IGZO films, as shown in Figure 6.9. Sub-bandgap absorption in the 100 mTorr deposited film was dominated by optical transitions within the tail states. This is evidenced by the linear shape of the absorption edge below the bandgap. In contrast, non-linear sub-bandgap absorption in the more conductive 20
mTorr deposited film suggests a substantial contribution from shallow defect states. In addition, this non-linear trend becomes more pronounced at low temperature, which suggests a carrier concentration dependence. Similar phenomena is not observed at low temperature in the more insulating 100 mTorr film, presumably due to a much lower defect state density.

Figure 6.10 shows the temperature dependence of the optical gap for four Eu:IGZO films, varying in oxygen pressure during deposition. The gap is observed to broaden with increasing oxygen pressure as well as with decreasing temperature. The dependence on oxygen pressure has been observed previously in Figure 6.1 and Figure
6.6 for both undoped and doped films, respectively. The dependence on temperature is expected as a result typical of semiconductor materials.

The bandgap dependence was successfully fit to both the Varshni and Fan models for all four Eu:IGZO thin films. Significant differences in the quality of fit are not observed in the range of experimentally limited temperatures. The two models tend to diverge near at very low and elevated temperatures as shown in Figure 6.10. At low temperatures, the Varshni model tends to a quadratic dependence on temperature, which may overestimate the bandgap dependence on temperature in this range compared to the Fan model. Over the same range, the Fan model predicts the bandgap is nearly independent of temperature and has been reported as a better fit in some instances[131, 132]. Temperatures well above room temperature are often required to obtain a good fit with the Varshni model and the lack of data in this temperature range results in widely varying parameter values, even for the similar material. As such, caution is required when presenting extracted parameters. With this in mind, the fit parameters for both models are given in Table 6.1.

In general, parameter values for both models are within expected ranges. The average phonon energy $\theta$ and the coupling constant $A$ tend to agree with data presented by refs. [131, 132]. In addition, it has been shown that Fan’s coupling constant is linear with the average phonon energy. Despite a small sample size, the data here suggest a similar trend. Values of $\beta$ of the Varshni model is in a range similar to that measured for ZnO[133]. However, the values of $\theta$ and $\beta$ for the 20 mTorr film are significantly lower than the more insulating films. Obtaining a linear fit for the Tauc curve in the 20 mTorr
film is difficult due to the presence of substantial sub-bandgap absorption, sometimes masking the true bandgap of the material. As such, obtaining an accurate description of the temperature-dependent bandgap is complicated due to the inherent temperature dependence of the sub-bandgap absorption. A better description of the temperature-dependent bandgap can be most reliably obtained for more insulating films as the defect states do not unnecessarily complicate bandgap determination.

Table 6.1. Fan and Varshni parameters for Eu:IGZO thin films.

<table>
<thead>
<tr>
<th>$P[O_2]$</th>
<th>$E_0$ (eV)</th>
<th>$A$</th>
<th>$\Theta$ (meV)</th>
<th>$E_0$ (eV)</th>
<th>$\alpha$ ($x10^{-3}$)</th>
<th>$\beta$ (K)</th>
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<td>3.378</td>
<td>0.1708</td>
<td>45.31</td>
<td>3.217</td>
<td>1.447</td>
<td>1338</td>
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<td>0.1330</td>
<td>36.11</td>
<td>3.155</td>
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<td>1010</td>
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<td>0.0134</td>
<td>6.11</td>
<td>3.122</td>
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<td>20.55</td>
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</tbody>
</table>

6.2.3 Cathodoluminescence

While undoped IGZO films demonstrated little or no cathodoluminescence, Eu doped films exhibited strong cathodoluminescence, owing to the presence of activated Eu$^{3+}$ ions in the host. Since Eu:IGZO films did not demonstrate observable PL emission, CL spectroscopy was used to study the behavior of Eu in IGZO thin films.

It was observed that Eu:IGZO produces characteristic Eu$^{3+}$ emission when deposited in increased oxygen pressures, as shown in Figure 6.11. For the 40 mTorr film, Eu emission is weak, but observable and increases in films deposited at higher oxygen pressures. Increasing from 80 to 100 mTorr results in roughly twice the CL intensity, integrated over the visible spectrum. The observed emission is again due to the $^5D_0$ to $^7F_1$
transitions in the Eu$^{3+}$ ion, with the most intense emission assigned to the $^{5}D_0$ to $^{7}F_2$ transition.

Figure 6.11. Room temperature CL spectra for 100, 40 and 20 mTorr Eu:IGZO thin films.

Reports of a-Si codoped by oxygen and erbium have indicated that the incorporation of O improves Er luminescence intensity[134-136]. The literature suggests the improvements by codoping samples stem from modification of the local environment, formation of Er-O complexes and increasing the solubility of Er in a-Si. These three phenomena work to either increase the efficiency or the population of optically active Er ions in the samples. This serves as one potential starting point for understanding the role of oxygen in Eu luminescence. Although the O content in these IGZO films is approximately 50 atomic percent, larger than that in codoped a-Si studies, there tends to
be an overall O deficiency in these films, which may result in competition among the constituent cations for available O. Another plausible scenario is that the luminescence intensity is dependent on the background carrier concentration, which is determined by the oxygen pressure during deposition. Further studies are required to better understand the interrelationship between optical emission from the rare-earth dopant and deposition conditions.

No PL signal was observed from these films, suggesting that efficient CL emission may be the result of direct excitation of the Eu ions in the host with limited contribution from indirect excitation mechanisms. The fact that CL was observed at all indicates that Eu:IGZO thin films could be used in TFEL devices where the Eu ion is again excited directly by impact ionization/excitation under high electric fields.

Low-temperature CL was also performed at temperatures down to 110 K. It was observed during the cooling cycle of the SEM stage that the characteristic luminescence from Eu\(^{3+}\) decreased in intensity with decreasing temperature, as shown in Figure 6.12. Emission at 125 K was about 35% of the room temperature intensity and increased somewhat as the temperature decreased to 110 K. This result likely contradicts the theory that the Eu\(^{3+}\) ions in IGZO are directly excited by the electron beam. Because indirect excitation mechanisms depend strongly on ionized carriers and trapping by localized defect states, it is likely that the decrease in emitted intensity is due to a reduction in efficient energy transfer processes at lower temperatures.
Figure 6.12. CL intensity during the cooling cycle. The CL intensity was quantified by measuring emission centered at the main emission features of the Eu:IGZO spectrum near 615 nm.
This chapter presents results on TFEL devices fabricated using novel Eu:Ga2O3 and Eu:IGZO phosphor layers. Europium doped gallium oxide thin film electroluminescent devices with bright red emission (611 nm) and relatively low threshold voltages of 60 V were produced using pulsed laser deposition. The use of transparent conducting electrodes of amorphous InGaZnO on transparent aluminum titanium oxide/indium tin oxide/7059 Corning glass substrates resulted in a device that is transparent throughout the visible spectrum. At 100 V, with 1 kHz excitation the luminance was 221 cd/m². Sawyer-Tower circuit analysis and time dependent emission measurements suggest that the charge trapping at the ATO/Ga2O3:Eu interface plays an important role in producing efficient emission.

Both host materials demonstrate characteristic Eu³⁺ emission with strong agreement between EL and CL spectra. The spectra from both hosts are surprisingly similar, which may provide some insight into the local structure of IGZO. Electronic properties of the TFEL devices are also discussed using a Sawyer-Tower circuit.

7.1 Europium Doped Gallium Oxide

This study investigates the design and characterization of an asymmetric europium doped Ga2O3 TFEL device structure. The use of transparent conducting oxides for electrodes results in a device that is transparent to visible wavelengths as
demonstrated in Figure 7.1. A transmission spectrum of the TFEL device shows good transparency through the visible region.

![Transmission Spectrum](image)

**Figure 7.1.** Optical transmission spectrum of the completed TFEL device, with a picture inset.¹

These devices are bright enough to be seen in normal room lighting, as shown in the picture inset in Figure 7.1 and Figure 7.2. However, in this study we use Sawyer-Tower circuit analysis following the methods described by Wager and Kier[85], and time dependent light emission characteristics to show that the trapping characteristics of the ATO/Ga₂O₃ interface are important in obtaining the high emission efficiency.

The observed electroluminescence and cathodoluminescence shown in Figure 7.2 is representative of the characteristic emission associated with atomic transitions observed in the Eu$^{3+}$ ions. The major peak at 611 nm corresponds to the $^5$D$_0$ to $^7$F$_2$ transition. Substantial emission is also observed as a shoulder of the 611 peak at 615 nm. This emission originates from the same $^5$D$_0$ to $^7$F$_2$ transition but is Stark shifted due to the particularly high sensitivity of this transition to the local crystal field[40]. In $\beta$-Ga$_2$O$_3$, Eu$^{3+}$ can occupy either the octahedral or tetrahedral gallium site[39], which would produce two similar but distinct emission lines. Other less prominent transitions near 578

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nm, 588 nm, 652 nm and 708 nm are the result of transitions from the $^5D_0$ states to the $^7F_0$, $^7F_1$, $^7F_3$ and $^7F_4$ states, respectively. From this spectrum, the chromaticity coordinates were calculated to be $(x = 0.629, y = 0.355)$.

In comparison with many other TFEL devices where the threshold voltage is 100-250 V the emission threshold voltage is relatively low at approximately 60 V as shown in Figure 7.3. The luminance of the devices excited by 1kHz square wave with RMS voltage of 100 V was 221 cd/m$^2$ which compares favorably with other reported results near 10-50 cd/m$^2$ for Ga$_2$O$_3$:Eu[36] and other red light emitting phosphors[95, 97] under similar excitation conditions. These results also exceed the requirements of the ISO 3664 (75 to 100 cd/m$^2$) and the newer ISO 12646 (80 to 120 cd/m$^2$) display standards that govern standard viewing conditions for proper color representation and reproduction. We conjecture that further improvements in light emission efficiency could be obtained using a symmetric device design and optimizing the Ga$_2$O$_3$ layer thickness. Emission is observable with the naked eye near 60 V for 1 kHz excitation and near 80 V for 60 Hz excitation. Plotting the intensity data on a log scale and finding the intercept with the x-axis $(y = 0.1 \text{ cd/m}^2)$ one finds the threshold voltages to be approximately 54 V for the 1 kHz and 60 Hz excitation.

There are practical implications in having electroluminescent devices operating near 100 V rather than 200-250 V, since typical single phase wall plug voltages are 120 V in the U.S. For battery powered devices, such as what might be required in a portable display device, the high voltages can be obtained using DC-DC converter-like circuits which are typically 80 to 95 percent efficient independent of the desired output voltage.
However, the power dissipated by the TFEL device depends on the square of the RMS current times the device impedance, or equivalently the RMS voltage squared divided by the total impedance. Thus for a given device impedance, halving the operating voltage results in a fourfold savings in power consumption.

The frequency dependence of the light output is shown in the inset of Figure 7.3, with the luminance reaching 221 cd/m² at 100 V for a 1 kHz square wave and 131 cd/m² for sinusoidal excitation. The intensity of the light emission reached a maximum near 3.9 kHz for 100V excitation, and then decreased monotonically.

Figure 7.3. Emitted EL intensity as a function of maximum applied voltage. The threshold for visible emission is about 60 V and a luminance of 221 cd/m² is achieved. Frequency dependent emission for a 100 V sinusoid is inset. The peak luminance occurs near 4 kHz.

Figure 7.4. EL intensity as a function time for a 65 and 95 V square wave with 50% duty cycle at 10 Hz. Note that at lower voltages, emission is only observed during the rising edge of the waveform. For higher voltages, emission is also observed for the opposite polarity, but is much weaker.¹

From the asymmetry in the device structure, one expects the dynamics of the electron injection from the ATO/Ga₂O₃ interface and the IGZO/Ga₂O₃ interface to be different and this is seen in the time dependent electroluminescence output data in Figure 7.4. Due to the relatively long radiative lifetime of the Eu³⁺ ion, the time dependent data was taken at 10 Hz with the alternating voltage applied to the IGZO top contact while the ITO bottom contact was grounded. At 65 V bias, the device emits a single observable light pulse per cycle during the positive half of the cycle. From the polarity of the voltage, this emission is from electrons injected from the ATO/Ga₂O₃ interface. When the applied voltage is increased near 100 V one finds a weaker pulse is emitted, corresponding to electrons originating from the IGZO contact.

This asymmetry was also examined using the Sawyer-Tower circuit as shown in Figure 7.5 where external charge that builds in the sense capacitor is plotted against the instantaneous voltage applied to the TFEL device. An 80 V bipolar pulse train was used to drive the device at 1 kHz (100 Hz) with a rise and fall time of 10 µs (100 µs) and a dwell time for each pulse of 100 µs (1 ms). The naming scheme for points on the Q-V plot is the same as in Wager and Keir[85].

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Figure 7.5. Q-V analysis for bipolar pulse trains at 0.1 and 1 kHz. The critical features of the Q-V loops are identified in the figure, as per [85].

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The abrupt changes from $E$ to $F$ and $A$ to $J$ denote the leakage charge during a long zero voltage portion of the pulse train. This leakage charge is due to electron emission from interface traps at either interface and is a function of the trap states as well as the magnitude of the polarization field at the interface. The polarity of the applied bias shows there is a greater leakage charge when electrons accumulate at the ATO/Ga$_2$O$_3$ interface ($A, J$) than at the IGZO/Ga$_2$O$_3$ interface ($E, F$). Thus, the number of traps being filled is greater at the ATO/Ga$_2$O$_3$ interface than at the IGZO/Ga$_2$O$_3$ interface where most of the charge simply recombines within the contact.

Similarly, the distinct transition from $C$ to $D$ and the absence of a similar transition near point $I$ is an indication that there is substantial transfer of relaxation charge to the IGZO/Ga$_2$O$_3$ interface and not to the ATO/Ga$_2$O$_3$ interface. Relaxation charge is the charge that flows across the phosphor while a constant maximum voltage is being applied to the device and as charge accumulates at either interface the electric field across the phosphor will decrease. Since points $C$ and $D$ are at positive voltages this indicates charge accumulation at the IGZO/Ga$_2$O$_3$ interface and similarly for a negative applied pulse, charge trapping occurs at the ATO/Ga$_2$O$_3$ interface. The shape of the transition from $C$ to $D$ shows that charge is transferred during the positive DC portion of the waveform, pointing to the release of charge from traps at the ATO/Ga$_2$O$_3$ interface. This transferred relaxation charge is approximately 28 and 0.22 µC/cm$^2$ per cycle at 100 Hz and 1 kHz, respectively. The lack of transferred charge during the negative DC portion of the waveform suggests the device is working more like a simple capacitor for negative voltages without transfer of trapped charge from the IGZO/Ga$_2$O$_3$ interface.
Electroluminescent light intensity is directly related to the probability (cross section) of impact ionization or excitation of the rare earth ion due to an energetic electron. In the case of the IGZO contact, electrons are injected into the Ga$_2$O$_3$ layer with relatively low energy and the high voltage is necessary to increase the electron energy above the Eu$^{3+}$ ionization threshold. The number of available electrons is low since there are relatively fewer charge traps. In the case of the ATO/Ga$_2$O$_3$ interface, a larger number of traps are present and we can view the concentration of interface trapped charge as a reservoir of available electrons. Some of these traps can also be at energies above the Ga$_2$O$_3$ conduction band and are filled during the large negative voltage pulse. Thus the number of available electrons for ionization is increased. Upon application of the positive pulse the charge, especially that from traps well above the Ga$_2$O$_3$ conduction band, can tunnel very energetically into the Ga$_2$O$_3$ layer. Thus both the population and kinetic energy of electrons from the ATO/Ga$_2$O$_3$ interface are increased by the presence of interface states.

