III-Nitride Nanostructures for Optoelectronic and Magnetic Functionalities: Growth, Characterization and Engineering

Dissertation

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By

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Abstract

Over the last two decades, group III-nitride compound semiconductor materials have revolutionized modern optoelectronics and high frequency devices. In this work, III-nitride based compound semiconductor nanostructures with tailor-made optoelectronic and magnetic functionalities are investigated. The first research vector concerns design, synthesis and characterization of novel ferromagnetic materials based on III-nitrides involving manipulation of magnetic dopants as well as heteroepitaxy of ferromagnetic materials. Synthesis of III-nitride-GdN epitaxial, ferromagnetic nanocomposites is developed using the technique of plasma assisted molecular beam epitaxy. Magnetic, structural and optical characteristics of these materials are tailored to yield nanocomposites which preserve the structural and semiconducting characteristics of GaN while integrating the ferromagnetic compound GdN. In the second part of this work, the growth, characterization and development of self-assembled III-nitride nanowire based ultraviolet light emitting diodes is explored. These devices are formed by a novel heterostructure which utilizes synthetic gradients in dipole moment per unit volume to mitigate many of the shortcomings of traditional thin film wide bandgap light emitting diode (LED) device designs for deep ultraviolet wavelengths. The optical and electronic characteristics of these devices are investigated by a number of spectroscopic methods. Combination of this heterostructure with the epitaxy of GdN on III-nitrides is found to yield a unique electrical device which allows
electrical modulation of narrow linewidth, ultraviolet Gd intra-f-shell fluorescence at significantly lower voltages compared to existing technology. During the course of this work, a number of unique scientific instruments were developed to aid research efforts in the Myers group. The design, construction and operation of a wide spectral bandwidth, ultrafast semiconductor photoluminescence characterization system, a spectroscopic probe station for high throughput measurements of deep ultraviolet LEDs and a modified closed cycle He cryostat for magnetic field dependent low level optoelectronic measurements is described. The dissertation closes with a discussion of various collaborative works of the author as well as a broad summary, conclusions and suggested future directions.
This work is dedicated to my beautiful love and wife, Elisabeth.
Acknowledgments

Success in modern science requires individuals to work collectively to solve the ever increasingly complex problems which we are dealt. The work described in this dissertation is no exception. Without the efforts and support of my friends and colleagues at OSU, many of the chapters of this dissertation would never have been written. I would like to begin by mentioning my fellow members of the Myers research group, particularly those senior graduate students who I came in under, learned a great deal from and spent the majority of my time with over the years. Santino Carnevale is an exceptional scientist, careful empiricist and a great friend. He was kind enough to teach me MBE growth, put up with my never ending questions about nuts and bolts on the system, and grow me many interesting samples to measure spectra and device characteristics from. We created a successful team with the PINLEDs project, now in its second graduate student generation and still going strong. Jing Yang is one of the nicest and most patient people I have ever met. She taught me thin film growth, x-ray diffractometry and atomic force microscopy and how to make plots that pleased the boss. Together, we got the now mature GdN nanocomposite project off the ground. I always look forward to her delicious Chinese cooking at group get-togethers.

I am forever indebted to the efforts of my advisor, Prof. Roberto Myers. He works tirelessly to provide funding for his students, comes up with publishable ideas,
is always willing purchase top shelf hardware and has encouraged and supported my
love of designing and constructing instrumentation throughout my years at OSU. I
particularly thank him for giving me the opportunity to design, construct and manage
a state of the art spectroscopy laboratory during the last four years.

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many students that have joined the group after me. I would like to thank them for
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a great empiricist, a rare and coveted combination of skills sure to bring him great
fame and success in his career. I feel secure in that the PINLEDs project now rests
in his capable hands. Zihao is one of the most dedicated, hardworking people that I
know. He is a tireless perfectionist who will not cease work until the task is complete.
In my third year, Brandon Giles, a physics student from UC Berkley joined the Myers
group. I knew from the start that Brandon would grow to replace me as the optics
guru of the group. We had a ton of fun designing and constructing a major cryostat
modification that enabled experiments that will become a substantial part of his and
other group members dissertations. I have taken great pleasure in watching him grow
his skills in Labview and instrumentation control over the last couple of years. In
my fourth and final year, two new students joined the Myers group. Brelon May,
who will take over the GdN NP project from me, has already shown great prowess as
a crystallographer and willingness to be a big help with MBE system maintenance.
John Jamison, our first group member with an undergraduate degree in MSE, has
already demonstrated the ability to learn optics and was a tremendous help with
getting most of the fab work for the spectroscopic probestation done in the physics student machine shop.

I would like to thank my fellow GEN930 MBE growers (Digbijoy Nath, Sriram Krishnamoorthy, Fatih Aykol, A.T.M. Sarwar, Santino Carnevale and Jing Yang) for all of their hard work during openings, system calibrations and recovery from the disaster that was the 2013 plasma source failure. I particularly want to acknowledge the work of the SEAL manager, Mark Brenner, who is responsible for all of the systems in DL095. We all endured significant hardship in order to bring the system back online in 2013 and will be forever closer for it.

During the course of the last four years, I have grown a passion for design and construction of scientific instruments. I have been extremely fortunate to have had access to the Physics Dept. student machine shop which is equipped with a full complement of manual machines and inspection equipment, so long as you can find it. I must thank the talented craftsman Josh Gueth, Jon Shover and Pete Gosser that run the shop in physics and have always been willing to answer my questions about techniques and operations on the machines as well as help me out to make a small part in a pinch.

I must also thank those individuals that encouraged me to stay the course in science and engineering during my undergraduate career and motivate me to pursue an advanced degree. My undergraduate advisors Prof. Bradley Trees and Prof. Robert Kaye and instructor Prof. Thomas Dillman at Ohio Wesleyan University provided direction and encouragement early on with my studies. Additionally, I was exceptionally fortunate to have the experience of interning in a small research and development company, BerrieHill Research Corporation, during my summers and
breaks from school during undergraduate. Under the direction of Dr. Tri Van, Dr. Jeffery Berrie and Dave Kuhl, I learned invaluable skills, habits and techniques that I continue to use and build on to this day. I very much look forward to working with these exceptional individuals again post-graduation.

I must thank my parents. Without their unending support and sacrifice, I would never have made it to this point in my professional development. My mother, Ann Kent, has always encouraged my curiosity and creativity. She allowed me to disassemble every mechanical thing in sight as a child, put up with my car projects in our crowded garage and my server farms in the basement. She taught me the joy of discovery. My father, William Kent, has always challenged me to push the limits of my knowledge. He taught me the love of science, the fascination with the natural world and the reward of hard work. Without his encouragement, financial support, exciting technical discussions and advice, I would never have been successful in pursuing a technical degree. My stepmother, Gayle Gyure, has taught me the need for balance in one's life. She has always encouraged me to further develop my creativity in areas not directly related to technical work, something I very much hope to do more of in years to come. I love you all.

Lastly, I thank my wife. Liz, you are the greatest joy in my life. Your support and encouragement over the last seven years that we have spent with each other has been unending and invaluable. This dissertation is but a mere stepping stone in the life we continue to build together.
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Chapter 1: Introduction and Overview of the Dissertation

Over the last three decades III-nitride semiconductor compounds (GaN, InGaN, AlGaN) have moved from relative technological obscurity towards near complete dominance in large portions of the semiconductor device market. This rapid emergence of III-nitride based solid state technology has been driven by a number of unique materials properties present in the system. The materials combine an extraordinarily large variation in bandgaps (5.3 eV) over a relatively small lattice constant range, giving rise to many possibilities for coherently strained heteropitaxial structures and bandgap engineering. Moreover, the presence of a direct bandgap over the full range of alloy compositions enables design and production of efficient solid state light emitters in the visible, near ultraviolet and potentially deep ultraviolet regions of the electromagnetic spectrum. The highly ionic character of atomic bonds in the system, combined with a non-centro symmetric crystal structure gives rise to large polarization fields in the semiconductor and large bound charge discontinuities at heterointerfaces, making possible high electron mobility transistors (HEMTs) as well as devices which are extremely tolerant to power fluctuations, electromagnetic pulses, radiation damage and thermal cycling.

Technologically, the largest impact of nitride based devices have been in the areas of solid state lighting and high power, high frequency transistors. Light emitting
diode (LED) solid state lighting devices based on the pseudobinary alloy InGaN have experienced considerable development over the last two decades and currently operate with wall plug efficiency greater than 50%[8]. Progress in this area has primarily been driven by government regulation designed to reduce energy consumption due to inefficient blackbody based light sources such as tungsten filament light bulbs. III-nitride optoelectronics have enabled commercial production of solid state lasers in the blue and near ultraviolet. The extraordinary tolerance[9] of nitride based devices to harsh environments involving ionizing radiation, high ambient temperatures and high electric fields have attracted much attention from the defense and aerospace industries over the years and resulted in a rapid adoption of III-nitride heterostructure based RF power devices.

This dissertation is principally concerned with the modification and enhancement of the native optical, electrical and magnetic properties of these compounds towards relevant technological applications. In the first part of the thesis, the functionalization of III-nitride compounds with ferromagnetism via a number of methods involving magnetic doping of heterostructures, epitaxial growth of embedded rare earth nanoparticles and growth of epitaxial, ferromagnetic thin films on GaN is investigated. This first section consists primarily of empirical work involving thin film growth by plasma assisted molecular beam epitaxy (PAMBE) and subsequent structural, magnetic, electrical and optical characterization via a number of complementary techniques. In the second half, the growth, design and development of a unique light emitting diode heterostructure based on self-assembled, catalyst free III-nitride nanowires are discussed. This device offers promise in overcoming some of the chief
limitations for developing efficient solid state light emitters which operate in the deep ultraviolet (UVB, UVC) bands of the electromagnetic spectrum.

In the process of performing the experimental work contained in this thesis, a number of unique, standalone scientific instruments were designed, constructed and developed by the author to aid in throughput, reproducibility and quality of the experimental data collected and analyzed in this dissertation. The design, construction calibration and development of these instruments are described in a number of the appendices.

Each of the chapters of the thesis consist of original, peer reviewed work of the author. Chapters will begin with a broad overview of the scientific problem, outlining real world device applications as well as societal implications of successful development. This is followed by a technical discussion of the fundamental physics which is directly relevant to the design and analysis of experiments, devices and equipment in each section. Next, details of the experimental techniques used in the collection and interpretation of the data are provided. Finally, the main scientific findings will be described, analyzed and summarized. Each chapter will conclude with a discussion of broad implications of the results as well as suggestions for future scientific and engineering work in area.
Chapter 2: Dilute magnetic doping of III-nitrides with Gadolinium

2.1 Integration of ferromagnetism with semiconductors.

The integration of magnetism with semiconductors, a field popularized by the success of the dilute magnetic semiconductor Ga$_{1-x}$Mn$_x$As[10], has been recently extended to nitrides with reports of ferromagnetism in dilute Gd$_x$Ga$_{1-x}$N alloys and successful heteroepitaxial growth of the rare earth ferromagnetic compound GdN on GaN. Control and manipulation of spins in semiconductors, an important area of research for the area of spin electrons (commonly abbreviated “spintronics”), requires development of materials which are either simultaneously magnetic and semiconducting or magnetic materials which can be epitaxially integrated with existing semiconductors. GaN is a very promising candidate material for development of a semiconductor spintronics system due to long spin coherence times and strong spin orbit coupling[11].

The area of spintronics seeks to accomplish the transmission and processing of information by manipulation of the spin quantum number of a given electronic state. The realization of a room temperature ferromagnetic semiconductor is an important goal for the field, because it would, in principle, allow for the combination of
information processing and storage in a single, monolithic device[1]. In order to accomplish this feat, suitable materials for spin injection and detection must be developed, which typically are ferromagnetic metals or semiconductors. Following the prediction of above room temperature Curie points in Mn-doped nitrides by Dietl and coworkers[12] in 2000 and subsequent report of room temperature ferromagnetism in Gd:GaN by Ploog’s group in 2005[13], the magnetic properties of Gd:GaN became of particular interest to spintronics related research.

Very few natively ferromagnetic semiconductors exist and those that do suffer from difficulties in preparation of adequate material quality and/or very low Curie temperatures[10]. More recently, non-magnetic semiconductors have been alloyed with magnetic ions such as Mn or Fe to yield materials which combines the properties of ferromagnets with a semiconductor[10]. These materials, known as ferromagnetic semiconductors have become an important area of inquiry in the field of spintronics, because they allow for epitaxially integrated material which can function as a spin polarizer or “injector” or equally as a spin filter or “detector”[10]. The mechanism of ferromagnetic ordering in these systems is inherently more complex due to the fact that delocalized charge carriers (electrons or holes) participate strongly. In general, ferromagnetic materials that possess charge carriers which actively participate in ferromagnetism, such as many $d$-shell magnetic metals (Fe, Ni), can be described by a spin split density of states (Fig. 2.1a.), whereby the spin-down electrons will be favored by an energy factor of the Zeeman splitting $g_e\mu_B H[14]$.

The most widely studied ferromagnetic semiconductor, Ga$_x$Mn$_{1-x}$As has shown much promise, yielding realization of many important devices and materials experiments. Notable has been demonstration of electric field gating of ferromagnetism
Figure 2.1: Dilute magnetic semiconductors. a. Spin split density of states, from Wolf and Awschalom[1] and b. Demonstration of electric field controlled ferromagnetism in (In,Mn)As, from Ohno[2] (Fig. 2.1) by Ohno in 2000, which conclusively demonstrated carrier-mediated ferromagnetism in GaMnAs[2], which has led GaMnAs to be the only material widely accepted as a “true” ferromagnetic semiconductor. Ferromagnetism in Ga$_{1-x}$Mn$_x$As proceeds not by the direct exchange interaction, but rather by interaction of spin polarized holes with localized Mn$^{2+}$ acceptors. This is called carrier-mediated ferromagnetism and is formally characterized by the RKKY interaction originally proposed by Ruderman and Kittel in 1954[15]. In this way, a dilute amount of a magnetic ion can give rise to long range magnetic order in a material, even if the individual magnetic ions do not couple magnetically to each other.