The waveform frequency dependence of the transferred relaxation leakage charge in Figure 4 is due to the longer dwell time during and between pulses for the 100 Hz signal. At 1 kHz the leakage and relaxation charge transferred is substantially less due to the dwell time being substantially shorter. This illustrates the interrelationship between the luminescence, the interface traps lifetime and excitation waveform.
7.2 Active Matrix Eu:IGZO Electroluminescent Pixel

7.2.1 Eu:IGZO Thin Film Electroluminescent Devices

Eu:IGZO TFEL devices were pulsed laser deposited at room temperature, making them compatible with flexible organic substrates such as PET. The resulting device stack, illustrated in Figure 7.6(a), is 80% transparent throughout the visible spectrum, as
shown in Figure 7.6(b) and (c). This high transparency is due to the wide bandgap of the constituent layers. The glass/ITO/ATO substrates are transparent further into the UV spectrum than the completed device, but the near-UV absorption is attributed mostly to absorption by the ITO top contact. This layer was deposited at room temperature, which reduces transparency in the UV, but remains transparent in the visible spectrum.

Photographs of the completed device are shown in Figure 7.6(c) and (d) in the off and on states, respectively.

![Figure 7.7. Electro- and cathodoluminescence spectra (left) and luminance voltage curves (right) for Eu:IGZO films and TFEL device. L-V curves are for 100 mTorr deposited Eu:IGZO phosphor excited by 100, 500 and 1000 Hz sinusoids.](image)

Emission from the 100 mTorr deposited Eu:IGZO TFEL device is shown in Figure 7.7 and compared to room-temperature CL emission from 20, 40 and 100 mTorr deposited films. There is excellent agreement among the spectral features between EL
and CL spectra with the only differences being ascribed to instrument resolution. Luminance-voltage curves for the TFEL device are presented in Figure 7.7. Peak EL emission was measured at less than 6 cd/m², substantially weaker than for Eu:Ga₂O₃ devices under similar conditions, though observable by the naked eye in a dark room.

Since CL emission was observed for 40, 80 and 100 mTorr deposited Eu:IGZO films, TFEL devices were also fabricated with 40 mTorr deposited phosphors to compare to the performance of 100 mTorr deposited phosphors. As shown in Figure 7.8, a TFEL device using the 40 mTorr phosphor emitted roughly one-sixth the luminance of the 100 mTorr phosphor. While 40 mTorr TFEL device appears to exhibit a much higher threshold voltage, near 70 volts, it is believed that this is due to limitations on instrument sensitivity.

![Figure 7.8. Luminance-voltage characteristics for 40 and 100 mTorr deposited Eu:IGZO TFEL devices. Both were excited with a 1 kHz sinusoid. The 100 mTorr phosphor is approximately six times brighter than the 40 mTorr phosphor.](image)

124
As with the Eu:Ga$_2$O$_3$ TFEL devices, time-dependent EL emission was investigated for both phosphors. Both devices demonstrated a the same polarity dependence observed for the Ga$_2$O$_3$ devices where a positive field, with respect to the grounded back contact, results in a stronger EL signal than does a negative field. This behavior is attributed to the asymmetric, single-dielectric structure of the TFEL devices. However, for these devices no EL response is observed during the negative applied pulse. This is attributed to the small size of the devices shown here (0.5 mm x 0.5 mm) and the low intensity of the EL signal.

![Figure 7.9](image)

**Figure 7.9.** Time-dependent EL emission from Eu:IGZO TFEL devices. A square pulse train of 50% duty cycle at 50 Hz was used to excite the devices. The trigger sequence from the waveform generator is shown at the top of the figure for comparison.

In addition, it was observed that the EL signal from the 100 mTorr film to decayed faster than that from the 40 mTorr film. The 40 mTorr device also continued
emitting until the polarity of the applied voltage was reversed, likely due to continued emission of carriers from long-lived traps. This is likely due to the substantial differences in background carrier density between the 40 and 100 mTorr Eu:IGZO films. The higher background carrier density of the 40 mTorr film results in a greater density of carriers that can be trapped at the interfaces. The intensity of EL emission from the 40 mTorr device is lower, which confirms that the 40 mTorr deposited film is a less efficient phosphor than the 100 mTorr film despite the possible advantages of higher carrier mobility or carrier density.

EL decay characteristics may be even more complex than those for PL as there are additional time-dependent factors which may obscure radiative decay phenomena. Quantitative analysis of EL decay at this point would be premature.

7.2.2 Active Matrix Pixel

Having developed novel rare-earth doped AOS TFEL phosphors and working devices, an integrated circuit was designed and fabricated that could operate as an active-matrix electroluminescent pixel. The circuit was designed as shown in Figure 7.10c, where TFTs T1 and T2 were fabricated using amorphous IGZO as the channel layer. An illustrated cross-section is shown Figure 7.10a, which describes how TFT T2 was integrated with the TFEL device. The resulting circuit is visible transparent, as shown in Figure 7.10b, owing to the use of wide bandgap materials for all layers, including interconnects. Complete fabrication and processing details are given in section 3.2.1. This is believed to be the first reported demonstration of an integrated active-matrix
electroluminescent pixel fabricated using amorphous oxide semiconductors for the TFT channel and light emitting layers.

Figure 7.10. A cross-section schematic showing the integration of a single TFT with the TFEL device (A), an image of a processed pixel chip (B) and the implemented circuit (C). Note the high transparency of the pixel chip. [137] © 2009 IEEE

The static characteristics of individual TFTs, including $I_{ds}$ vs. $V_{ds}$ and $\sqrt{I_{ds}}$ vs. $V_{gs}$ curves were measured and are shown in Figure 7.11. It was determined that the TFTs are high quality enhancement mode devices that demonstrate hard saturation. An $I_{on}/I_{off}$ ratio greater than $10^8$ and an-off state leakage current on the order of 1 pA is achieved according to the $\sqrt{I_{ds}}$ vs. $V_{gs}$ transfer curves. The subthreshold swing of 300 mV/decade
was extracted from the transfer characteristics, indicating linearity that meets requirements for fast transient response of TFTs.

Using standard FET equations, the threshold voltage (~1 V) was determined by extrapolating the linear portion of the $\sqrt{I_{ds}}-V_{gs}$ curve to zero (inset in Figure 7.12) and a saturation field effect mobility, $\mu_{sats}$, of 7 cm$^2$/V·s was extracted. This mobility value is lower than previous devices and is most likely caused by reduced interface quality between the channel and dielectric layers. It is recognized that TFTs are non-ideal devices and standard FET equations do not completely model their behavior. A more generic form of mobility extraction proposed by Hoffman has been carried out and $\mu_{avg}$, which quantifies the average mobility of the cumulative induced channel charge as a
function of $V_{GS}$ in the linear regime, is plotted in Figure 7.12. Both measures of carrier mobility are in good agreement.

![Figure 7.12. Carrier mobility plotted as a function of gate voltage for an IGZO TFT in the linear regime. A $\sqrt{I_{ds}}-V_{gs}$ plot where the linear portion has been extrapolated to zero to determine the threshold voltage is inset. [137] © 2009 IEEE](image)

The individual transient behavior of a single TFT ($W/L = 800/100$) was characterized using a waveform generator to individually pulse either $V_{ds}$ or $V_{gs}$. To measure the response to a changing $V_{gs}$, the gate voltage was pulsed from 0-10V with a 50% duty cycle while applying 10 V$_{DC}$ to the drain. Subsequently, $V_{ds}$ was pulsed from 0-5 V with a 50% duty cycle while 10 V$_{DC}$ was applied to the gate contact.
As shown in Figure 7.13, the response of the TFT to a change in $V_{ds}$ is faster than to a change in $V_{gs}$. The slow response to a pulsed $V_{gs}$ is mostly due to the large area of the TFTs. The response to a pulsed $V_{ds}$ is quicker because the TFT channel is already formed as $V_{ds}$ is pulsed. These devices have not been optimized for high-speed operation, but seem capable of operating at the frequencies required by modern displays.

![Figure 7.13. Single TFT transient response. $V_{ds}$ (left) is pulsed 0-10 V and $V_{gs}$ (right) is pulsed 0-5 V. The trigger waveform represents a TTL output from the waveform generator. [137] © 2009 IEEE](image)

More important for pixel operation is the transient response of the interconnected TFTs T1 and T2. The results shown in Figure 7.14 demonstrate that these large devices are capable of operating at 120 Hz, which is a common operating frequency for modern LCD displays. The frequency response could be substantially improved through the use of a gate insulator with a higher relative dielectric constant, or by reducing the TFT active area. Faster IGZO TFTs have since been fabricated and used in 5 and 7-stage ring
oscillators, operating at frequencies over 2 MHz, with a propagation delay near 50 ns per stage. These new devices were fabricated using an atomic layer deposited Al₂O₃ dielectric, resulting in improved interface quality as compared to the SiNx dielectric used here. The channel dimensions were also substantially smaller.

Figure 7.14. Transient response for two interconnected TFTs. The drain current from T2 is plotted as a function of time. The drain bias on T1 (top) is modulated from 0-10 V at 120 Hz with a gate voltage of 10 V. The gate bias on T1 (bottom) is modulated from 0-5 V at 120 Hz with a drain bias of 10 V. In both tests, the T2 drain bias is 10 V. [137] © 2009 IEEE

The spectral output of the Eu:IGZO TFEL device is shown in Figure 7.15, and is characteristic of the Eu³⁺ dopant where the most intense emission results from transitions from the ⁵D₀ state to the ⁷F₁ manifold. The main emission peak is at 615 nm, due to the ⁵D₀ to ⁷F₂ transition in the rare earth ion. The absence of observable blue emission is evidence that the optically active Eu ions in the phosphor are predominantly trivalent. The narrow emission peaks can be useful for display devices as the result is a color with high spectral purity and the lack of emission from the IGZO host preserves the spectral purity.
purity of the Eu dopant. CIE color coordinates based on the EL emission were found to be (0.621, 0.362), which agree well with previous successful red TFEL devices[89].

Figure 7.15. EL spectrum from the Eu:IGZO TFEL device. The device was excited by a 300 Hz sinusoid with a peak voltage of 70V. [137] © 2009 IEEE

TFEL devices are pulsed in nature due to their design. As such, an important feature of a TFEL is the time dependence of the luminescence, which is a combination of the capacitive behavior of the device as well as the radiative exponential decay of the involved excited states. Due to the use of rare-earth dopants, the EL decay can be quite long-lived, depending on the host material. In this study, we observed an exponential decay time constant comparable to other Eu-doped oxide hosts[111], as shown in Figure 7.16. It should be noted that this short decay time makes these TFEL devices suitable for display applications requiring modulation at 120 Hz or more. There is little discussion
among the literature on luminescence from IGZO, thus the characteristics of radiative decay in this material are unknown.

Figure 7.16. Time dependent electroluminescence from the TFEL device. [137] © 2009 IEEE

The output intensity of an individual TFEL device was characterized as a function of the applied AC voltage. In Figure 7.17, the device was driven by a 300 Hz sinusoid with a peak voltage from 40 to 100 V. The device threshold is near 40 V, but EL intensity increases rapidly beyond 40 V until it saturates near 65 V. From 65 V to 100 V, less than 10% change in EL intensity is observed. The largest recorded photodiode current corresponds to a brightness of 2.5 cd/m² and can be seen by eye in a dark room.

The EL intensity could be modulated, or turned off altogether, using the gate input to TFT T2. Here, the driving waveform is the same 300 Hz sinusoid, but the peak
voltage is set to 70 V and Vgs2 is varied from 8 to 16 VDC for two TFT sizes (W/L = 800/200 and 800/100). As shown in Figure 7.17, both TFTs were capable of modulating the output of the TFEL device over a wide range of optical intensity and with a clear threshold for luminance.

Three important features are observed to depend on the TFT channel length: 1) the EL luminance threshold, 2) the sensitivity of the TFEL device to the applied gate bias and 3) the maximum observed TFEL luminance. Another interesting observation is that the EL intensity saturates at high Vgs, with intensity well below which the TFEL device emits at the same applied AC voltage.

Figure 7.17. Demonstration of TFEL device emission modulated by a TFT. EL intensity as a function of excitation voltage for an individual Eu:IGZO TFEL device (left), excited by a 300 Hz sinusoid. The peak EL intensity corresponds to approximately 2.5 cd/m². EL intensity (right) for a TFT-modulated TFEL device with a peak applied voltage of 70 V at 300 Hz. The channel length of the modulating TFT are shown in the figure next to the corresponding data. [137] © 2009 IEEE
As a simplification, this may be explained by discussing the TFT as a variable current-limiting device in series with the TFEL. The instantaneous current through a TFEL device can be quite large as the polarity of the applied electric field is reversed. In this scenario, the instantaneous current flowing through the TFEL is modulated by the TFT. A reduction in current through the TFT results in a proportional reduction in TFEL emission. The effect of the channel length is then approximately consistent with TFT device theory. An increased channel length reduces the drain current in both saturation and linear regions of operation and is a likely factor in effects 1) and 3). Furthermore, in the linear region of operation, an increased channel length negatively affects the transconductance of the device, which may impact 2). This is a complex system and requires further investigation to fully understand the mechanisms at work in TFEL device modulation.
8 Conclusions

8.1 Europium-Doped Gallium Oxide

The author has prepared europium-doped monoclinic Ga$_2$O$_3$ thin films with dopant concentrations of 2.4, 5, 10 and 20 mole percent by pulsed laser deposition. He found that undoped films and those with low dopant concentrations (2.4 mole percent or less) resulted in polycrystalline monoclinic thin films with crystalline grains in multiple orientations. As the concentration was increased, crystalline grains tended toward a single orientation.

Photoluminescence (PL) was used to investigate the bright red emission from the intra-4f transitions of the Eu$^{3+}$ dopant. Using continuous-wave photoluminescence (CWPL) techniques, the author’s results indicate the emission intensity increases with increasing europium concentration up to the 10% film followed by a substantial decrease in intensity for the 20% film.

With assistance from collaborators, time-integrated and time-resolved PL (TIPL and TRPL) was used to analyze the radiative decay characteristics of transitions from the $^5D_0$ state to the $^7F_J$ ($J = 0$ to 4) manifold. Radiative decay was parameterized by a biexponential decay with distinguishable fast and slow components. The slow component has been previously reported as primarily responsible for the observed emission while the fast component was attributed to a separate energy transfer mechanism. In this study, the slow component of the biexponential decay was observed
to remain approximately constant for the 2.4 and 5% doped films and was in good agreement with previous studies on the same material with lower Eu concentrations. However, the lifetime of the slow decay mechanism decreased substantially for the 10 and 20% doped films, indicating the onset of parasitic energy transfer, corroborating CWPL and TIPL results. Thus, the optimal doping level for Eu:Ga$_2$O$_3$ occurs between 5 and 10 mole percent.

The author has also characterized the refractive index, thickness and absorption coefficient of each of these films using Swanepoel’s method by designing and implementing a MATLAB script that successfully extracted these parameters from a measured transmission spectrum. The results of the MATLAB implementation could then be used to simulate a transmission spectrum for that film. Simulated and measured data were in good agreement, though some refinement is required to optimize the determined thickness and refractive index. Further revisions would likely include an iterative method to fit the simulated spectrum as a final step. The author characterized the refractive index and thickness independently using prism-coupling and a stylus profilometer, respectively, to confirm the results extracted using Swanepoel’s method. In most cases, the extracted and measured values were in good agreement.

8.2 Europium-Doped Gadolinium Oxide

The author pulsed laser deposited europium-doped Gd$_2$O$_3$ thin films under varying conditions to observe differences between the monoclinic and cubic phase of the host.
The author obtained monoclinic Gd₂O₃ films over a range of oxygen pressures during pulsed laser deposition but the cubic phase was only obtained at 50 mTorr. TIPL and TRPL were used to both characterize the luminescent properties but to also corroborate the structural differences between the phases.

By TEM and x-ray diffraction, the author observed that Eu:Gd₂O₃ films deposited at 5 and 50 mTorr were monoclinic and cubic, respectively. High-resolution TEM imaging revealed fine crystalline grains 10-20 nm in size while electron and x-ray diffraction identified the respective phases of the films. Films were polycrystalline as evidenced by the ring-like nature of the electron diffraction patterns and multiple diffraction peaks observed by XRD.

TIPL spectroscopy revealed bright red emission owing to intra-4f transitions within the Eu³⁺ dopant. However, differences between the monoclinic and cubic phases were observed in the fine structure of the respective PL spectra, most notably in the region corresponding to the \(^5\)D₀ to \(^7\)F₂ transition. This transition, which is often used to probe the structure of materials, is particularly sensitive to the local structure surrounding the dopant to the large angular momentum change in the transition (\(\Delta J = 2\)). PL features from both films were compared to a detailed, site-selective spectroscopy study performed on monoclinic Eu:Gd₂O₃. All features in the PL spectrum of the monoclinic film could be ascribed to the energy levels reported in the earlier study while only a few of the emission features matched.

TRPL was used to study differences in decay characteristics of the coinciding spectral features of the monoclinic and cubic films. The results were fit to single- and
biexponential decay models and unique characteristics were determined for the monoclinic and cubic films. Thus, spectrally similar features from the monoclinic and cubic films were coincidental and not the result of the presence of cubic phase material in the monoclinic film or vice versa.

Crystal-field calculations, performed by Dr. John Gruber, corroborated these results. Level splittings for the cubic Eu:Gd₂O₃ were determined theoretically and compared to experimental results with excellent agreement, again confirming that the 50 mTorr deposited films were cubic phase. It was also observed that the energy level splittings for Eu³⁺ in cubic Gd₂O₃ are remarkably similar to cubic Eu:Y₂O₃. This is due to the cubic crystal structure shared by the two hosts with similar lattice parameters.

### 8.3 Europium-Doped IGZO

Amorphous Eu:IGZO thin films were pulsed laser deposited by the author at room temperature to observe their absorptive and luminescent properties which were then compared to that of undoped IGZO films. This work is thought to be the first on any rare-earth doped amorphous oxide semiconductor and as such represents the preliminary stages of research into luminescence from rare-earth doped AOS materials.

Previous collaborative studies indicated an ability to control the carrier concentration over several orders of magnitude in undoped IGZO thin films by adjusting the oxygen pressure during deposition. This feature is ascribed to the formation of n-type point defects which may form more readily under lower oxygen pressures. Films
deposited at 5 mTorr oxygen pressure or more are semiconducting with carrier mobility above 10 cm^2/V-s and are transparent over the visible spectrum. Deposition in less than 1 mTorr of oxygen resulted in semi-metallic films with non-ideal optical transmission.

The author prepared IGZO films doped with europium by pulsed laser deposition. The author observed that as-deposited films demonstrated characteristic red Eu^{3+} cathodoluminescence emission, owing to the intra-4f transitions of the ion. The intensity of the emission was found to vary with the deposition oxygen pressure for films deposited at 20, 40, 80 and 100 mTorr. Only films deposited at higher pressures (> 40 mTorr) demonstrated observable, characteristic Eu^{3+} luminescence. Low pressure deposited films did not emit observable luminescence. Low temperature CL experiments (110 K) resulted in a decreased CL intensity compared to that at room temperature, indicative of a thermally activated excitation process. No photoluminescence was observed from any of the Eu:IGZO thin films.

Temperature-dependent optical transmission measurements were conducted on the Eu:IGZO films by the author from which the optical bandgap could be determined by the commonly used Tauc equation. Measurements over the range of 80 K to room temperature allowed fitting of the temperature-dependent bandgap to Varshni and Fan models. Both models adequately described the data over this temperature range, but diverge, as expected, at low and elevated temperatures. The Varshni and Fan parameters for the 20 mTorr film are very different from those corresponding to higher pressure deposited films. This is ascribed to difficulty in determining the bandgap of the 20 mTorr film due to sub-bandgap absorption in this film by shallow defect states contributing to
the increased background carrier density. More insulating films showed dramatically less
sub-bandgap absorption, simplifying bandgap determination from transmission spectra.

8.4 Thin Film Electroluminescent Devices

Europium doped Ga₂O₃ thin film electroluminescent devices were fabricated by the
author using pulsed laser deposited phosphor and top contact ITO layers. The use of
wide bandgap materials for the contacts, insulator and phosphor layers on a glass
substrate resulted in a device that was transparent throughout the visible spectrum.

Bright red electroluminescence was obtained owing to the intra-4f transitions of the
trivalent Eu dopant. Peak emission observed at 611 nm was ascribed to the efficient ⁵D₀
to ⁷F₂ radiative transition in Eu³⁺. The EL emission was recorded at 221 cd/m² for 100 V
square wave excitation at 1 kHz, with a threshold near 50 V. These metrics are both
improvements over other reported red Ga₂O₃ EL phosphors at similar voltages. In
addition, the chromaticity coordinates of the device are similar to earlier reports of red
phosphors using sulfide hosts that were deemed state of the art. These results confirm
that Eu:Ga₂O₃ represents a viable alternative for next-generation red EL phosphors.

The asymmetric structure of the device, with only one insulating layer, resulted in
asymmetric optical and electronic properties as observed by the author. Monitoring the
EL emission and applied voltage as a function of time revealed that the emitted intensity
was greater when a positive voltage rather than negative was applied to the top contact of
the device, indicating that device efficiency depended on the interface between the
phosphor layer and the underlying insulator. Charge-voltage (Q-V) analysis revealed that more charge was being stored at this interface compared to the ITO/phosphor interface. In order for this stored charge to be useful, it must be above or near the conduction band of the phosphor in order to improve EL emission intensity. The large bandgap of the Ga$_2$O$_3$ phosphor thus places certain constraints on the band structure of the insulating layer.

The author subsequently fabricated and characterized amorphous Eu:IGZO TFEL devices using only room-temperature processes, making it compatible with commercially important flexible polymer substrates. The device stack is again transparent through the visible spectrum due to the wide bandgap of the materials used. This TFEL device emitted characteristic red EL due to the Eu$^{3+}$ dopant. However, the emitted EL intensity was approximately 6 cd/m$^2$ for a 100 mTorr deposited phosphor layer, much less than that required for display applications though observable with the naked eye in a dark room. The threshold for EL emission remains near 50 V. Using the same asymmetric device structure as for the Eu:Ga$_2$O$_3$ TFEL devices resulted in similarly asymmetric device operation both in terms of optical emission and charge storage characteristics. To the best of the author’s knowledge, this is the first example of a rare-earth doped TFEL device phosphor.

Using the Eu:IGZO TFEL device technology, a transparent active-matrix EL pixel was fabricated using only IGZO-based devices. A two-TFT circuit was successfully implemented that could modulate the EL emission from the TFEL device over a range of emission intensities with good reproducibility. Large TFTs were used so as to avoid high
current densities in this initial demonstration. The author observed that, despite large channel dimensions, individual and interconnected TFTs could be modulated at better than 120 Hz – a common refresh rate used in modern LCD displays. The use of smaller TFTs in the active-matrix backplane would improve the transient response considerably. Five- and seven-stage ring oscillators have since been fabricated at NCSU using IGZO channel TFTs with much smaller dimensions that oscillated at frequencies over 2 MHz with a supply voltage of 25 V.

The author demonstrated that EL emission from the TFEL device could be modulated using a series TFT by varying the applied gate bias from 8 to 16 VDC. Over this range of voltages, a TFT with 800 µm x 100 µm (W/L) channel dimensions could effectively control EL emission from an ‘off’ state to nearly the full brightness of the device obtained with the same driving voltage. To the best of the author’s knowledge, this is also the first example of an active-matrix pixel that uses AOS materials for the backplane TFTs as well as the light emitting element.

8.5 Considerations for Future Work

The results presented in this work demonstrate gallium oxide may represent a viable red EL phosphor for future TFEL devices, both in terms of chromaticity as well as emitted intensity. The devices fabricated here exhibit lower threshold and greater intensity at a given voltage than many similar devices reported in the literature. Future work should focus on developing the phosphor material for improved EL emission
through optimization of dopant concentration, using the results presented in Chapter 4 as a guide. With regard to the TFEL device, the phosphor and dielectric layers could be optimized. Optimization of layer thicknesses could potentially lower device threshold and improve device efficiency.

There has been recent interest in rare-earth doped sesquioxide ceramics for high power disk lasers. The work presented in Chapters 4 and 5 indicate that Ga$_2$O$_3$ and Gd$_2$O$_3$ are well suited as hosts for rare-earth dopants. The long radiative lifetimes observed for both hosts makes these interesting materials for laser gain media. Gd$_2$O$_3$ may prove particularly interesting for high-power lasers as the presence of substitutional Eu$^{3+}$ ions did not alter the local structure of the host, which suggests that the thermal properties of Gd$_2$O$_3$ may not substantially degrade with doping.

Europium doped IGZO thin films have been developed and integrated into a working active matrix pixel circuit. Future work in this area should focus on the fabrication of faster TFTs, brighter phosphor materials and device design. Faster TFTs have been fabricated using smaller channel dimensions. This improved transient response has been demonstrated by an IGZO ring oscillator circuit operating at over 2 MHz. However, tradeoffs between device speed and current-carrying capacity must be considered. The high channel mobility of IGZO TFTs is beneficial in this regard by improving both the saturation current density and transient response of a TFT with a given size.

Further improvements may be made in the phosphor layer itself. Amorphous IGZO was first reported in 2004 and thus relatively little is known about this material system, inhibiting speculation regarding what improvements may be possible. The results
discussed in Chapter 7 represent the sum total of the literature on rare-earth doped IGZO thin films. As such, further investigation is required to better understand the effects of deposition oxygen pressure on the electronic and optical properties of IGZO thin films.
9 References


10 Appendices
11 Appendix A: Material Deposition and Characterization

11.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a non-equilibrium deposition technique whereby a high-power, pulsed laser is focused onto a target with the desired composition. As the laser impinges on the target, the high power density and short duration results in the formation of an energetic plasma at the target. The very short duration of the laser pulse causes the energetic species (~1-20 eV) in the plasma to be propelled away from the target and onto a substrate some short distance away. The motivation for developing the PLD technique was to achieve flash evaporation of material using short pulses of radiation from a laser[138].

A concise history of PLD technology is presented by Chrisey in ref. [138] and is summarized here. PLD of thin films was reported as early as 1965 using ruby lasers[139] but the technique was limited in the types of materials and the film thicknesses that could be deposited. As laser technology developed, so did PLD through the use of CO$_2$[140] or Nd-doped glass lasers[141]. These new laser systems were capable of faster repetition rates as well as shorter pulses which allowed deposition of thicker films. The CO$_2$ laser, with emission at 10.6 microns, increased the variety of materials that could be deposited by using radiation in the infra-red spectrum. It was then that researchers were able to demonstrate faithful transfer of target composition to the deposited films.
This faithful transfer of target composition is the result of the short pulse durations used to ablate the target material which allows congruent ablation of the target to take place. In this way, PLD as a technique benefitted from the advent of reliable Q-switched lasers with ever increasing peak power in the 1970’s. Additionally, the introduction of shorter wavelength lasers, either through the use of non-linear optics or novel gain media, improved films deposited by PLD by reducing splashing and further improving compositional fidelity. Shorter laser wavelengths also added to the variety of materials which could be deposited by PLD[138].

Successful demonstration of high-temperature superconductors deposited by PLD in the early to mid 1980’s greatly accelerated interest in the technique[142]. At that time, laser technology had progressed sufficiently that high-power pulsed lasers of a variety of wavelengths were available, enabling deposition of a vast variety of materials and alloys at an affordable price.

The PLD technique is continually being developed and refined. The largest drawback to the technique is “splashing” of micron-scale particulates from the target onto the surface of the film. Such defects are unacceptable for production processes in commercial applications and a great deal of effort has gone into reducing this effect. Solutions may be as mundane as reducing laser power at the expense of deposition rates or be more complicated such as using particle filters to remove species of greater mass[143] or using novel deposition geometries[144]. Over the last decade, the range of materials deposited by PLD continued to expand and now also includes organic semiconductor layers[145, 146].
The thin films discussed here were deposited using a modified PLD system from Neocera, and is illustrated by Figure 11.1. The system consists of an 18” diameter spherical, high-vacuum chamber with a quartz laser window. The system is capable of reaching 10⁻⁸ Torr and operating between high-vacuum and up to 100-500 mTorr pressure. The vacuum system consists of a 520 l/s Pfeiffer TMU 521P turbomolecular pump backed by a diaphragm pump. Atmospheric control is achieved using a pneumatically controlled throttling gate valve between the chamber and the turbo pump. Three mass flow controllers (MFCs) are used to backfill the chamber with either oxygen, argon or both.

![Diagram](image)

**Figure 11.1. The pulsed laser deposition system.** The schematic illustration (left) indicates the major components required for deposition. The photograph (right) demonstrates the deposition process. The whitish-blue plume is observed, originating at the target surface (not visible) and propagating towards the substrate holder.

A Lambda-Physik Compex 201 KrF (248 nm) excimer laser is used to ablate polycrystalline targets of the desired composition. Laser power is typically between 150
and 300 mJ per 20 ns pulse (peak power on the order of 10 MW), with a pulse rate of 10 Hz. The energy density at the target is estimated at ~2-4 J/cm².