In spite of its success as a prototype material for spintronics, Ga$_x$Mn$_{1-x}$As is hampered by a below room temperature Curie point and poor solubility of the Mn ion in GaAs, leading to the necessity of low temperature highly non-equilibrium growth and thus high defect content in the material. Because of this, the community has been actively seeking out materials which could offer higher solubility of magnetic dopants
and function at room temperature, which has led to development of many novel ferromagnetic oxides and nitrides[16]. Ferromagnetism in dilutely Gd-doped GaN prepared by NH$_3$ molecular beam epitaxy ([Gd] $\approx 10^{18}$ cm$^{-3}$) was originally reported by Dhar and coworkers in 2005[13, 17]. In addition to an above room temperature Curie point, they showed that the saturation magnetization of their samples, when normalized to the amount of Gd incorporated, was orders of magnitude larger than the expected moment due to the seven unpaired electrons of Gd$^{3+}$ ion, causing them to label the magnetism “colossal”. This result of the “colossal” magnetic moment quickly became highly controversial, as multiple groups found that the magnitude of the moment varied wildly between growths at identical conditions and sample’s magnetization appeared to decrease with time[18]. Subsequent investigations of Gd-ion-implanted material confirmed Dhar’s initial results, but were equally silent as to the mechanism of magnetic ordering or the interaction of Gd the free carriers of the films[19, 20]. Following these initial reports, Lo, et. al. fashioned an AlGaN/GaN high electron mobility transistor heterostructure, which they subjected to Gd ion implantation[21]. This device was characterized by low temperature magnetotransport studies, whereby the authors were able to observe anomalous behavior in the Hall effect signal and n-type conduction in the electron sheet charge at the AlGaN/GaN interface, indicating coupling of charge carrying electrons to the magnetization of the lattice.

The report by Khaderbad, et. al. [20] outlines the effect of annealing the films after ion implantation. They showed a net decrease in the magnetization after annealing, which suggest that the interaction of Gd with a thermodynamically unstable set of defects in the structure is responsible for the observation of ferromagnetism. This
hypothesis was further supported by the work of Bedoya-Pinto and colleagues[22], who, by conducting variable temperature magnetotransport studies on Gd:GaN films grown by MBE, concluded that their material exhibited variable range hopping transport, which is known to occur in semiconductors with a critically large amount of point defects. Unfortunately, the process of ion implantation imparts a very large amount of structural defects on the sample and thus it is difficult to make sound conclusions about native defects based on such studies. Davies and coworkers[23] then showed that when Gd is co-implanted with Si, considerably larger magnetic moments result. Furthermore, they showed magnetization data for field orientations, both in and out of the plane of the sample, which showed a striking type of anisotropy, that the out of plane field orientation (eg. $H \parallel [0001]$) gave considerably larger magnetization values. This result taken at face value is counterintuitive, given that thin films typically exhibit strong preference for in-plane magnetization, due to shape anisotropy. Out of plane preference demonstrates intrinsic anisotropy in these materials. Mishra and colleagues[24] later reported photoconductive spectroscopy investigations of Gd:GaN films which indicated a characteristic defect level around 3.0eV that increased in intensity when Gd is added to the system.

These experimental results sparked much interest among theorists eager to explain the puzzling existence of “excess” magnetic moment. Most studies utilized density functional theory, which has become popular in recent years due to demonstration of the ability to predict configurational energies for various types of defect structures and ferromagnetic ordering in semiconductors[25]. To date, the agreement amongst individual studies as to which defect is responsible for the anomalous ferromagnetism in Gd:GaN is relatively poor. However, multiple groups[26, 27] have been able to show
energetic favorability of ferromagnetic spin configurations of native defect-Gd centers which result in a moment larger than that due to the Gd$^{3+}$ ion alone, an important step along the road toward understanding of the magnetism in this system. Recently, Roever and colleagues published a detailed, systematic account of the difficulties in controlling and understanding this material[18]. Notably, they provided data over multiple years which demonstrated the difficulties involved with preparing materials which were consistently magnetic as well as the fact that the magnetic moment of the few successful samples decreased with time.

In summary, as of 2011, much work remained to understand and be able to manipulate the anomalous magnetism present in the Gd:GaN system. It was clear that the magnetic moment depends strongly on material quality and, in fact, seems to be inversely proportional to the quality of the samples. Toward this end, this material was synthesized in the Myers’ research group by PAMBE and its behavior was characterized. Magnetic, electronic and structural investigations are the topic of this chapter.

2.2 Atomic Origins of Magnetism

The phenomenon of magnetism in materials is fundamentally quantum mechanical in origin and arises from quantization of the orbital and spin angular momentum of electrons. In fact, classical mechanics famously predicts that all materials are non-magnetic if a continuum of angular momentum values are allowed, as originally shown by Bohr in his doctoral dissertation[28]. Magnetism manifests itself in terms of three principal mechanisms: the deformation of atomic orbitals due to a field gradient, the induced magnetic moment due to circulation of electrons around the nucleus,
known as the “orbital” contribution, and, finally, the intrinsic moment or “spin” of electrons. The first mechanism gives rise to the phenomena of diamagnetism, which is present in all materials, regardless of electron configuration. The second and third mechanisms are fundamental to our understanding of the phenomena of paramagnetism and ferromagnetism and only occur in materials with specific electron configurations. In solids, the orbital contribution to the total angular momentum is quenched[14] and thus ferro/paramagnetism in these materials is based solely upon interaction of the spin angular momenta of electrons in a lattice[29]. Only elements which contain unpaired electrons and therefore non-zero spin angular momentum in their orbitals may contribute to spontaneous magnetic ordering. The three major types of magnetism can be described in terms of their effect on the bulk property of susceptibility, $\chi$, which is, in general, a second rank tensor and is a measure of how responsive a material is to an applied magnetic field. The susceptibility is formally described as the proportionality between the magnetization, $M$, and the applied magnetic field $H$[30]

$$M = \chi H.$$ (2.1)

The diamagnetic response of a material manifests itself as a weak repulsion to applied magnetic fields, and can be derived using a semiclassical approach, where orbital radii from the Bohr model are taken into account. Gradients in the magnetic field causes an acceleration of electrons which form a “current loop” around the nucleus, in such a direction that they induce a magnetic moment in opposition to the applied field. Because the electrons do not lose energy in their orbits, the diamagnetic response persists even when there is no field gradient, but a static field. All materials exhibit
diamagnetic behavior, but atoms with filled orbital energy levels give the strongest response. This response can be measured in terms of the bulk property of susceptibility, $\chi$ which will have values less than zero for diamagnets and is given by\[30\]

$$\chi = -\frac{N\mu_0 Ze^2}{6m_e\langle r^2 \rangle_{av}}, \tag{2.2}$$

where $N$ is the number of atoms per unit volume, $\mu_0$ is the permeability of free space, $Z$ is the number of electrons in a given orbital, $e$ is the electron charge, $m_e$ is the electronic mass and $\langle r^2 \rangle_{av}$ is the square of the average value of orbital radii.