Substrates are mechanically mounted to an inconel 600 plate that can be heated up to 950°C. The plate is rotated to promote uniform film deposition. Targets are mounted on a carousel and can be rastered and rotated to avoid pitting at the surface. The carousel can hold up to six 1” targets, or three 2” targets, allowing users to deposit multi-layered film stacks in a single vacuum cycle.

Ablation targets are made in-house from raw powders of the desired materials. Binary metal oxides are made directly from the metal oxide powder itself and can also be doped by careful addition of another powder. In the case of Eu:Ga₂O₃, for example, Eu₂O₃ powder is mixed in the desired ratio with Ga₂O₃ powder by suspension of both in ethanol. The suspended mixture is shaken overnight in a beaker at room temperature using an orbital shaker at 120 RPM until the ethanol evaporates. The dried mixture is removed from the beaker and ground using a mortar and pestle before pressing. Using a 1” diameter bore with two pistons, the powder is pressed into a 1” diameter disk at up to 5000 psi and then sintered in air at up to 1700 °C for 6 hours. The bore and pistons are each lubricated on the circumferential surfaces with oleic acid, an organic lubricant that is burned off during sintering, to avoid binding of the hardened steel pieces.

High temperature sintering a pressed powder target produces a solid body by reducing the size of pores in between crystal grains and increasing grain size in the target. The end result is a body that is denser and more robust than the pressed powder[147]. Slow heating and cooling rates (~5 °C/min) are used to avoid thermal shock to the target,
crucible or furnace work tube. Sintering processes are carried out at temperatures high enough to encourage material diffusion on the atomic scale, but low enough to maintain a solid phase. For these sesquioxide ceramics, the melting point can be quite high due to their strong ionic bonds.

Experience has shown that the mass of powder used for a target is dictated by the density and compressibility of the mixture. For Ga$_2$O$_3$ targets, 6-8 g of powder is used and results in a very dense sintered target. In contrast, Al$_2$O$_3$ targets use 2-3 g of powder and are pressed to only about 2000 psi.

Preparation of IGZO targets is a longer process. The IGZO composition used in this investigation had a molar ratio of 1:1:10 of In$_2$O$_3$:Ga$_2$O$_3$:ZnO, resulting in an atomic ratio of 1:1:5 of In:Ga:Zn. The three oxide powders are mixed together in the desired molar ratio as described above, and then ground with an agate mortar and pestle. The ground powder is then calcined at 1000 °C for 2 hours in air to remove volatile fractions. This critical step prior to pressing results in denser and more robust targets than without calcining. If the IGZO is to be doped, with Eu$_2$O$_3$ for example, the dopant may be added after calcining.

### 11.2 Optical Transmission and Absorption

Two experimental apparatus were used to obtain optical transmission data from thin films. The first was using a Perkin-Elmer Lambda 9 dual beam spectrophotometer with a spectral range from 200 to 3200 nm. Two light sources and two optical detectors were used to obtain this wide spectral range. A dual beam spectrophotometer continuously
compares the transmitted intensity of a reference and a sample beam, to correct for spectral variations in the emission of the source and responsivity of the detectors, making this a highly accurate measurement technique.

The other apparatus was designed to measure temperature-dependent shifts of the absorption band edge in the UV spectrum. To achieve this, a broad-band 30 W deuterium (D₂) arc lamp was used to illuminate the sample inside a Janis cryostat with quartz windows. Fused silica lenses were used to focus and couple the transmitted light into a fiber-coupled Ocean Optics USB2000 CCD spectrometer, sensitive from approximately 200 to 1000 nm. The cryostat can be operated with liquid helium (4 K) or liquid nitrogen (77 K). The temperature is monitored by a calibrated silicon diode connected to a Lakeshore temperature controller. A built-in resistive heater in the sample mount allows for temperature control.

11.2.1 Optical Determination of the Bandgap

Optical transmission measurements can be used to determine a number of properties of thin film samples including refractive index, thickness and the optical absorption edge. By measuring the transmitted intensity as a function of wavelength, one can determine the absorption coefficient of the sample using equation (11.2), where \( T \) is the normalized transmitted optical intensity, \( \alpha \) is the absorption coefficient with units of inverse length, and \( t \) is the thickness of the sample. Equation (11.2) however, is simplified in that it does not account for reflection at the surface of the film.
The absorption coefficient can be used to determine the band gap of a semiconductor and also the nature of the band gap (direct or indirect). Qualitatively, the absorption coefficient of a direct-gap semiconductor follows the square root of the photon energy as described by equation (11.3), where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the bandgap of the material and $A$ is a material constant that includes physical parameters such as effective mass and refractive index\cite{148}. Thus, a plot of the square of the absorption coefficient should be linear with energy and the x-intercept indicates the optical bandgap of the film.

$$\alpha = A\sqrt{(h\nu - E_g)} \quad (11.3)$$

The analysis for an amorphous semiconductor is different. As discussed earlier, the Bloch theorem cannot be applied to amorphous semiconductors due to the lack of translational symmetry and thus, electron states cannot be described by well-defined $k$-values\cite{63}. A direct result of the inapplicability of the Bloch theorem to such materials, is that all radiative transitions are phonon assisted to provide the necessary momentum change. Thus, such analysis cannot be used to determine the optical bandgap of an
amorphous semiconductor. Rather, a method has been proposed by Tauc, et al[149] that can be used to determine the optical bandgap of amorphous films and is given by (11.4).

\[ \sqrt{\alpha E} = A(E - E_g) \]  \hspace{1cm} (11.4)

It is possible to determine the bandgap energy \( E_g \) by plotting the left-hand-side of (11.4) as a function of energy. The linear portion of this plot can be extrapolated to the x-axis and the x-intercept equals the bandgap. However, significant sub-bandgap absorption can be observed and this absorption edge tail is attributed to intra-band absorption by localized defect states below the mobility edge[149].

While Tauc’s method is widely accepted for determining the bandgap of amorphous materials[150, 151], alternative methods have been proposed by Cody et al[129] and Vorlicek et al[130] that may offer greater consistency in bandgap determination. Cody’s and Vorlicek’s methods, described by equations (11.5) and (11.6) respectively, are similar to Tauc’s method in how the bandgap is determined, but differ in their form. That is, a function of both the absorption coefficient and photon energy is plotted against photon energy and the linear portion extrapolated to the energy axis. The intercept denotes the bandgap. The methods of Tauc, Cody and Vorlicek each give different results due to the different expressions on the left hand sides of their respective equations.
The argument in favor of Cody’s or Vorlicek’s methods is improved linearity in the spectral region near the absorption edge[152], which reduces error associated with bandgap determination. As a result of the reduced linearity in Tauc’s method, film thickness can skew the determined bandgap[129]. Since these methods were first derived between 1966 and 1982, the literature has compared the effectiveness of Cody’s model against Tauc’s for both narrow[153, 154] and wide bandgap[155] semiconductors. In the narrow gap examples, both methods seem to produce similar results with respect to bandgap determination. In wider bandgap materials, Cody’s model not only predicts the bandgap well, but can also accurately model ellipsometric data with better results than Tauc’s method. However, it should be noted that Tauc’s method remains the most commonly used of the three.

11.2.2 Low-Temperature Transmission Measurements

By varying the temperature of the sample during transmission measurements, one can observe the absorption band edge shift to higher energy. This is an often reported phenomenon and has been successfully modeled empirically by Varshni[156] and semi-empirically by a number of others[157-159]. The Varshni model takes the form shown in (11.7) where \( \alpha \) and \( \beta \) are empirical constants and \( E(0) \) is the bandgap at zero temperature.
Those who argue against the Varshni model point out that $\beta$ is supposedly related to the Debye temperature but in some cases has a negative value after fitting to experimental data[157-159].

$$E(T) = E(0) - \frac{\alpha T^2}{T - \beta} \quad (11.7)$$

A common alternative to the Varshni model, is one with a Bose-Einstein occupation term to describe an average phonon energy in the material. Variants of this concept have been reported with reasonable success after fitting to experimental data. One such variant is described by equation (11.8)[158, 159] where the constant $A$ has units of energy, $\theta$ is an average phonon energy in units of temperature, $T$ is the temperature and $E(0)$ is the bandgap at zero temperature. Equation (11.8) can be modified to give the phonon energy in eV, rather than units of temperature as shown in (11.9) where $k_B$ is Boltzmann’s constant in units of eV/K.

$$E(T) = E(0) - A \left( 1 + \frac{2}{e^{\theta/T} - 1} \right) \quad (11.8)$$

$$E(T) = E(0) - A \left( 1 + \frac{2}{e^{\theta/k_BT} - 1} \right) \quad (11.9)$$
That this model is deemed semi-empirical comes from the reasoning behind bandgap expansion at reduced temperatures. Two mechanisms are thought to be responsible for bandgap expansion: (1) thermal contraction of the solid lattice and (2) a temperature dependence of the electron-lattice interaction[156]. The contribution of lattice contraction on the width of the bandgap is reported to be less than 20% and thus a semi-empirical model with a term describing phonon statistics leads to satisfactory results[157-159].

11.2.3 Swanepoel’s Method
A very useful method for analyzing optical transmission data for thin films has been devised and presented by Swanepoel[123]. This section describes an implementation of Swanepoel’s method for extracting optical parameters from transmission data. The method is based on the analytical expression for transmission through a thin film on a substrate and is manipulated to allow extraction of wavelength-dependent refractive index and absorption coefficient values as well as film thickness with reported accuracy comparable to or better than 1%. Previous analytical techniques often made use of iterative numerical methods but with increased complexity and reduced accuracy. Significant portions of the method are outlined in
Appendix B: Swanepoel’s Method.

In order to implement Swanepoel’s method, MATLAB scripts were written to produce the envelope functions using an interpolation scheme between the extrema points of the fringes. Using the formulas derived by Swanepoel it was possible to extract the refractive index, absorption coefficient and film thickness. The MATLAB scripts are included in the appendix, section 13.

The MATLAB implementation (transmission.m) was divided into two main tasks: (1) determining the envelope functions (envelope.m) and (2) calculating optical parameters using Swanepoel’s equations (swanepoel1.m). In the first task, the envelope functions were devised in a piece-meal form. In the regions of weak or no absorption, the envelope functions were derived from interpolating between the Fabry-Perot fringe maxima and minima points using a cubic-spline interpolant. A publicly available MATLAB script was used to determine fringe maxima and minima values (peakdet.m). In the strong absorption region, the envelopes were set equal to the measured transmission curve.

Swanepoel’s equations were implemented in a separate script using the envelope functions and fringe peak positions as inputs. In the transparent and weak absorption regions, refractive index and absorbance values could be determined independently for each transmission data point. In the strong absorption region, the refractive index and absorbance cannot be independently determined. Using Sellmeier and Cauchy models, the refractive index could be extrapolated to shorter wavelengths, enabling determination of the absorbance. The results of both models are compared.
Lastly, by plotting the half-integer fringe order as a function of \( n/\lambda \), one can determine the film thickness and fringe order number from the slope and \( y \)-intercept simultaneously. This film thickness can then be used to determine the absorption coefficient from the absorbance data.

### 11.3 Scanning Electron Microscopy

Scanning electron microscopy is a highly versatile tool that allows high-resolution surface imaging of conducting samples as well as analysis of optical properties and composition. An image of the sample is formed by rastering a focused electron beam along the sample surface. As energetic electrons (~1-30 keV) interact with the sample, a number of observable signals are produced including: backscattered electrons, secondary electrons, photons and x-rays. These various signals are detected and an image is constructed by mapping the detected intensity as a function of position.

Backscattered electrons (BSE) are primary electrons (those from the original probing electron beam) which have scattered backwards from the sample due to collisions with heavy nuclei near the surface. Due to the relationship between the nuclear mass and backscattered electron yield, an image constructed from BSE has “phase contrast” but does not reveal much information regarding topography.

Secondary electrons (SE) are electrons that are ejected from the sample surface but are not themselves part of the original electron beam. As a primary electron interacts with the sample, it may impart sufficient energy to an electron so as to free it to vacuum. Energies of secondary electrons (10’s of eV) are much lower than that of BSE (keV-
range) and so reveal information regarding the topography of the sample. This is because of the relatively short distance a SE can travel through a solid with its low energy. A SE produced near the surface is more likely to escape and be detected than one produced further into the sample. Fine topography, for example, provides contrast because the SE produced within such features can more easily escape.

Photon emission (cathodoluminescence) is most often used to study the electronic structure of the sample under investigation. Cathodoluminescence (CL) from semiconducting or insulating samples is often the result of band-band recombination. In this application, CL becomes a very important tool for studying optical emission from wide bandgap materials where a light source of appropriate wavelength is not available. Additionally, adjusting the beam energy in a CL experiment allows the user to probe deeper below the surface and can be essential for analyzing quantum wells and other layered structures, for example[160]. This is something that photoluminescence cannot readily do, as the optical intensity decreases exponentially with thickness into the sample. The range of the electron beam through a sample can be modeled using Monte Carlo simulations, such as Casino, which helps to correlate the observed luminescence to a particular layer in the structure.

The SEM used in these experiments is a JEOL JSM-6400 thermionic emission microscope with a tungsten filament cathode. The microscope has a working energy range of 1-30 keV though the cathode design limits beam energy to ~1-20 keV for optimum results. The microscope has been fitted with an Oxford Instruments MonoCL monochromator for CL analysis. A parabolic mirror is inserted into the specimen
chamber which collects and focuses the luminescence into a light guide coupled to a
grating monochromator. The dispersed luminescence is detected by a thermoelectrically
cooled photomultiplier tube (PMT). The sensitive range of the PMT is approximately 190
to 900 nm with a maximum wavelength resolution of 0.5 nm. Microscope parameters
were 5 keV beam energy at a magnification of 1000x, unless otherwise noted.

A cryogenic cold stage has been fitted inside the specimen chamber as well,
permitting imaging and spectroscopy at temperatures as low as 110 K. Nitrogen gas
circulates through a liquid nitrogen dewar and into the cold stage. Pre-cooled nitrogen
gas from a liquid nitrogen cylinder is often used to reduce the amount of cryogen used
during sample cooling. The temperature is monitored using a calibrated platinum wire
resistor embedded in the cold stage and a heater can be used to maintain a set
temperature.

11.4 Photoluminescence

Photoluminescence provides a method to analyze the electronic structure of thin
films. While optical absorption allows for determination of the optical bandgap and in
some cases, refractive index and thickness, it does not provide much information on
defect states in thin film samples. The density of these states is weak and much thicker
samples are required to observe absorption. However, PL emission from these defect
states is more easily observed. Photoluminescence experiments can be divided into two
major categories: continuous wave and pulsed excitation.
11.4.1 Continuous Wave

Continuous wave PL (CWPL) is a technique to observe luminescence from radiative transitions in a steady state. That is, the populations of various excited states remain, on average, constant. This type of analysis provides information regarding the energy levels of various states involved in radiative transitions and can be often used to observe the existence of excitons or defect states, for example.

CWPL experiments at NCSU have been carried out using a variety of UV LED light sources with peak wavelengths from 250-350 nm and optical powers on the order of 0.1-1 mW. UV and visible emission spectra were obtained using an Ocean Optics fiber coupled USB4000 CCD spectrometer. Near IR spectra were obtained using a thermoelectrically cooled BWTek InGaAs CCD spectrometer, sensitive from 0.9 to 1.7 microns. Assorted UV blocking filters were used to remove unwanted excitation from the luminescence spectra. Power-dependent PL measurements were also made possible through the use of metallic neutral density filters on fused silica substrates.

11.4.2 Pulsed Excitation

Using a pulsed laser source for PL allows two types of experiments: time integrated (TIPL) and time resolved (TRPL) PL. TIPL experiments are similar to CWPL experiments in that the result is an emission spectrum, however the results may be very different. The width of the optical pulse is typically much shorter than the radiative decay rates of excited states and as a result, the sample does not equilibrate. Thus, in contrast to CWPL, TIPL measurements reflect non-equilibrium conditions in the sample
and the relative intensities of emission peaks may be very different from those observed under equilibrium conditions.

TRPL is an effective method to determine the radiative decay characteristics of excited states where the luminescence intensity over a given spectral bandwidth is monitored as a function of time. Determination of spontaneous radiative lifetimes is made possible using the above apparatus. The spontaneous emission rate from an excited state (2) to a lower energy state (1) is given by

\[
\frac{\partial N_2}{\partial t} = -A_{21}N_2 \tag{11.10}
\]

\[
N_2(t) = N_2(0)e^{A_{21}t} \tag{11.11}
\]

\[
\frac{N_2(t)}{N_2(0)} = \exp\left(-\frac{t}{\tau}\right) \tag{11.12}
\]

where \(A_{21}\) is the Einstein coefficient for spontaneous emission, the negative reciprocal of which is often denoted as a time constant \(\tau\) called the radiative lifetime. Equation (11.12) can also be normalized to the initial excited state population \(N_2(0)\) giving a relative decay from unity as in (11.12).

Time resolved and time integrated photoluminescence was carried out using a frequency tripled Ti:sapphire pulsed laser source, which can excite the samples directly. Alternately, the pulsed laser can be used to drive an optical parametric amplifier to fine tune the pump wavelength. In this case, the OPA is pumped by a 1 kHz regenerative amplifier seeded by the 80 MHz Ti:sapphire oscillator operating at 780 nm. The data
were analyzed with a 0.3 m focal length Acton spectrometer and detected by a liquid nitrogen cooled Princeton Instruments CCD. The excitation could be attenuated using a series of metallic neutral density filters.

11.5 X-Ray Diffraction

X-ray diffraction is a structural characterization technique that can provide information regarding the crystalline structure, orientation and uniformity of a thin film, bulk or powder sample.

X-rays incident on a periodic structure will diffract in the same way as light does, provided that Bragg’s law (below) is satisfied. In (11.13), $d$ is the period of the diffracting structure, $m$ is a positive non-zero integer corresponding to the order of the diffraction, $\lambda$ is the wavelength of the incident radiation and $\theta$ is the angle between the incident radiation and the periodic structure. The order number $m$ is often assigned a value of unity in the Bragg equation for x-ray diffraction experiments since higher order diffractions are accounted for by a corresponding increase in $d$[161].

\[
m\lambda = 2d \sin \theta \tag{11.13}
\]

\[
\frac{m\lambda}{2d} = \sin \theta \tag{11.14}
\]

In (11.14), the absolute value of right-hand side cannot exceed unity which requires that $\lambda$ and $d$ be comparable in magnitude. It follows then that diffraction gratings
used in optical experiments have groove densities on the order of 600 per mm, corresponding to a pitch of 1.66 microns which is comparable to optical wavelengths. X-ray wavelengths are typically in the range of 0.5 to 2.5 angstroms[161], and so can be diffracted by periodic structures on a similar length scale, such as atomic planes in solids. The most commonly use x-ray wavelength is that of the copper Kα doublet, which often resolved into the individual Kα₁ (1.5405 angstroms) and Kα₂ (1.5444 angstroms) lines, with the latter emission filtered for improved accuracy.

The most common configuration for XRD experiments is called θ-2θ and is illustrated in Figure 11.2. In this configuration, the angle between the incident radiation and the diffracting planes is again θ, while the angle between the transmitted and diffracted radiation is 2θ. As θ is scanned over the desired range of angles, the angle 2θ is maintained by moving the x-ray detector appropriately. In this way, the x-ray source and detector are always positioned in a way to detect diffracted radiation when Bragg’s law is satisfied. For most samples, the transmitted radiation shown in Figure 11.2 does not extend through the sample due to strong absorption of x-rays. However, it is instructive to show it here for purposes of discussing the method.
Diffraction from thin films has certain advantages and disadvantages over bulk or powder samples. If the thin film is deposited on a well understood crystalline substrate, such as sapphire, then diffraction from the substrate can be used to calibrate the positions of the x-ray source and detector. However, due to the reduced thickness of thin films, the diffracted intensity is very small compared to that of similar bulk samples. In most cases however, diffraction from thin films is still strong enough to be detected, provided that diffraction from the substrate does not occur at similar values of $\theta$.

Results from $\theta$-2$\theta$ experiments are commonly plotted as a graph of diffracted intensity versus the angle 2$\theta$ with a single peak for single crystal samples or multiple peaks in the case of polycrystalline materials. The diffracting planes can be identified by comparing the experimental results with a set of known data from the International
Center for Diffraction Database (ICDD). However, this is only possible assuming that the user has at least some prior knowledge of the sample’s composition.

XRD data was obtained from facilities at NCSU and Duke University’s Shared Materials Instrumentation Facility (SMIF). At NCSU, a Rigaku DMax III diffractometer was used with a copper x-ray tube using the unresolved Kα doublet. The radiation wavelength was a weighted average of the two lines, with the weight of the Kα₁ being twice that of the Kα₂, corresponding to their relative intensities. Measurements using the SMIF facilities were obtained using a Philips X’pert PRO MRD diffractometer with a filtered Cu Kα₁ source. The incident beam passes through an x-ray mirror, and a parallel plate collimator is affixed to the detector. In both cases, the experiments were carried out using a θ-2θ configuration.

11.6 Transmission Electron Microscopy

Transmission electron microscopes (TEM) are highly versatile instruments that can obtain high-resolution images of a variety of samples as well as crystallographic information. An important distinction between TEM and SEM analysis, is that an SEM can provide high-resolution images of the surface of a sample while a TEM obtains information regarding the interior of a sample by virtue of the electron transparency of thin samples. The thinness of TEM samples can be on the order of up to two or three hundred nanometers and can cause some difficulty in preparing such samples.

The high-resolution imaging capability of TEMs comes from the high kinetic energy of electrons in such experiments (~100-400 keV), which reduces the DeBroglie
wavelength. For example, at 200 keV, the electron wavelength is 2.51 pm after considering relativistic effects[162] which is important to note as the Rayleigh criterion for resolution estimates that the minimum resolvable distance between two features is one-half the wavelength of radiation used to observe it. For an optical microscope, this translates to a resolution of about 200-350 nm for visible light with wavelength 400-700 nm. For a 200 keV electron beam, the theoretical limit is approximately 1.25 pm. Aberrations in electron optics however, reduce the resolving power of all electron microscopes to features larger than the predicted Rayleigh limit. Advances in electron optics since the 1970’s have greatly improved TEM resolution to the point of being able to resolve atomic columns in crystalline samples.

Contrast in TEM images arises from scattering of electrons by the sample. This contrast can be divided up into two types for traditional TEM experiments: (1) mass-thickness contrast and (2) diffraction contrast. Mass-thickness contrast is the result of variations of mass (Z), density (\(\rho\)) and thickness (t) of the sample[162]. Diffraction contrast occurs for crystalline or polycrystalline samples and is used to form bright-field (BF) and dark-field (DF) images. Examples of diffraction contrast are often found in observing crystalline defects such as dislocations.

The ability of a TEM to obtain a diffraction pattern and an image from a sample is born out of its complex electron optics system. Three lenses exist in a typical TEM that affect the electron after interacting with the sample: objective lens (OL), intermediate lens (IL) and projector lens (PL) as illustrated in Figure 11.3. Each of these may actually be groups of lenses, rather than a single lens, but the effect is the same. Using parallel
illumination of the sample, the diffraction pattern is formed at the back focal plane of the OL and the image is formed at a somewhat greater distance. The important functional change between imaging and diffraction mode is object distance of the IL. More specifically, changing the IL focal length results in the IL object being either the diffraction pattern or the sample image. The projector lens and objective lens are unchanged during this process[162]. Additionally, the objective aperture and selected area diffraction (SAD) apertures must be swapped. While these do not change the functionality of the microscope, they substantially improve the results by limiting the diameter of the electron beam, reducing spherical aberrations in imaging and physically limiting the area from which diffraction information is collected.
Figure 11.3. TEM operation for selected area diffraction and imaging. For diffraction (left), the SAD aperture is inserted to physically limit the sample area contributing to the diffraction pattern. For imaging (right), the OL aperture improves imaging results by reducing highly off-axis beams, reducing the effects of spherical aberration. The grey circles represent diffraction spot formations at intermediate stages of projection. The grey arrows represent the various image planes at intermediate stages of projection.

For crystalline samples, a diffraction pattern (DP) will consist of a series of spots while for polycrystalline samples the DP will consist of rings. The formation of rings versus spots arises from the random relative orientation of grains of the same crystalline phase. The finer the grain size, the smoother the diffraction rings will appear as a greater distribution of orientations is observed by the electron beam.
While more information can be extracted from single crystal samples, the crystalline phase can still be determined from polycrystalline samples as in XRD experiments. This is done by measuring the radius of the diffracted rings and calculating the corresponding interplanar distance. These distances are then compared to known spacings in the ICDD database for assignment.

Calculation of the interplanar spacing was achieved using a calibrated reciprocal length provided by the microscope. On each DP there is a scale bar and an associated length. The measured length of the bar (in pixels) is thus the radius of a diffraction ring produced by a set of planes with an interplanar distance given by the displayed length. This ratio can be used then to determine the interplanar distance of the set of planes provided one can accurately measure the ring radius. ImageJ is open source analytical software developed by the National Institutes of Health (NIH) that is often used by electron microscopists for such measurements. In this work, to measure the radius of the rings, ImageJ was used to draw a circle overlapping the diffraction ring. Properties of the circle, such as area from which one can calculate the radius, are output by the program.

\[
\frac{\text{known spacing (nm)}}{\text{scale bar (pixels)}} = \frac{d \text{ (nm)}}{\text{measured radius (pixels)}}
\]

(11.15)

\[
d \text{ (nm)} = \frac{\text{measured radius (pixels)}}{\text{scale bar (pixels)}} \cdot \text{known spacing (nm)}
\]
The TEM results presented in this work were obtained using a Hitachi HF2000 microscope at the Analytical Instrumentation Facility at NCSU using a 200 keV electron beam from a cold field emission electron source. Images and diffraction patterns were recorded using a 4 megapixel CCD camera with an overall camera length of 20 cm (?) for diffraction patterns.

To simplify TEM sample preparation, thin films of interest were deposited directly onto amorphous silicon nitride (SiNx) membranes supported by a 3 mm silicon ring, designed to fit into a standard TEM sample holder. The membranes are 50 nm thick and have shown very high electron transparency in imaging and diffraction type experiments. Additionally, the membranes are rugged enough to withstand pulsed laser deposition of thin films at high temperatures and high vacuum processes. Membranes were supplied by Protochips, Inc (Raleigh, NC).

11.7 Rutherford Backscattering Spectrometry

Rutherford Backscattering Spectrometry (RBS) was used to determine composition and density of some deposited thin films. This technique was made available to us by Dr. J. Derek Demaree at the Army Research Lab in Aberdeen, MD and offers multiple advantages over other techniques. X-ray photoelectron spectroscopy (XPS) or secondary ion mass spectroscopy (SIMS) are available and often used, however RBS offers non-destructive depth profiling of samples without need for calibration standards.

The advantages of RBS stem from the use of energetic light ions such as protons or alpha particles to probe the sample. Light ions with MeV-range energy are incident on
the sample and backscatter after colliding with nuclei in the sample. The energy with which the particles backscatter is proportional to the particle’s energy at the time of collision and the masses of the energetic particle and sample nuclei. Unless the incident particle backscatters from nuclei at the sample surface, the energy of the particle at the time of collision is less than its original energy. Energy loss mechanisms of light ions in solids is well understood and stopping powers can be calculated using software packages like SRIM (the Stopping and Range of Ions in Matter), allowing for accurate, standard-less depth profiling of a sample. Depending on beam energy and sample composition, the range of a light ion can be several microns, but the escape depth of backscattered particles is substantially less, allowing RBS to effectively probe a thickness of up to approximately one micron or more.

In contrast, XPS can only examine a few nanometers into the surface of sample. Depth profiling can be achieved by repeatedly sputtering the surface atoms away in between measurements. SIMS is commonly used to profile atomic concentrations as a function of depth but requires a standard of similar known composition and is a destructive measurement. Quantitative x-ray spectroscopy can be used to determine the composition of a sample, but also requires a known standard for comparison.

For the data presented here, 2.0 MeV He\(^+\) ions were incident on the sample surface with the particle detector positioned at 170\(^\circ\) backscatter angle. The detector solid angle is estimated at 5 millisteradian. Data were analyzed by fitting in the computer simulation program RUMP to determine film composition and density.
11.8 Atomic Force Microscopy

Atomic force microscopy (AFM) is a common surface analysis technique with a vertical resolution of a few nanometers. Here, a silicon cantilever with a fine tip is brought in close proximity with the surface of a sample while a small laser spot illuminates the back of the cantilever and is reflected towards a position-sensitive photodetector. The cantilever is mechanically clamped to a piezoelectric holder and, by applying an ac voltage to this holder, the holder and cantilever oscillate. As the oscillating cantilever scans across the sample surface, the reflected laser beam oscillates on the detector. Topographic features on the sample surface are thus detected by a change in phase and amplitude of oscillation of the laser’s position on the detector. This technique is useful for analyzing the roughness of a thin film or mesa profiles after etching or lift-off steps, for example.

The AFM scans presented here were acquired using a Digital Instruments Nanoscope IIIa tapping mode AFM. The tool is supported by a table with an air suspension system to reduce noise due to mechanical vibrations. The RMS noise floor of the instrument is better than 0.05 nm, which represents the observed signal due to noise. Signals above this floor should be considered significant.

11.9 Four-point probe

The four-point probe technique is useful for measuring the electrical resistance of a variety of conducting and semiconducting samples. The main advantage of the
technique is the use of a four-terminal measurement as opposed to two terminals for measuring the resistance.

In this method, four equally spaced in-line contacts are placed on the sample surface as illustrated in Figure 11.4. A current is forced to flow through the sample by the outer two contacts while the voltage is measured by the inner two. Using a voltmeter with sufficiently high input impedance reduces the current flowing through the inner two contacts, minimizing the effects of contact resistance on the overall measurement. In contrast, a two-terminal measurement suffers from contact resistance as the voltage sensing probes also carry the current, resulting in a non-trivial series contact resistance.