The relationship between angular momentum of an electron and its magnetic moment can be derived classically, but it is more important to note that two distinct quantum mechanical contributions to the electron’s angular momentum exist. The first is the orbital angular momentum, which is determined by the azimuthal quantum number, $l$ and gives a contribution of\[30\]

$$m_{\text{orbital}} = \mu_B \sqrt{l(l + 1)} \tag{2.3}$$

to the total magnetic moment of an electron. The second contribution is made by the electron’s intrinsic, or “spin” angular momentum, originally demonstrated by Stern and Gerlach in 1922\[31\], which is given by the spin quantum number, $m_s$ whose moment along an applied field (typically taken as the $z$-direction) is given by

$$m_z = -g_e \mu_B m_s \tag{2.4}$$

where $g_e = 2.002319$ is the $g$-factor for free electrons derived from quantum electrodynamics\[30\], $\mu_B$ the Bohr magneton, which is the natural unit of magnetic dipole moment for electrons and $m_s$ the spin quantum number. Electron spin is the dominant magnetic moment in solids, responsible for ferromagnetic interactions, due to the fact the the crystal field causes orbital angular momenta of electrons to average to exactly zero\[14\].
By applying the expression of the energy of a magnetic dipole in a field, we can see that the relationship between angular momentum and magnetic moment will give rise to an energy splitting between electrons with different values for total angular momentum:

\[ E = -\mu_0 \mathbf{m} \cdot \mathbf{H} \]  

(2.5)

In the case in which spin angular momentum is the sole contribution to total angular momentum, as is the case for solids, this simplifies to be

\[ E = g_e\mu_0 \mu_B m_s H. \]  

(2.6)

Thus, the spin “down” \((m_s = -1/2)\) electron will be lowered in energy and the spin “up” \((m_s = +1/2)\) will be raised in energy. This gives rise to the observation of Zeeman splitting, which is observed between spectral lines of atoms and solids subjected to a magnetic field. This energy splitting will become important in the consideration of magnetic semiconductors and metals.

The phenomena of ferromagnetism was originally treated by Weiss in 1907[32], following the development of the Langevin theory of paramagnetism and the Curie law for paramagnets. Using the assumption of a “Molecular Field”, which in his model functioned as an additional component to the total magnetic field acting on the material, he was able to predict the behavior of susceptibility with temperature as well as the existence of a point at which the thermal energy in the system would be sufficient to override the energetic benefit of magnetic ordering, known as the “Curie Point”, \(T_c\). His analysis can be summarized in the Curie-Weiss law:

\[ \chi = \frac{C}{T - \theta}, \]  

(2.7)
where $C$ is the Curie constant, $T$ is the temperature and $\theta$ is the Curie temperature, $T_c$, which is linearly related to the magnitude of the molecular field. According to the modern quantum mechanical understanding of magnetism, this “molecular field” in solids is actually due to the coupling of spin angular momenta between electrons in a lattice to produce a net magnetization parallel to the field.

To understand the mechanisms involved in para- and ferromagnetism, we must first develop the concept of the exchange interaction, since it is at the heart of the energetic favorability of the ferromagnetic state, as shown by Heisenberg, nearly a century ago[29]. The concept of exchange is best demonstrated by derivation of the electronic energy levels of the first excited state of the two electron He atom. Following Atkins[33], the Hamiltonian operator, $\mathcal{H}$, which describes all potential and kinetic energies in the system can be written purely in terms of electrostatic potential energies as

$$\mathcal{H} = -\left(\frac{\hbar^2}{2m_e}\right)\left(\nabla_1^2 + \nabla_2^2\right) - \left(\frac{2e^2}{4\pi\epsilon_0 r_1}\right) - \left(\frac{2e^2}{4\pi\epsilon_0 r_2}\right) + \left(\frac{e^2}{4\pi\epsilon_0 r_{12}}\right).$$

In the above Hamiltonian, the first term describes the kinetic energy of each electron in its orbit around the nucleus, the second and third term are due to the coulombic potential that the electrons experience due to the two protons in the helium nucleus. The final term is due to the mutual coulombic repulsion of the electrons orbiting the nucleus. The Schrödinger equation, which is a partial differential equation describing the energies and locations of electrons can be written as

$$\mathcal{H}\psi(r_1, r_2) = E\psi(r_1, r_2),$$

where the square of the wavefunction, $|\psi(r_1, r_2)|^2$ can be interpreted as the positional probability density of the electron and $E$ is the energy of the state corresponding
to $\psi(r_1, r_2)$. Although analytical solution of Schrödinger’s equation for the helium Hamiltonian is intractable, approximate solutions can be obtained using the method of time independent perturbation theory[33], whereby the unperturbed Hamiltonian is taken to be a superposition of two hydrogenic (i.e. analytical solutions of Schrödinger’s equation for the hydrogen atom) Hamiltonians,

$$\mathcal{H}^{(0)} = \mathcal{H}_1 + \mathcal{H}_2 \quad \text{where} \quad \mathcal{H}_i = -\left(\frac{\hbar^2}{2m_e}\right)(\nabla_i^2) - \left(\frac{2e^2}{4\pi\epsilon_0 r_i}\right).$$

(2.10)

The functional form of the unperturbed wavefunction for the ground state of He is given by

$$\psi(r_1, r_2) = \psi_{n_1,l_1,m_{l_1}}(r_1)\psi_{n_2,l_2,m_{l_2}}(r_2)$$

(2.11)

where the subscripts $n$, $l$ and $m_l$ are the principal, azimuthal and magnetic quantum numbers, which together determine the radial and angular distribution of the wavefunction. The solution of the energy for the ground state is given by[33]

$$E = 2E_{1s} + K.$$  

(2.12)

Where $E_{1s}$ is the ground state energy of a hydrogen atom and $K$ is the Coulomb integral

$$K = \left(\frac{e^2}{4\pi\epsilon_0}\right)\int \int |\psi_{n_1,l_1,m_{l_1}}(r_1)|^2 \left(\frac{1}{r_{12}}\right) |\psi_{n_2,l_2,m_{l_2}}(r_2)|^2 d\tau_1 d\tau_2,$$

(2.13)

which can be understood to describe the electrostatic potential of two interacting bulk volumes of charge given by $-e(|\psi_{n_i,l_i,m_{l_i}}(r_i)|^2) d\tau_i$.

To gain insight into the origin and nature of the exchange interaction, we must consider the first excited state of the helium atom, e.g. where one electron occupies the 1s orbital, with quantum numbers $(n_1,l_1,m_{l_1})$ and the other occupies the 2s, with quantum numbers $(n_2,l_2,m_{l_2})$. Complication quickly arises however, when it
becomes clear that there must exist two equivalent and degenerate unperturbed wavefunctions, \( \psi_{n_1,l_1,m_{l_1}}(r_1) \psi_{n_2,l_2,m_{l_2}}(r_2) \) and \( \psi_{n_2,l_2,m_{l_2}}(r_1) \psi_{n_1,l_1,m_{l_1}}(r_2) \), because it must be equally probable for the electron at \( r_1 \) and \( r_2 \) to be in the excited state. Because of this degeneracy in unperturbed states, solutions must be obtained using degenerate first order perturbation theory\[33\], the resulting eigenfunctions, \( \psi_{\pm}(r_1, r_2) \) are given by forming linear combinations of the degenerate wavefunctions via the method of Slater determinants\[33\]

\[
\psi_\pm(r_1, r_2) = \frac{1}{\sqrt{2}} (\psi_{n_1,l_1,m_{l_1}}(r_1) \psi_{n_2,l_2,m_{l_2}}(r_2) \pm \psi_{n_2,l_2,m_{l_2}}(r_1) \psi_{n_1,l_1,m_{l_1}}(r_2)) . \tag{2.14}
\]

The corresponding energies are given by

\[
E = E_{n_1} + E_{n_2} + K \pm J , \tag{2.15}
\]

where \( E_{ni} \) are the hydrogenic energies of each electron, \( K \) is the Coulomb integral discussed previously and \( J \) is denoted the exchange integral,

\[
J = \left( \frac{e^2}{4\pi \epsilon_0} \right) \int \int \psi^*_n(r_1) \psi^*_m(r_1) \left( \frac{1}{|r_1|} \right) \psi_n(r_2) \psi_m(r_2) \, d\tau_1 \, d\tau_2 , \tag{2.16}
\]

which has no classical analog. The exchange integral can be qualitatively interpreted as the quantum mechanical perturbation to the Coulomb integral, \( K[33] \). Note that the value of \( J \) is always positive which means that the degeneracy of \( \psi_{\pm} \) is lifted, with the \( \psi_- \) state being \( 2J \) lower in energy than the \( \psi_+ \) state.