Figure 11.4. Typical four-point probe experiment for a thin film on an insulating substrate. The film thickness $t$, probe spacing $s$ and sample diameter $d$ are labeled on the schematic.
The four-point probe technique does have certain limitations with respect to sample geometry. Three correction factors exist to compensate for film thickness ($F_1$), lateral extent ($F_2$) and proximity of the probes to the sample edge as compared to the probe spacing ($F_3$) [163]. In most measurements of this type, the four contacts are spaced relatively close together, on the order of 40 to 80 thousandths of an inch (approximately 1 to 2 mm), which is sufficiently small that provided the contacts are near the sample center, this effect can be neglected. Thus, for most cases $F_3 = 1$. The other two correction factors can be determined using the following:

$$\rho = 2\pi s F \frac{V}{I}$$

$$F = F_1 F_2 F_3$$

$$F_1 = \frac{t}{s} \frac{1}{2 \ln 2}$$

$$F_2 = \frac{\ln 2}{\ln 2 + \ln \left[ \left( \frac{D}{s} \right)^2 + 3 \right] / \left[ \left( \frac{D}{s} \right)^2 - 3 \right]}$$

(11.16)

(11.17)

where $t$ is the film thickness, $s$ is the contact spacing and $D$ is the diameter of a circular sample. For a sample 10 mm in diameter, and a probe spacing of one mm, $F_2$ is approximately 0.92 so the overall correction factor and resistivity formula are
Resistivity measurements were made using a Lucas 302 four-point probe stand and a tungsten probe head with 0.040” contact spacing and a constant force of 85 grams. The current was sourced using a Keithley 220 programmable current source and the voltage sensed by a Keithley 6517a electrometer.

\[
F = 0.92 \frac{t}{s} \frac{1}{2 \ln 2}
\]

\[
\rho = 0.92 \frac{\pi}{\ln 2} \frac{tV}{I}
\]

\[
\rho = 4.17t \frac{V}{I}
\]

11.10 Van der Pauw Hall Effect

The Hall Effect accounts for the generation of a perpendicular electric field when a magnetic field is applied perpendicular to the direction of current flow. This electric field effectively counteracts the Lorentz force produced by the interaction between the moving electrons and the perpendicular magnetic field. The voltage resulting from this electric field is commonly called the Hall voltage, \(V_H\), and is experimentally measured to calculate the Hall coefficient, \(R_H\). In equation (11.19), \(t\) is the sample thickness, \(B\) is the magnetic field and \(I\) is the current through the sample[163].
Electronic properties can be subsequently extracted from the Hall coefficient according to equation (11.20) where \( p \) and \( n \) are the hole and electron densities, respectively, \( b \) is the ratio of the electron mobility to hole mobility, \( r \) is the scattering factor and \( q \) is the fundamental unit of charge. The scattering factor is a coefficient with value between 1 and 2 that varies for different scattering mechanisms including lattice scattering \((r = 1.18)\), ionized impurity scattering \((r = 1.93)\) or neutral impurity scattering \((r = 1)\). The scattering factor is usually unknown and so for simple Hall experiments, is approximated as unity[163]. For \( p \) and \( n \) type semiconductors equation (11.20) reduces to equations (11.21) and (11.22), respectively.

\[
R_H = \frac{t V_H}{B I} \tag{11.19}
\]

\[
R_H = \frac{r(p - b^2 n)}{q(p + bn)^2} \tag{11.20}
\]

\[
R_H = \frac{r}{qp} \tag{11.21}
\]

\[
R_H = -\frac{r}{qn} \tag{11.22}
\]
Carrier density and mobility can be calculated using the following set of equations[163]. The Hall mobility differs from the conductivity mobility in extrinsic cases where the scattering factor $r$ is not unity, though it is often assigned this value. This is still a commonly accepted discrepancy and assumptions about the scattering factor should be explicitly described.

$$p = \frac{r}{qR_H}$$  \hspace{1cm} (11.23)

$$n = -\frac{r}{qR_H}$$

$$\mu_H = \frac{|R_H|}{\rho} = |R_H|\sigma$$  \hspace{1cm} (11.24)

The work of van der Pauw later removed the geometric restrictions by describing a method to apply the Hall effect technique to samples of arbitrary shape, provided they had no internal gaps.
12 Appendix B: Swanepoel’s Method

It is assumed that the sample geometry is that of a thin film on a thick substrate whose thickness is orders of magnitude larger than the film’s and whose absorption is nearly zero through the region of interest for the film. Such is the case for the samples analyzed here, as the films were approximately 650 nm thick and were deposited on double side polished sapphire substrates over 300 µm thick. The large bandgap of sapphire ensures minimal absorptive losses in the region of interest and double-polishing virtually eliminates scattering losses. The rigorous model in (12.1) has been previously derived for such a sample geometry.

\[ T = \frac{Ax}{B + Cx + Dx^2} \]

\[ A = 16s(n^2 + k^2) \]

\[ B = [(n+1)^2 + k^2][(n+1)(n+s^2)+k^2] \]

\[ C = [(n^2-1+k^2)(n^2-s^2+k^2)-2k^2(s^2+1)]2\cos\varphi - k[2(n^2-s^2+k^2)+(s^2+1)(n^2-1+k^2)]2\sin\varphi \]

\[ D = [(n-1)^2+k^2][(n-1)(n-s^2)+k^2] \]

\[ \varphi = 4\pi \frac{nd}{\lambda} \]

\[ x = \exp(-\alpha d) \]

\[ \alpha = 4\pi \frac{k}{\lambda} \]
It is possible to fit this model to experimental transmission data, but would be more complex than the method of Swanepoel. Here, the extinction coefficient $k$ is set to zero, which is a good approximation over the transparent region for the thin film and greatly simplifies the above set of equations to the form shown in (12.2).

$$T = \frac{Ax}{B + Cx \cos \varphi + Dx^2}$$

$$A = 16sn^2$$

$$B = (n + 1)^3(n + s^2)$$

$$C = 2(n^2 - 1)(n^2 - s^2)$$

$$D = (n - 1)^3(n - s^2)$$

$$\varphi = 4\pi \frac{nd}{\lambda}$$

$$x = \exp(-\alpha d)$$

The cosine term in the denominator describes the oscillatory nature of the transmission spectrum due to the Fabry-Perot fringes. Thus, the envelope functions describing the maximum and minimum transmission are given by equation (12.3).

$$T_{\text{max}} = \frac{Ax}{B + Cx + Dx^2}$$

$$T_{\text{min}} = \frac{Ax}{B - Cx + Dx^2}$$
For analytical purposes, the envelope functions are each treated as continuous functions of the film and substrate refractive indices, which are themselves continuous functions of wavelength. Using \( T_{\text{max}} \) and \( T_{\text{min}} \) it is possible to determine the refractive index and extinction coefficient continuously as a function of wavelength by simplifying each term through a different portion of the spectrum: transparent, weak/medium absorption and strong absorption.

In the transparent region, it is assumed that \( x \) is unity, thus \( \alpha \) is zero, which gives:

\[
T_{\text{max}} = \frac{2s}{s^2 + 1}
\]

(12.4)

This reveals that the maximum transmission envelope is governed by the substrate transmission, or more specifically the refractive index, in the transparent region. Thus, the deviation of the maximum transmission envelope from the substrate transmission indicates the onset of optical absorption in the film. The minimum envelope allows calculation of the film index in this region according to the following:

\[
n = \left[ M + \left( M^2 - s^2 \right)^{1/2} \right]^{1/2}
\]

\[
M = \frac{2s}{T_{\text{min}}} - \frac{s^2 + 1}{2}
\]

(12.5)
As the film becomes absorbing, the refractive index and extinction coefficient can be calculated using both maximum and minimum envelope functions according to equation (12.6).

\[
n = \left[ N + \left( N^2 - s^2 \right)^{1/2} \right]^{1/2}
\]

\[
N = 2s \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} + T_{\text{min}}} - \frac{s^2 + 1}{2}
\]

(12.6)

In the region of weak and medium absorption, \( x \) is no longer unity, and must be determined from the refractive index and envelope functions. Swanepoel describes two expressions for the absorbance using either the maximum (12.7) or minimum (12.8) transmission envelope. Both forms arrive at nearly identical results.

\[
x = \frac{E_M - \sqrt{E_M^2 - \left( n^2 - 1 \right)^3 \left( n^2 - s^4 \right)}}{\left( n - 1 \right)^3 \left( n - s^2 \right)}
\]

\[
E_M = \frac{8n^2 s}{T_{\text{max}}} + \left( n^2 - 1 \right) \left( n^2 - s^2 \right)
\]

(12.7) (12.8)
In the region of strong absorption, the refractive index and absorbance cannot be
determined independently, thus the index data from other spectral regions must be
extrapolated to shorter wavelengths. To accomplish this extrapolation, refractive index
data could be fit to the two-term Cauchy relation in (12.9) where $A$ and $B$ are empirical
costants. $A$ is unitless and $B$ has units of length squared.

$$n = A + \frac{B}{\lambda^2} \quad (12.9)$$

The Sellmeier equation, below, is another commonly used model for fitting of refractive
index values.

$$n^2 = 1 + \sum_{k=1}^{K} \frac{B_k \lambda^2}{\lambda^2 - C_k} \quad (12.10)$$

In equation (12.10) $B_k$ and $C_k$ are empirical constants where the former is unitless and the
latter in units of inverse length squared. A good fit is typically achieved using two terms
(K=1), but more precise extrapolation can be achieved using additional terms. Benefits are marginal for values of K beyond three.

Once refractive index data has been fitted to either the Cauchy or Sellmeier relations and subsequently extrapolated, the absorbance can be calculated using equation (12.11). In the presence of strong absorption, the transmission envelopes converge to a single curve $T_0$.

\[
x \approx \frac{(n-1)^3(n+s^2)}{16n^2s}T_0
\]

(12.11)

Lastly, the thickness of the film can be determined by the fringe spacing using (12.12) where $n$ is the refractive index, $d$ the film thickness, $\lambda$ the wavelength and $m$ is the order number for transmission maxima (integer) and minima (half-integer), respectively.

\[
2nd = m\lambda
\]

(12.12)
Equation (12.12) can be rewritten in the following way:

\[ 2nd = \left( m_1 - \frac{L}{2} \right) \lambda \]
\[ \frac{L}{2} = 2d \left( \frac{n}{\lambda} \right) - m_1 \]
\[ L = 0, 1, 2, \ldots \]  

(12.13)

where \( m_1 \) is the fringe order number and \( L \) is a positive integer. By plotting \( L/2 \) versus \( n/\lambda \) and then performing a linear fit, the film thickness is given by one-half the slope and the order of the first fringe is equal to the y-intercept.

Once the thickness is known, the absorbance data can be used to determine the absorption coefficient. An equation for absorbance in terms of the film absorption coefficient and thickness is given in (12.2) which can be solved for the absorption coefficient as in (12.14).

\[ \alpha = \frac{-\log x}{d} \]  

(12.14)
13 Appendix C: MATLAB Implementation

The following sections contain the MATLAB code used to implement Swanepoel’s method described previously. Effort has been made to document the code so that someone familiar with Swanepoel’s method and MATLAB may improve upon or correct this implementation. The script peakdet.m was released to public domain by its author and was downloaded for use in this work from the MATLAB file exchange website (http://www.mathworks.com/matlabcentral/fileexchange/).

13.1 Transmission.m

```matlab
function [trans, tmax, tmin, nf, nf_int, k, alpha, d, lambda]=transmission

mask = 400;

%Import data from Excel spreadsheet
[filename, pathname, filterindex]=uigetfile(’*.xls’);
data = xlsread(filename);
lambda = data(:,1);
trans_raw = data(:,2);

%Find peaks
dt = 0.001; %threshold for peak determination
trans=smooth(lambda, trans_raw, 10); %’rlowess’);
[tmax, tmin]=peakdet(trans, dt);

%Sapphire Substrate index (default)
%Data from Melles Griot website at discrete lambda
%Interpolated for intermediate values
ns = [1.8337 1.7970 1.7858 1.7754 1.7731 1.7718 1.7708 1.7660];
lams = [265.2 351.1 404.7 488 514.5 532 546.1 632.8];
ns_int = interp1(lams, ns, lambda, ’cubic’);
Ts = 2.*ns_int./(ns_int.^2+1);

%Find fringe max/min and envelope functions
[Tmax, Tmin, lambda1, lambda2]=envelope(lambda, trans, tmax, tmin, Ts);
figure(1)
```

hold on;
plot(lambda, trans, 'b');
plot(lambda, Ts, 'g');
plot(lambda(1:length(Tmax)), Tmax, 'k');
plot(lambda(1:length(Tmin)), Tmin, 'k');
plot(lambda(tmax(:,1)),tmax(:,2), 'ro');
plot(lambda(tmin(:,1)),tmin(:,2), 'rx');
hold off;

%Calculate index and absorbance in weak/med absorption
[nf] = swanepoel1(Tmax, Tmin, lambda, ns_int, lambda1, lambda2);

%Extrapolate index data into strongly absorbing region
%Extrapolate calculated index values using 2-term Cauchy relation
figure(2)
[cf_, gof] = cauchyfit(lambda(1:length(Tmax)), nf, mask);
Cauchy = coeffvalues(cf_);
nf_int = Cauchy(1)+Cauchy(2)./lambda.^2;

%Absorbance calculation
for j = 1:length(Tmax)
    Emax(j) = ((8*nf_int(j)^2*ns_int(j))/Tmax(j))+(nf_int(j)^2-1)*((Tmax(j)-1)^3* ns_int(j)^2)/((nf_int(j)-1)^3*(nf_int(j)+ns_int(j)^2));
    x(j) = (Emax(j)-sqrt(Emax(j)^2-(nf_int(j)^2-1)^3*(nf_int(j)^2-ns_int(j)^4)))/((nf_int(j)-1)^3*(nf_int(j)-ns_int(j)^2));
end

%Calculate absorbance in absorbing region using extrapolated index data
%for k = 1:length(lambda)
%    if lambda(k) <= lambda2
%        x(k) = Tmin(k)*(nf_int(k)-1)^3*(nf_int(k)+ns_int(k)^2)/(16*nf_int(k)^2*ns_int(k);
%    end
%end

[d, m, cf_lin, gof_lin]=thickness(tmax, tmin, nf_int, lambda);

alpha = -log(x)/d;
lam_short = lambda(1:length(alpha));
lam_short = lam_short,'

k = (alpha.*lam_short)/(4*1000000*pi);
figure(3)
plot(lambda(1:length(alpha)), alpha)
disp('Film thickness:')
disp(d)
disp('Fringe order:')
disp(m)
disp('Linear Fit results:')
disp(cf_lin)
disp(gof_lin)

disp('Cauchy results:')
disp(cf_)
disp(gof)

%Prepare output for EXCEL spreadsheet
labels= {'Wavelength', 'n', 'k', 'alpha (per cm)', 'Fitted n'};
data_out(1:length(lambda),1) = lambda;
data_out(1:length(nf),2) = nf;
data_out(1:length(k),3) = k;
data_out(1:length(alpha),4) = alpha;
data_out(1:length(nf_int),5) = nf_int;

[M, N] = size(data_out);

for m=1:M
    for n=1:N
        if data_out(M,N) == 0
            data_out(M,N) = NaN;
        end
    end
end

%Output data to EXCEL spreadsheet
(outfile, outpath) = uiputfile('*.xls', 'Save data to');
xlswrite(outfile, labels, 'A1:E1');
xlswrite(outfile, data_out, 'A2:E600');

13.2 Envelope.m

function [max_interp, min_interp, lambda1, lambda2]=envelope(wavelength, trans, tmax_raw, tmin_raw, Ts)

%[max_interp, min_interp, lambda1]=transmission(wavelength, trans, dt)
%Locate peaks in vector trans, with peak threshold dt.
%lambda1 is boundary between weak/med absorption and transparency.
%lambda2 is boundary between weak/med absorption and strong absorption.