The wavefunctions \( \psi_+(r_1, r_2) \) and \( \psi_-(r_1, r_2) \) are called “spin-antisymmetric” and “spin-symmetric”, respectively. This is due to the fact that the probability density of these functions evaluated at \( r_1 - r_2 = 0 \) are a maximum value and zero, respectively.
We know from the Pauli exclusion principle that electrons in an orbital with the same spin quantum number must not overlap spatially. Thus, $\psi_+(r_1, r_2)$ describes a configuration where the 1s and 2s electrons have opposite spins $|\uparrow\downarrow\rangle$ and $\psi_-(r_1, r_2)$ describes a configuration where the 1s and 2s electrons have aligned spins $|\uparrow\uparrow\rangle$, in bra-ket notation. Note that it is the aligned spin state or ferromagnetic state, $|\uparrow\uparrow\rangle$, which is energetically favored. Thus, it is the phenomena of the exchange interaction which gives rise to the energetic favorability of ferromagnetic ordering. It should be noted that in solids, crystal symmetry and super-exchange interactions can give rise to a negative value of the exchange integral which leads to the antiferromagnetic state $|\uparrow\downarrow\rangle$ being preferred\[14\] The simplest picture of exchange driven ordering in a ferromagnetic solid was originally treated by Heisenberg\[29\]. He assumed a lattice of atoms, with a localized electron with spin $s_i$ at each lattice point. The Hamiltonian for the system can be written

$$\mathcal{H} = -2 \sum_{ij} J_{ij} s_i \cdot s_j,$$  

(2.17)

where $J_{ij}$ is the exchange interaction between two spins $s_i$ and $s_j$ and has the property that lattice points $i$ and $j$ must be nearest neighbors, otherwise $J_{ij}$ will be zero. Heisenberg’s model works well in materials with highly localized moments, which are close enough that they can directly couple to each other and thus is a good model for many rare earth ferromagnets, whose magnetically-active $f$ orbitals are relatively isolated from charge carriers. In this case the process of magnetization proceeds by direct exchange, whereby neighboring spins couple to ferromagnetically to each other, driving the formation of domains and long range spin order, which produces a net magnetization in the material and results in the observation of magnetic hysteresis. Magnetic hysteresis is a phenomenon whereby application of a field opposite to the
direction of magnetization of a material will not produce a change in direction of magnetization until a critical field value, termed the coercive field, $H_c$. The net magnetization will then increase until all spins are aligned to the applied field and thus, the magnetization is at its saturation value, $M_s$. Given this discussion, it can be qualitatively understood that the Curie temperature, $T_c$, of a material is the temperature at which the thermal energy of a system becomes equal to the energy benefit of ferromagnetic ordering, which leads to a randomization of spins in the system and destruction of long range spin order.

2.3 Growth and Characterization of Bulk Gd:GaN

Following the report of colossal room temperature ferromagnetism in GaN doped with a dilute amount of Gd atoms by Ploogs group in 2005, many research groups became interested in confirming and expanding on the observation of room temperature ferromagnetism in this system. Gd is an attractive candidate as a magnetic dopant in nitrides due to its comparable ionic radius to Ga and isoelectronic ionization state with the group III elements in nitrides. This leads to substitution incorporation on the Ga site which is uncharged, $\text{Gd}^\text{X}_{\text{Ga}}$ in Kroger-Vink notation. In addition, Gd possesses the most strongly correlated electronic structure of the lanthanides, possessing $4f^7$ grounds state spin of $s_z=7/2$. As discussed previously, when doped with Gd, these films exhibit saturation magnetizations that are much larger than can be explained by the moment of Gd alone. Our work on Gd:GaN has focused on understanding the origins and mechanism of the anomalous ferromagnetism in this material and attempting to exhibit control over its magnitude and reproducibility, which has until recently remained an elusive target.
Initially, samples similar to those reported by Ploog and coworkers were prepared and their magnetic and structural properties were characterized. Using the technique of PAMBE, 500nm Gd:GaN epilayers were grown on AlN templates. Structural characterization by x-ray diffractometry of these samples revealed an asymmetric peak in the 2θ scan, indicating a tensilely strained GaN layer, likely due to the rather large ionic radius difference between Gd$^{3+}$ and Ga$^{3+}$ ions (38%).

![Magnetic and structural properties of MBE grown Gd:GaN.](image)

**Figure 2.2:** Magnetic and structural properties of MBE grown Gd:GaN. **a.** Low and High temperature magnetic hysteresis scans **b.** Comparison of experimental XRD pattern to simulated spectrum.

Magnetic characterization via SQUID magnetometry of these films (Fig. 2.2) shows both room temperature and low temperature ferromagnetism, as expected from previous reports, as well as a normalized moment far in excess of the atomic moment of Gd$^{3+}$ ($7\mu_B$/Gd). Note that room temperature and low temperature yield strikingly similar hysteresis scans. Magnetic characterization of these samples is in actuality, quite difficult since their moments are on the order of 0.1 emu/cm$^3$, resulting in moments which are near the detection limit of SQUID magnetometers.
Various long term studies of this material performed by the author and undergraduates Brittany Niles and Laura Manuel as well as other groups[18] have shown that the ferromagnetism observed in these compounds is transient and not environmentally stable over multi-month durations. Moreover, strong correlation of ferromagnetic moment appear to exist with extended defect content. To study this more in depth, a series of samples were prepared in a co-loaded fashion. On a Si(111) substrate, a GaN on Sapphire, AlN on Sapphire, Si(111) wafer chip were bonded. Growth of a Gd:GaN film on this substrate yielded three samples with similar structures, but widely different extended defect content. Analysis of magnetic characteristics showed a striking inverse correlation of normalized moment with film quality.

The origin of the colossal moment in Gd:GaN sparked much debate and research after the initial report in 2005. The rather widely accepted explanation in the community is that the incorporation of Gd into GaN gives rise to many defect states[22], not un plausible given the size mismatch, which can then order ferromagnetically. Each of these defect states adds 2-3 $\mu_B$. The Gd ions themselves, however are determined to be paramagnetic. This results in a moment much larger than due to Gd alone. A plausible explanation for the defect responsible could be the large number of threading dislocations present in these films. Unfortunately, this defect based model suggests that control and manipulation of magnetism in these structures in systematic ways common to semiconductors will be rather difficult, which has more or less caused them to be abandoned as ferromagnetic semiconductor candidates.
2.4 Investigation of interaction of Gd and charge carriers in GaN/AlGaN 2DEGs

Exploring the possibility of exchange interaction between charge carriers in nitrides and gadolinium dopants is necessary condition for demonstration of a dilute magnetic semiconductor in III-nitrides. Toward this end, we investigated this possibility by designing a set of samples where Gd dopant atoms are incorporated at varying distances from a GaN/AlN two dimensional electron gas (2DEG) (Fig. 2.3). Utilization of the 2DEG heterostructure, which is widely used in GaN/AlGaN HEMTs due to its high mobility electrons for FETs[9], allowed us to study the possibility of interaction by looking at the most extreme case, high electron concentration, high dopant amounts of Gd. Samples were initially grown by PAMBE on semi-

Figure 2.3: Calculated band diagram for AlN/GaN 2DEG heterostructure showing Gd δ-doping locations for high overlap and low electron overlap samples.
insulating MOCVD grown Fe:GaN on sapphire templates from Lumilog. Regrowth on GaN/sapphire templates, though widely used for optoelectronics, presents a number of significant challenges for electrical devices. It has been widely demonstrated that the regrowth interface will be heavily populated with donor states[34], leading to large buffer leakage currents for lateral transport devices such as FETs. After the growth of these samples was optimized, samples with identical amounts of Gd placed at varying distances from the 2DEG were prepared and their magnetic properties were characterized by SQUID. From the data shown in Fig. 2.4, it can be observed that all samples exhibit a ferromagnetic open hysteresis loop, although the coercivity is rather small at $\leq 50$ Oe. Moreover, samples exhibit ferromagnetic hysteresis both at low temperature and at room temperature (300K). Samples where the Gd overlaps with the 2DEG peak electron density (0.4nm from interface) exhibit a reduction in

Figure 2.4: Magnetic properties of Gd:2DEG heterostructures. Low temperature (a.) and room temperature (b.) Hysteresis for samples with Gd located directly overlapping electron density and far away.
saturation magnetization compared with samples which have Gd incorporated 10nm from the heterointerface. These data suggest that conduction band electron actually hinder magnetic coupling between the Gd ions. The free spins from Gd are entirely in the f-shell which is a non-bonding orbital and thus is not expected to interact strongly with conduction band carriers in the semiconductor, so it is surprising that any effect is seen at all. This may be explained by the presence of free spins on native defects in nitrides contributing to the measured magnetic moment.

Furthermore, when the orientational anisotropy of these films are measured they are observed to show enhanced magnetization for the magnetic field applied along the c-axis of the semiconductor, out of plane of the film. This is in contrast to what is expected for magnetization in thin films, which should exhibit a preference for magnetization in the plane of the film due to shape anisotropy. The observed anisotropy is also observed in bulk Gd:GaN films, suggesting that it is intrinsic to the mechanism of Gd induced magnetism present in these films.

Next, magnetotransport experiments involving lateral transport in the 2DEG of the heterostructure were designed and executed. This involved design and fabrication of 1-3-3-1 Hall bars, designed according to ASTM F76 standard for Hall measurements of semiconductors (Fig. 2.5). These were large area devices which allowed simultaneous collection of magnetoresistance, resistivity and hall voltage during measurements. Devices were prepared by photolithographic patterning, mesa etching with an ICP-RIE tool and subsequent metallization using an electron-beam evaporator.

Initial measurements for these devices showed some promise in that nonlinearities in the hall voltage, which are characteristic of the anomalous Hall Effect, were observed, as shown in Fig. 2.6 Unfortunately, subsequent systematic electrical characterization
of these devices revealed that a substantial amount of conduction was likely taking place through the buffer or a highly conductive regrowth interface, causing delocalization of the current from the 2DEG region where magnetic dopants were present.

In order to alleviate this issue, a new set of samples was prepared using a specially designed heteroepitaxial growth on SiC. SiC substrates see extensive use in RF power devices such as GaN/AlGaN HEMTs due to their ability to form truly insulating buffer layers as well as their high crystalline quality and thermal conductivity[35]. Using a heterostructure employed by Prof. Siddharth Rajan’s (OSU ECE) research group[36], which uses a columnar AlN nucleation layer followed by defective GaN and then a thick layer of high quality GaN before the AlN cap samples with exceptionally low buffer leakage characteristics were prepared. Extensive magnetotransport characterization was carried out on these samples by Zihao Yang, the results of which are shown in Fig. 2.7. All samples exhibit nonlinearities in the Hall voltage, as well as show mostly Lorentz dominanted magnetoresistance behavior. However, when the
Figure 2.6: Initial observation of temperature dependent non-linearity in the Hall voltage vs. Field in Gd:2DEG heterostructures

Figure 2.7: Demonstration of poor correlation between magnetic hysteresis in Gd:2DEG heterostructure and magnetotransport phenomena

nonlinear Hall voltage is compared to a given samples magnetization curve, it becomes clear that Hall voltage does not directly track magnetization, indicating that
the effect being observed is not due to the anomalous hall effect (AHE), since that should be directly proportional to magnetization. Moreover, comparison of all samples, including a Gd-free control sample, reveals similar behavior in all three samples. From this it is concluded that GaN/AlGaN 2DEGs themselves exhibit some nonlinearity in the Hall voltage with magnetic field, but this non-linearity is unrelated to Gd ions, which seem to have no effect on the actual magnetotransport properties.

2.5 Conclusions and outlook for magnetic doping of III-nitrides

Successful reproduction of literature results in the form of magnetic characteristics of bulk doped Gd:GaN was successful. Additionally, the potential for interaction between Gd$^{3+}$ ions and conduction band electrons in III-nitride heterostructures was systematically investigated. Although, some effect on the magnitude of magnetization with Gd$^{3+}$-electron overlap parameter was observed, no strong interaction between spin polarized Gd$^{3+}$ ions and conduction band electrons in GaN was determined to exist. Although there continues to be some activity in this area involving searching for various other dopant candidates, most groups have moved away from Gd:GaN as a potential room temperature dilute magnetic semiconductor due to problems with sample aging, growth reproducibility and lack of strong magnetism-carrier interactions, our group being no exception.
Chapter 3: Epitaxial, Ferromagnetic GdN/GaN Nanocomposites

In parallel with interest in Gd:GaN over the last few years has been exploration of integration of the rare earth ferromagnetic compound GdN with GaN to function as a material for spin injection and detection, plus investigation of the properties of epitaxial semiconductor-ferromagnet heterostructures in nitrides. As mentioned previously, devices for semiconductor spintronics require efficient ferromagnetic spin injection and detection layers, which currently are composed of either dilute magnetic semiconductor (DMS) or metallic layers. Within the family of III-nitride compounds, no epitaxial spin injector is currently well-developed this is in contrast to III-As/P materials which have demonstrated epitaxial GaMnAs and Fe. For the preservation of spin coherence through the device, interface and crystalline quality are key considerations and epitaxial integration gives rise to the highest possible quality, and thus could give rise to more efficient device function. As mentioned in the previous section, dilute Gd:GaN, though offering the promise of room temperature ferromagnetism and realization of a nitride-based DMS, has proven to be a difficult material to control[18] due to the poorly understood nature of magnetic ordering in the system. GdN, in contrast is understood to be a Heisenberg ferromagnet[37] with $T_c$ around 70 K. Furthermore, unlike most other rare earth pnictide compounds, which are well established
to be semimetals, thin GdN layers have been predicted[27, 38, 39] to be indirect gap semiconductors, a claim which is consistent with recently reported absorption features for thin GdN films[40]. This leads to the possibility of a well understood ferromagnet, which is possibly also a semiconductor, that could be epitaxially integrated with wurtzite III-nitride compounds. Although this integration does not solve the problem of room temperature functionality, it does offer the potential to investigate the III-nitride system for various spintronics applications.