%Slt width correction.
S=0;
for h = 2:length(tmax_raw)
    wmax(h)=tmax_raw(h-1,1)-tmax_raw(h,1);
    tmax(h,2)=tmax_raw(h,2)+(tmax_raw(h,2)*S/wmax(h))^2;
    tmax(h,1)=tmax_raw(h,1);
end
for g = 2:length(tmin_raw)
    wmin(g)=tmin_raw(g-1,1)-tmin_raw(g,1);
    tmin(g,2)=tmin_raw(g,2)-(tmin_raw(g,2)*S/wmin(g))^2;
    tmin(g,1)=tmin_raw(g,1);
end

tmax(1,:)=tmax_raw(1,:);
tmin(1,:)=tmin_raw(1,:);

%Set envelope functions equal to transmission spectrum in high
%absorption
%up to the first observed extrema point

merge = 0.77;

if tmax(1,1) < tmin(1,1)
    %max_interp(1:tmax(1,1)) = trans(1:tmax(1,1));
    %min_interp(1:round(0.8*tmin(1,1))) = trans(1:round(0.8*tmin(1,1)));
    max_interp(1:round(merge*tmax(1,1))) =
    trans(1:round(merge*tmax(1,1)));
    min_interp(1:round(merge*tmax(1,1))) =
    trans(1:round(merge*tmax(1,1)));
    lambda2=wavelength(tmax(1,1));
    flag = 1;
else
    %min_interp(1:tmin(1,1)) = trans(1:tmin(1,1));
    %max_interp(1:round(0.8*tmin(1,1))) = trans(1:round(0.8*tmin(1,1)));
    min_interp(1:round(merge*tmin(1,1))) =
    trans(1:round(merge*tmin(1,1)));
    max_interp(1:round(merge*tmin(1,1))) =
    trans(1:round(merge*tmin(1,1)));
    lambda2=wavelength(tmin(1,1));
    flag = 0;
end

%Parabolic interpolation to get transmission envelope
N = length(max_interp);
M = length(min_interp);

%Limit envelope length to furthest fringe extreme
maxTmax=max(tmax(:,1));
maxTmin=max(tmin(:,1));
if maxTmax > maxTmin
    max_int = maxTmin;
else max_int = maxTmax;
end

tmax1(1,1)=N;  %round(0.8*tmax(1,1));
tmax1(1,2)=trans(N);  %round(0.8*tmax(1,1));
tmin1(1,1)=M;  %round(0.8*tmin(1,1));
tmin1(1,2)=trans(M);  %round(0.8*tmin(1,1));
for j = 1:length(tmax)
    tmax1(j+1,:)=tmax(j,:);
end

for k = 1:length(tmin)
    tmin1(k+1,:)=tmin(k,:);
end

disp('Left click to move point 1 nm to the left. Right click to shift right. Middle click to END')
for a = 2:length(tmax1)
    button = 0;
    diff = 0;
    while button ~= 2
        max_interp(N+1:length(trans)) = interp1(wavelength(tmax1(:,1)),
            tmax1(:,2), wavelength(N+1:length(trans)), 'pchip');
        figure(1)
        clf
        hold on
        axis([wavelength(tmax1(a,1))-25 wavelength(tmax1(a,1))+25
            tmax1(a,2)-.1 tmax1(a,2)+.1])
        plot(wavelength(1:length(max_interp)), max_interp);
        plot(wavelength, trans, 'r');
        plot(wavelength(tmax1(a,1)), tmax1(a,2), 'bo')
        hold off
        [x,y, button] = ginput(1);
        if button == 1
            diff = -1;
        elseif button == 3
            diff = +1;
        else diff = 0;
        end
        tmax1(a,1) = tmax1(a,1)+diff;
        tmax1(a,2) = trans(tmax1(a,1));
    end
end

disp('Left click to move point 1 nm to the left. Right click to shift right. Middle click to END')
for a = 2:length(tmin1)
    button = 0;
    diff = 0;
    while button ~= 2
        min_interp(M+1:length(trans)) = interp1(wavelength(tmin1(:,1)),
            tmin1(:,2), wavelength(M+1:length(trans)), 'pchip');
        figure(1)
        clf
        hold on
        axis([wavelength(tmin1(a,1))-25 wavelength(tmin1(a,1))+25
            tmin1(a,2)-.1 tmin1(a,2)+.1])
        plot(wavelength(1:length(min_interp)), min_interp);
        plot(wavelength, trans, 'r');
        plot(wavelength(tmin1(a,1)), tmin1(a,2), 'bo')
        hold off
        [x,y, button] = ginput(1);
        if button == 1
            diff = -1;
        elseif button == 3
            diff = +1;
        else diff = 0;
        end
        tmin1(a,1) = tmin1(a,1)+diff;
        tmin1(a,2) = trans(tmin1(a,1));
    end
end
axis([wavelength(tmin1(a,1))-25 wavelength(tmin1(a,1))+25
tmin1(a,2)-.1 tmin1(a,2)+.1])
plot(wavelength(1:length(min_interp)), min_interp);
plot(wavelength, trans, 'g');
plot(wavelength(tmin1(a,1)), tmin1(a,2), 'bo')
hold off

[x, y, button] = ginput(1);
if button == 1
diff = -1;
elseif button == 3
diff = +1;
else diff = 0;
end

tmin1(a,1) = tmin1(a,1)+diff;
tmin1(a,2) = trans(tmin1(a,1));
% tmin1(a,:
% diff
end
end

[max_interp(N+1:max_int), ex1, ex2] = ppinterp(wavelength(tmax1(:,1)),
tmax1(:,2), wavelength(N+1:max_int));
[min_interp(M+1:max_int), ex3, ex4] = ppinterp(wavelength(tmin1(:,1)),
tmin1(:,2), wavelength(M+1:max_int));

max_interp=max_interp(1:max_int);
min_interp=min_interp(1:max_int);

% Find boundary of weak/med absorption and transparent regions
for m = 1:length(max_interp)
    if max_interp(m) < Ts(m)
        lambda1 = wavelength(m);
        % Film is transparent for lambda longer than lambda1
    end
end
end

close(1);

13.3 Peakdet.m

function [maxtab, mintab]=peakdet(v, delta)
% PEAKDET Detect peaks in a vector
% [MAXTAB, MINTAB] = PEAKDET(V, DELTA) finds the local
% maxima and minima ("peaks") in the vector V.
% A point is considered a maximum peak if it has the maximal
% value, and was preceded (to the left) by a value lower by
% DELTA. MAXTAB and MINTAB consists of two columns. Column 1 contains indices in V, and column 2 the found values.

% Eli Billauer, 3.4.05 (Explicitly not copyrighted).
% This function is released to the public domain; Any use is allowed.

maxtab = []; 
mintab = [];

v = v(:); % Just in case this wasn't a proper vector

if (length(delta(:)))>1 
    error('Input argument DELTA must be a scalar'); 
end

if delta <= 0 
    error('Input argument DELTA must be positive'); 
end

mn = Inf; mx = -Inf; 
mnpos = NaN; mxpos = NaN;

lookformax = 1;

for i=1:length(v)
    this = v(i);
    if this > mx, mx = this; mxpos = i; end 
    if this < mn, mn = this; mnpos = i; end

    if lookformax
        if this < mx-delta 
            maxtab = [maxtab ; mxpos mx]; 
            mn = this; mnpos = i; 
            lookformax = 0;
        end
    else
        if this > mn+delta 
            mintab = [mintab ; mnpos mn]; 
            mx = this; mxpos = i;
            lookformax = 1;
        end
    end
end

13.4 Swanepoel1.m

function [nf] = swanepoel1(Tmax, Tmin, wavelength_raw, ns_int, lambda1, lambda2)
%Swanepoell.m
%Calculates film index, absorption coefficient and thickness of a thin
%film on a substrate using only optical transmission data, according
%to the method by Swanepoel.

% [nf]=swanepoel(Tmax, Tmin, lambda1, lambda2)
%nf: Film index as a function of wavelength

wavelength = wavelength_raw(1:length(Tmax));

%Calculate index and absorbance in transparent and weak absorption
regions
for j = 1:length(wavelength)
    if wavelength(j) > lambda1
        %Transparent region
        M(j) = (2*ns_int(j)/Tmin(j)) - 0.5*(ns_int(j)^2+1);  
        nf(j) = sqrt(M(j)+sqrt(M(j)^2-ns_int(j)^2));
    elseif wavelength(j) <= lambda1
        if wavelength(j) > lambda2
            %Weak/med absorption
            N(j) = 2*ns_int(j)*(Tmax(j)-Tmin(j))/(Tmax(j)*Tmin(j))+0.5*(ns_int(j)^2+1);  
            nf(j) = sqrt(N(j)+sqrt(N(j)^2-ns_int(j)^2)
        end
    end
end

13.5 Thickness.m

function [d, m, cf_, gof]=thickness(tmax_raw, tmin_raw, nf, wavelength)

%Thickness calculation
ext(1:length(tmin_raw)) = tmin_raw(:,1);
ext(length(tmin_raw)+1:length(tmin_raw)+length(tmax_raw)) = tmax_raw(:,1);
ext = sort(ext, 'descend');
less = 0;
for m = 1:length(ext)
    if ext(m) > length(wavelength)
        less = less+1;
    end
end
ext_arr(1:length(ext)-less,1) = wavelength(ext(1+less:length(ex)));
ext_arr(1:length(ext)-less,2) = nf(ext(1+less:length(ext)));
A = ext_arr(:,2)./ext_arr(:,1);
l=[0:length(A)-1].*0.5;
[cf_, gof]=modefit(A,l);
coeffs2 = coeffvalues(cf_);
d=coeffs2(1)*1e-7;
m=round(-coeffs2(2));
13.6 Cauchyfit.m

function [cf_, gof] = cauchyfit(lambda,n, mask)
%CAUCHYFIT    Create plot of datasets and fits
%   [CF_, GOF] = CAUCHYFIT(LAMBDA,N)
% Fits the refractive index n as a function of wavelength to
% the 2-term Cauchy dispersion relation. Applies a mask to ignore
% data in the highly absorbing region.
% Returns the model data (including coefficients) and the goodness
% of fit parameters.
% Creates a plot, similar to the plot in the main curve fitting
% window, using the data that you provide as input. You can
% apply this function to the same data you used with cftool
% or with different data. You may want to edit the function to
% customize the code and this help message.
% Number of datasets:  1
% Number of fits:  1

% Data from dataset "n vs. lambda":
% X = lambda:
% Y = n:
% Unweighted
%
% This function was automatically generated on 09-Jun-2009 15:26:02

% Set up figure to receive datasets and fits
f_ = clf;
figure(f_);
set(f_, 'Units', 'Pixels', 'Position', [440.667 243 680 484]);
legh_ = []; legt_ = {}; % handles and text for legend
xlim_ = [Inf -Inf]; % limits of x axis
ax_ = axes;
set(ax_, 'Units', 'normalized', 'OuterPosition', [0 0 1 1]);
set(ax_, 'Box', 'on');
axes(ax_); hold on;

% --- Plot data originally in dataset "n vs. lambda"
lambda = lambda(:);
n = n(:);
h_ = line(lambda,n,'Parent',ax_, 'Color', [0.333333 0 0.666667],...
    'LineStyle','none', 'LineWidth',1,...
    'Marker', '.', 'MarkerSize',12);
xlim_1 = min(xlim_1,min(lambda));
xlim_2 = max(xlim_2,max(lambda));

206
legh_(end+1) = h_;  
legt_(end+1) = 'n vs. lambda';

% Nudge axis limits beyond data limits
if all(isfinite(xlim_))
    xlim_ = xlim_ + [-1 1] * 0.01 * diff(xlim_);
    set(ax_,'XLim',xlim_)
end

% --- Create fit "Cauchy_2term"
% Apply exclusion rule "mask2"
%if length(lambda)~=600
%   error('Exclusion rule "mask2" is incompatible with lambda');
%end
ex_ = false(length(lambda),1);
ex_([]) = 1;
ex_ = ex_ | (lambda <= mask); %change to variable!!
fo_ = 
fitoptions('method','NonlinearLeastSquares','Robust','On','Algorithm','Levenberg-Marquardt');
ok_ = isfinite(lambda) & isfinite(n);
st_ = [0.07007463906274 0.3773896748545 ];
set(fo_,'Startpoint',st_);
set(fo_,'Exclude',ex_(ok_));
ft_ = fittype('A+B/x^2',...
    'dependent',{'y'},'independent',{'x'},...
    'coefficients',{'A', 'B'});

% Fit this model using new data
if sum(~ex_(ok_))<2  %% too many points excluded   
    error('Not enough data left to fit ''%s'' after applying exclusion rule ''%s''.','Cauchy_2term','mask2')
else
    [cf_, gof] = fit(lambda(ok_),n(ok_),ft_,fo_);
end

% Or use coefficients from the original fit:
if 0
    cv_ = { 1.889031506289, 12829.71172443};
    cf_ = cfit(ft_,cv_{:});
end

% Plot this fit
h_ = plot(cf_,'fit',0.95);
legend off;   % turn off legend from plot method call
set(h_(1),'Color',[1 0 0],...
    'LineStyle','-','LineWidth',2,...
    'Marker','none', 'MarkerSize',6);
legh_(end+1) = h_(1);
legt_{end+1} = 'Cauchy_2term';

% Done plotting data and fits. Now finish up loose ends.
hold off;
leginfo_ = {'Orientation', 'vertical'};
h_ = legend(ax_, legh_, legt_, leginfo_{:}); % create and reposition legend
set(h_,'Units','normalized');
t_ = get(h_,'Position');
t_(1:2) = [0.558578,0.498623];
set(h_,'Interpreter','none','Position',t_);
xlabel(ax_,'');               % remove x label
ylabel(ax_,'');               % remove y label

13.7 Modefit.m

function [cf_, gof] = modefit(A,L)
%MODEFIT    Create plot of datasets and fits
%   MODEFIT(A,L)
%   Creates a plot, similar to the plot in the main curve fitting
%   window, using the data that you provide as input. You can
%   apply this function to the same data you used with cftool
%   or with different data. You may want to edit the function to
%   customize the code and this help message.
%   
%   Number of datasets:  1
%   Number of fits:  1

% Data from dataset "L vs. A":
%   X = A;
%   Y = L;
%   Unweighted
%
% This function was automatically generated on 10-Jun-2009 14:36:49

% Set up figure to receive datasets and fits
f_ = clf;
figure(f_);
set(f_,'Units','Pixels','Position',[440.667 243 680 484]);
legh_ = []; legt_ = {};  % handles and text for legend
xlim_ = [Inf -Inf];       % limits of x axis
ax_ = axes;
set(ax_,'Units','normalized','OuterPosition',[0 0 1 1]);
set(ax_,'Box','on');
axes(ax_); hold on;

% --- Plot data originally in dataset "L vs. A"
A = A(:);
L = L(:);
**Code Snippet**

```matlab
h_ = line(A,L,'Parent',ax_, 'Color', [0.333333 0 0.666667],...
    'LineStyle', 'none', 'LineWidth', 1, ...
    'Marker', '.', 'MarkerSize', 12);
xlim_(1) = min(xlim_(1), min(A));
xlim_(2) = max(xlim_(2), max(A));
legh_(end+1) = h_;
legt_(end+1) = 'L vs. A';

% Nudge axis limits beyond data limits
if all(isfinite(xlim_))
    xlim_ = xlim_ + [-1 1] * 0.01 * diff(xlim_);
    set(ax_,'XLim',xlim_)
end

% --- Create fit "fit 1"
fo_ = fitoptions('method','LinearLeastSquares','Robust','On');
ok_ = isfinite(A) & isfinite(L);
ft_ = fittype({'2*x', '1'},
    'dependent','y','independent','x',
    'coefficients',{'a', 'c'});
% Fit this model using new data
[cf_, gof] = fit(A(ok_),L(ok_),ft_,fo_);

% Or use coefficients from the original fit:
if 0
    cv_ = { 625, -3.25};
    cf_ = cfit(ft_,cv_{:});
end

% Plot this fit
h_ = plot(cf_,'fit',0.95);
legend off; % turn off legend from plot method call
set(h_(1), 'Color', [1 0 0],...
    'LineStyle', '-', 'LineWidth', 2,...
    'Marker', 'none', 'MarkerSize', 6);
legh_(end+1) = h_(1);
legt_(end+1) = 'fit 1';

% Done plotting data and fits. Now finish up loose ends.
hold off;
leginfo_ = {'Orientation', 'vertical'};
h_ = legend(ax_, legh_, legt_, leginfo_{:}); % create and reposition
legend
set(h_, 'Units', 'normalized');
t_ = get(h_, 'Position');
t_(1:2) = [0.293137, 0.783747];
set(h_, 'Interpreter', 'none', 'Position', t_);
xlabel(ax_, ''); % remove x label
ylabel(ax_, ''); % remove y label
```

---

209
## Appendix D: Eu\(^{3+}\) Level Splittings in Cubic Gd\(_2\)O\(_3\)

Table 14.1. Photoluminescence peaks observed from the \(^5\)D\(_0\) → \(^7\)F\(_J\) levels in Eu:Gd\(_2\)O\(_3\).

<table>
<thead>
<tr>
<th>(2s^{2+1}L^J)</th>
<th>(\lambda_a^b) (nm)</th>
<th>(E_{exp}) (cm(^{-1}))</th>
<th>Trans.(^c)</th>
<th>(\Delta E) (cm(^{-1}))</th>
<th>(E_{calc}) (cm(^{-1}))</th>
<th>(E_{Y2O3}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^7)F(_0)</td>
<td>580.6</td>
<td>17219</td>
<td>(A_1)→(Z_1)</td>
<td>0</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>(^7)F(_1)</td>
<td>587.8</td>
<td>17008</td>
<td>(A_1)→(Y_1)</td>
<td>211</td>
<td>199</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>592.6</td>
<td>16870</td>
<td>(A_1)→(Y_2)</td>
<td>349</td>
<td>349</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>599.4</td>
<td>16678</td>
<td>(A_1)→(Y_3)</td>
<td>541</td>
<td>555</td>
<td>543</td>
</tr>
<tr>
<td>(^7)F(_2)</td>
<td>611.0</td>
<td>16362</td>
<td>(A_1)→(X_1)</td>
<td>857</td>
<td>874</td>
<td>859</td>
</tr>
<tr>
<td></td>
<td>613.0</td>
<td>16308</td>
<td>(A_1)→(X_2)</td>
<td>911</td>
<td>909</td>
<td>906</td>
</tr>
<tr>
<td></td>
<td>613.9</td>
<td>16286</td>
<td>(A_1)→(X_3)</td>
<td>933</td>
<td>933</td>
<td>949</td>
</tr>
<tr>
<td></td>
<td>625.0</td>
<td>16000</td>
<td>(A_1)→(X_4)</td>
<td>1219</td>
<td>1226</td>
<td>1217</td>
</tr>
<tr>
<td></td>
<td>629.8</td>
<td>15874</td>
<td>(A_1)→(X_5)</td>
<td>1345</td>
<td>1377</td>
<td>1380</td>
</tr>
<tr>
<td>(^7)F(_3)</td>
<td>650.6</td>
<td>15366</td>
<td>(A_1)→(W_1)</td>
<td>1853</td>
<td>1856</td>
<td>1847</td>
</tr>
<tr>
<td></td>
<td>651.5</td>
<td>15346</td>
<td>(A_1)→(W_2)</td>
<td>1873</td>
<td>1870</td>
<td>1867</td>
</tr>
<tr>
<td></td>
<td>652.6</td>
<td>15319</td>
<td>(A_1)→(W_3)</td>
<td>1900</td>
<td>1911</td>
<td>1907</td>
</tr>
<tr>
<td></td>
<td>655.0</td>
<td>15264</td>
<td>(A_1)→(W_4)</td>
<td>1955</td>
<td>1946</td>
<td>1949</td>
</tr>
<tr>
<td></td>
<td>656.9</td>
<td>15219</td>
<td>(A_1)→(W_5)</td>
<td>2000</td>
<td>2018</td>
<td>2021</td>
</tr>
<tr>
<td></td>
<td>633.0</td>
<td>15079</td>
<td>(A_1)→(W_6)</td>
<td>2140</td>
<td>2129</td>
<td>2130</td>
</tr>
<tr>
<td></td>
<td>662.1</td>
<td>15099</td>
<td>(A_1)→(W_7)</td>
<td>2120</td>
<td>2152</td>
<td>2160</td>
</tr>
<tr>
<td>(^7)F(_4)</td>
<td>686.7</td>
<td>14558</td>
<td>(A_1)→(V_1)</td>
<td>2661</td>
<td>2670</td>
<td>2669</td>
</tr>
<tr>
<td></td>
<td>693.3</td>
<td>14419</td>
<td>(A_1)→(V_2)</td>
<td>2800</td>
<td>2797</td>
<td>2800</td>
</tr>
<tr>
<td></td>
<td>695.6</td>
<td>14373</td>
<td>(A_1)→(V_3)</td>
<td>2846</td>
<td>2832</td>
<td>2846</td>
</tr>
<tr>
<td></td>
<td>704.1</td>
<td>14199</td>
<td>(A_1)→(V_4)</td>
<td>3020</td>
<td>3019</td>
<td>3014</td>
</tr>
<tr>
<td></td>
<td>706.3</td>
<td>14154</td>
<td>(A_1)→(V_5)</td>
<td>3065</td>
<td>3067</td>
<td>3080</td>
</tr>
<tr>
<td></td>
<td>707.9</td>
<td>14118</td>
<td>(A_1)→(V_6)</td>
<td>3101</td>
<td>3116</td>
<td>3119</td>
</tr>
<tr>
<td></td>
<td>710.8</td>
<td>14065</td>
<td>(A_1)→(V_7)</td>
<td>3154</td>
<td>3174</td>
<td>3163</td>
</tr>
<tr>
<td></td>
<td>711.9</td>
<td>14043</td>
<td>(A_1)→(V_8)</td>
<td>3176</td>
<td>3186</td>
<td>3178</td>
</tr>
<tr>
<td></td>
<td>712.6</td>
<td>14029</td>
<td>(A_1)→(V_9)</td>
<td>3190</td>
<td>3198</td>
<td>3190</td>
</tr>
</tbody>
</table>

\(^{a}\)Terminal multiplet manifold for radiative transition originating at \(^5\)D\(_0\) manifold.

\(^{b}\)PL spectrum obtained at 78 K.

\(^{c}\)Transitions between labeled Stark levels.

\(^{d}\)Calculated crystal field splitting. See Table 14.5.

\(^{e}\)Comparable Stark sublevels in C\(_2\) sites in cubic Eu:Y\(_2\)O\(_3\)\[124\].
Table 14.2. Photoluminescence peaks observed from the \( ^5D_1 \rightarrow ^7F_J \) levels in Eu:Gd_2O_3.

<table>
<thead>
<tr>
<th>2s( ^{2S+1} )L( ^J )</th>
<th>( \lambda ) (nm)</th>
<th>( \lambda ) (cm(^{-1}))</th>
<th>Trans.</th>
<th>( \Delta E ) (cm(^{-1}))</th>
<th>( E_{\text{calc}} ) (cm(^{-1}))</th>
<th>( E_{\text{Y}_2O_3} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^7F_0 )</td>
<td>527.7</td>
<td>18945</td>
<td>B(_1)→Z(_1)</td>
<td>0</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>( ^7F_1 )</td>
<td>533.8</td>
<td>18732</td>
<td>B(_1)→Y(_1)</td>
<td>213</td>
<td>199</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>537.5</td>
<td>18600</td>
<td>B(_1)→Y(_2)</td>
<td>345</td>
<td>349</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>543.0</td>
<td>18405</td>
<td>B(_1)→Y(_3)</td>
<td>540</td>
<td>555</td>
<td>543</td>
</tr>
<tr>
<td>( ^7F_2 )</td>
<td>552.8</td>
<td>18088</td>
<td>B(_1)→X(_1)</td>
<td>857</td>
<td>874</td>
<td>859</td>
</tr>
<tr>
<td></td>
<td>554.4</td>
<td>18034</td>
<td>B(_1)→X(_2)</td>
<td>911</td>
<td>909</td>
<td>906</td>
</tr>
<tr>
<td></td>
<td>554.1</td>
<td>18044</td>
<td>B(_1)→X(_3)</td>
<td>935</td>
<td>933</td>
<td>949</td>
</tr>
<tr>
<td></td>
<td>564.0</td>
<td>17726</td>
<td>B(_1)→X(_4)</td>
<td>1219</td>
<td>1226</td>
<td>1217</td>
</tr>
<tr>
<td></td>
<td>567.6</td>
<td>17600</td>
<td>B(_1)→X(_5)</td>
<td>1345</td>
<td>1377</td>
<td>1380</td>
</tr>
<tr>
<td>( ^7F_3 )</td>
<td>582.6</td>
<td>17160</td>
<td>B(_1)→W(_1)</td>
<td>1850</td>
<td>1856</td>
<td>1847</td>
</tr>
<tr>
<td></td>
<td>585.4</td>
<td>17078</td>
<td>B(_1)→W(_2)</td>
<td>1867</td>
<td>1870</td>
<td>1867</td>
</tr>
<tr>
<td></td>
<td>586.9</td>
<td>17044</td>
<td>B(_1)→W(_3)</td>
<td>1901</td>
<td>1911</td>
<td>1907</td>
</tr>
<tr>
<td></td>
<td>588.3</td>
<td>16995</td>
<td>B(_1)→W(_4)</td>
<td>1950</td>
<td>1946</td>
<td>1949</td>
</tr>
<tr>
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\(^a\)Terminal multiplet manifold for radiative transition originating at \( ^3D_1 \) manifold.
\(^b\)PL spectrum obtained at 78 K.
\(^c\)Transitions between labeled Stark levels.
\(^d\)Calculated crystal field splitting. See Table 14.5.
\(^e\)Comparable Stark sublevels in C\(_2\) sites in cubic Eu:Y\(_2O_3\)[124].
Table 14.3. Photoluminescence peaks observed from $^5D_1 \rightarrow ^7F_j$ levels in Eu:Gd$_2$O$_3$.

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$^a$Terminal multiplet manifold for radiative transition originating at $^3D_1$ manifold.

$^b$PL spectrum obtained at 78 K.

$^c$Transitions between labeled Stark levels.

$^d$Calculated crystal field splitting. See Table 14.5.
Comparable Stark sublevels in C₂ sites in cubic Eu:Y₂O₃[124].

Table 14.4. Photoluminescence peaks observed from \(^{5}D_2\rightarrow^{7}F_j\) levels in Eu:Gd₂O₃.

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<th>Trans.(^d)</th>
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\(^a\)Terminal multiplet manifold for radiative transition originating at \(^{3}D_2\) manifold.
bPL spectrum obtained at 78 K.
cTransitions between labeled Stark levels.
dCalculated crystal field splitting. See Table 14.5.
eComparable Stark sublevels in C2 sites in cubic Eu:Y2O3[124].
fPossible magnetic dipole transitions from C3i site.

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<td>3067</td>
<td>-2</td>
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<td>V\textsubscript{6}</td>
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<td>3116</td>
<td>-15</td>
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<tr>
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<td>3164</td>
<td>-10</td>
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<tr>
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<td>-10</td>
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<td>V\textsubscript{9}</td>
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<td>3198</td>
<td>-9</td>
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<tr>
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<td>3785</td>
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<tr>
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<td>3825</td>
<td>3817</td>
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<td>U\textsubscript{4}</td>
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<tr>
<td>U\textsubscript{5}</td>
<td>3900</td>
<td>3898</td>
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Table 13.5 (continued)

<table>
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<th>U</th>
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<td>U8</td>
<td>4131</td>
<td>4124</td>
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<td>U10</td>
<td>4234</td>
<td>4234</td>
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<tr>
<td>U11</td>
<td>4244 (^f)</td>
<td>4248</td>
<td>-4</td>
</tr>
</tbody>
</table>

\[^5D_0\] A1  | 17219 | 17216 | 3  |

\[^5D_1\] B1  | 18945 | 18935 | 10 |
\((18972)\) B2 | 18960 | 18961 | -1 |
\((10)\)     B3  | 19010 | 19029 | -19|

\[^5D_2\] C1  | 21371 | 21376 | -5 |
\((21439)\) C2 | 21376 | 21386 | -10|
\((8.5)\)    C3  | 21403 | 21393 | 10 |
C4  | 21499 | 21494 | 5  |
C5  | 21546 | 21540 | 6  |

\(^a\) Multiplet manifolds; first parenthesis indicates experimental barycenter; second parenthesis indicates standard deviation for that manifold.
\(^b\) Stark sublevels of manifold; transition between sublevels given in Table 14.1 and Table 14.2.
\(^c\) Based on \(^5D_0\rightarrow\(^7F_0\) transitions (Table 14.1) and \(^5D_2\rightarrow\(^7F_5\) transitions (Table 14.4).
\(^d\) Calculated splitting; parameters given in Table 14.5.
\(^e\) Total of 43 levels used in modeling the splitting; \(\sigma = 9.8 \text{ cm}^{-1}\).
\(^f\) Obtained from deconvoluted PL spectrum.