Additionally to magnetic applications, rare earth semimetal/III-V semiconductor nanocomposites have been shown to exhibit a number of intriguing optical and electronic phenomena stemming from production of midgap states in the semiconductor host. These states have been shown to facilitate efficient tunneling in reverse biased p-n junctions in ErAs/GaAs, ErSb/GaSb[41] and most recently GdN/GaN[42]. Additionally, these midgap states result in ultrashort carrier lifetimes, giving rise to recombination times less than a picosecond, a useful property for design of ultrafast photoconductive switches and synthesis of THz radiation[43].

3.1 Heteroepitaxy of dissimilar crystal structures

In addition to the complications of lattice mismatch in traditional heteroepitaxy, where the crystal structure is continuous between films with different chemical compositions and lattice constants, epitaxial growth of materials with distinct crystal structure gives rise to many additional challenges[44]. First, one must consider the differences in surface energies of adlayer and substrate, which strongly influences growth mode. Next, the crystal symmetries of adlayer and substrate must be considered. Particularly notable is a potential discontinuity in the presence of an inversion
center in the space group of adlayer and substrate, as this can lead to formation of antiphase domain boundaries and therefore multiplicity in possible epitaxial orientations of the epilayer[44].

The discontinuity in crystal symmetry along the growth direction is a particular problem for integration of GdN with nitrides, due to the lower symmetry of the rock salt structure along the growth direction (Fm\(\overline{3}m\)) than the host (P6\(_3\)mc in the case of wurtzite). Complete films of GdN on wurtzite III-Nitrides have been shown to be epitaxial with the relationship GdN[111]||GaN[0001] but containing two rotational variants due to crystal symmetry considerations, which can be observed by an off-axis \(\phi\) scan in x-ray diffractometry and when overgrown with GaN, result in a polycrystalline overlayer[45]. Thirdly, lattice mismatch must be considered as it dictates the maximum thickness of the film before nucleation of interface misfit dislocations. Finally, thermodynamic stability of the adlayer must be considered, as subsequent processing or growth steps can lead to unintended compound formation or diffusion through the bulk. This is a substantial problem for GdN, which is observed to readily react with oxygen to form Gd\(_2\)O\(_3\).

Much progress has been made in this field over the past thirty years, ranging from successful growth of fcc and bcc metals on GaAs[46, 47] to demonstration of NiAs-structure compounds on GaAs such as MnAs[48] and finally, thermodynamically stable rare earth-pnictide (ErAs,ErSb) compounds on III-As/Sb compounds, which have led to a number of novel optoelectronic applications[43, 49, 50, 41]. In addition, the rare earth monopnictide GdN has been shown to be readily grown on wurtzite III-nitride compounds[45, 7].
3.2 PAMBE growth of compound semiconductors

All III-nitride heterostructures discussed in this thesis were grown in a Veeco GEN930 plasma assisted molecular beam epitaxy system. The technique of molecular beam epitaxy, a staple of compound semiconductor growth techniques, combines precision control of layer thickness and composition with an exceptionally pure ultrahigh vacuum (<1E-10 Torr base pressure) environment. The system employed in this work is equipped with solid elemental source Knudsen effusion cells for group III elements (Ga, Al, In, Mg, Si, Gd) and a radio frequency (RF) plasma source for active nitrogen. Fluxes are measured and calibrated using a shielded ion gauge mounted to the backside of the continuous azimuthal rotation (CAR) sample mount.

All thin film nitrides in this work are grown via standard metal rich conditions of approximately 2x the Ga:N stoichiometric flux (1.9E-7 Torr). This causes an adlayer of liquid Ga to develop on the surface of the semiconductor which acts as a surfactant during growth, yielding smooth (<1nm rms) step-flow type surface morphologies. During growth the surface reconstruction is monitored using the technique of reflective high energy electron diffraction (RHEED) which provides an indicator of surface structure as well as morphology.

3.3 Properties and Structure of GdN

Prior to the work described in this dissertation, two groups had reported successful heteroepitaxial growth of GdN on GaN by MBE. Scarpulla and coworkers[45] grew coalesced films of GdN at low temperature with two rotational variants and a polycrystalline overlayer of GaN, they demonstrated that the films had the epitaxial relationship of GdN[111]||GaN[0001] and showed that the GdN films contained two
rotational variants by conducting rotational x-ray diffraction (XRD) analysis of an off-axis peak. Other groups have successfully synthesized material by reactive ion sputtering on bulk AlN templates. Yoshitomi and coworkers recently reported measurement of direct and indirect gap optical absorption features which compare well with theoretically predicted energies[27, 39].

Although there is a limited amount of experimental literature pertaining to GdN at this point, we can learn many lessons from the existing work in the closely related RE-As/Sb on GaAs/Sb structures. Development of those materials led to exciting magnetic, photonic, and transport properties and applications. The similarities in chemistries of the rare earth elements and the similarities in symmetry of the zincblende and wurtzite structures allow for extension of many results from RE-As/GaAs growth to GdN on III-nitrides.

3.4 Heteroepitaxial Growth and Characterization of GdN thin films on GaN

In order to reproduce the results of Scarpulla and coworkers, GdN thin films on UID GaN templates were prepared by PAMBE. During growth, the RHEED pattern changes gradually from a GaN 1x1 to GdN 2x4 and then to a somewhat complex, spotty pattern indicating 3D growth of the expected bivariant structure expected due to symmetry considerations. GdN has been reported to lack air stability, gradually forming Gd$_2$O$_3$ when exposed to air. Unpassivated films, as grown, exhibit a dark color until removal from the vacuum environment, and then their appearance becomes gradually transparent. Growth was conducted at 550C, as measured by an IR pyrometer and using Gd flux of 3.67E-8 Torr, nitrogen flux of 2E-5 Torr and power of 350W.
Films were characterized by x-ray diffractometry which indicated, as expected that there exists an epitaxial relationship between the GdN and GaN given by GdN\[111\]|GaN\[0001\]. The magnetic characterization (Fig. 3.1) of these films show near ideal mean field ferromagnetic behavior, indicated by a temperature decay of magnetic moment following the relationship derived by Heisenberg, as well as clear, open hysteresis loops. However, the lack of complete in-plane symmetry continuity in the growth direction, as well as poor air stability of the GdN layer, greatly limits possible use of GdN in semiconductor heterostructures. Multiple methods were employed to successfully passivate the GdN films in-situ during growth ranging from overgrowth of polycrystalline GaN to deposition of thin layers of Al and allowing them to oxidize upon removal from the growth chamber, the latter of which was the most successful in achieving passivation. The GaN capping layer was visibly polycrystalline by RHEED and did not prevent the GdN from oxidizing upon introduction of the sample to ambient.

Figure 3.1: Magnetic characteristics of PAMBE grown GdN thin films
3.5 Epitaxial Ferromagnetic Nanoislands of Cubic GdN in Hexagonal GaN

In this section, which is adapted from a previous publication by the author[3], the epitaxial integration of discrete cubic GdN nanoparticles in a continuous, high crystalline quality GaN matrix is described. Although the growth of coalesced epitaxial GdN films on III-nitrides by molecular beam epitaxy (MBE)[45, 51] and by reactive ion sputtering on AlN[40] has been previously reported, formation of discrete GdN islands within a continuous, epitaxial III-nitride matrix has until now, yet to be explored. Epitaxial growth of dissimilar crystal structures is in general met with many challenges[52], but the rare earth pnictides (RE-Pn:EuO, ErAs.) have been shown to grow well on zincblende III-V semiconductor compounds[44]. Most widely studied has been the epitaxial integration of semi-metallic ErAs in InGaAs[43], which has resulted in novel high speed photodetectors and THz sources[50]. The mechanism of ErAs embedded nanoparticle growth in GaAs has been proposed[49] to proceed first by incomplete layer formation of ErAs islands on the surface followed by epitaxial lateral overgrowth of the uncovered GaAs.

The epitaxial integration of GdN with GaN is attractive for a number of reasons. First, the dilute doping of III-Nitrides with Gd has attracted a large amount of attention in recent years initially for its promise of utilization of the intra-f-shell UV optical transitions of Gd in AlN[53] and subsequently for the search of a room temperature dilute magnetic semiconductor following the report of room temperature ferromagnetism in Gd:GaN[13, 22, 23]. Gd is attractive for its magnetic properties, possessing the most strongly correlated electronic structure of the lanthanides, with 4f ground state of spin 7/2. Devices for semiconductor spintronics require efficient
ferromagnetic spin injection and detection layers, which currently are composed of either dilute magnetic semiconductor (DMS) (GaMnAs) or metallic Fe layers. No epitaxial spin injector is currently available in the III-nitride materials system. For the preservation of spin coherence through the device, interface and crystalline quality are key considerations. Dilute Gd:GaN, though offering the promise of room temperature ferromagnetism and realization of a nitride based DMS has proven to be a difficult material to control\[18\] due to its poorly understood defect mediated mechanism of ferromagnetism. GdN, in contrast is a well understood classical ferromagnet\[37\] with $T_c$ around 70K. Furthermore, unlike most other RE-Pn, which are well established to be semimetals, thin GdN layers has been predicted\[27, 38, 39\] to be indirect gap semiconductors, a claim which is consistent with recently reported absorption features for thin GdN films\[40\]. This leads to the possibility of a controllable ferromagnetic semiconductor which can be epitaxially integrated with GaN and may be able to be manipulated by doping of the particles or the host. In addition to intriguing magnetic properties, embedded GdN nanoparticles in GaN could potentially function as carrier recombination centers, giving rise to ultrafast photoconductivity in the same fashion as RE-As particles in III-arsenides.

For the epitaxial structure of the matrix to remain single crystalline, the layer coverage of the rock salt GdN must remain incomplete, allowing for epitaxial lateral overgrowth of the surrounding matrix. This is due to the lower symmetry of the rock salt structure (Fm$\overline{3}$m) than the host (P$6_3$mc in the case of wurtzite). Complete films of GdN on wurtzite III-Nitrides have been shown to be epitaxial with the relationship GdN[111]||GaN[0001] but containing two rotational variants due to crystal symmetry.
considerations, which can be observed by an off-axis $\phi$ scan in x-ray diffractometry and resulting in a polycrystalline overlayer of GaN[45].

![Figure 3.2: Growth and Calibration of GdN-GaN nanocomposites. STEM micrographs and RHEED characterization during growth. Adapted from Ref. [3]](image)

Samples were prepared using the technique of plasma assisted molecular beam epitaxy (PAMBE). In a Veeco GEN930 PAMBE system equipped with a Ga, Gd effusion cell, and nitrogen plasma source. To study the GdN island formation threshold, a calibration stack consisting of increasing effective thicknesses of GdN are deposited from 0.2 ML to 2.4 ML in between 10 nm GaN spacers on a GaN buffer layer grown on an AlN on sapphire (KYMA) template at a substrate temperature of 730 C, nitrogen flux of $2 \times 10^{-5}$ Torr and III/V ratio of 2. During the period of GdN growth, the Ga shutter is closed, meaning only Gd and N are being deposited, although there is a
residual amount of Ga present on the surface. To analyze the onset of GdN island formation, the samples were characterized by cross-sectional, atomic resolution TEM using an FEI Titan3 80-300 Probe-Corrected Monochromated (S)TEM, as can be seen in Fig. 3.2a. Up to 1.2 ML GdN, no change in the structure of the heavily Gd

doped region is observed, however at 1.2 ML, discrete clusters of highly concentrated Gd atoms appear. From the atomic resolution data shown in Fig.3.2b, cubic particles of GdN are observed in the 1.4 ML layer. From image analysis of the STEM data[54], the lattice parameter of cubic GdN in GaN is measured to be 4.8±0.1Å and the nanoparticle size is roughly 2.6 nm x 3.6 nm. After 1.2 ML and up to 2.4 ML, GdN particles with clearly cubic structure surrounded by a hexagonal GaN matrix can be seen with the major change with additional Gd deposition being increased lateral growth, suggesting that the height of the nanoparticle is self limited and further growth will proceed by lateral expansion of the GdN islands, which is similar to what has been observed for Er-Pn in III-As nanoparticle structures[41]. It should
be noted that in order to procure STEM images of nanocomposites, TEM foils were first prepared using a FIB tool. This process exposes the buried GdN nanoparticles to air and may cause conversion of the GdN to Gd$_2$O$_3$. Preliminary studies have shown enhanced oxygen content around nanoparticle regions, although stoichiometry has not been established.

During growth, the surface reconstruction was monitored using reflection high energy electron diffraction (RHEED) operating at 10 kV and cathode current of 1.4 A, results are shown in Fig. 3.2c. For the first 0.4 ML of GdN coverage, the pattern is representative of the wurtzite Ga-face 1×2 reconstruction. After 0.5 ML and until 1.2 ML of GdN the pattern changes to a 2×4 reconstruction. Past 1.2 ML of coverage, the wurtzite 1×2 pattern again is visible, indicating a temporary change in the surface structure during growth of the GdN layer.

After calibration of the GdN precipitation threshold, the heterostructure show in Fig. 3.3a, consisting of a GaN buffer on an AlN template on sapphire (KYMA) and a 50 period superlattice of alternating 10nm udf-GaN and 2.4 ML GdN layers was prepared under identical growth conditions as the calibration structure. Cross sectional STEM images, shown in Fig.3.3b, using a Technai F20 operating in HAADF imaging mode, which provides atomic number contrast, shows expected discrete GdN particles in a GaN matrix with GaN spacer thickness of 11.8±0.4nm and GdN layer thickness of 5.6±0.3 nm obtained from image analysis. Another interesting feature is the appearance of threading dislocations terminating at GdN nanoparticles, which has been suggested to occur for Er-Pn particles in III-As/Sb[41], which exhibit a similar morphology to GdN/GaN nanocomposites. The structure of the sample was further characterized by high resolution x-ray diffractometry using a Bruker D8 triple axis
system. Diffraction data shown in Fig. 3.3b. exhibits clear epitaxial orientation of the GdN [111] to the wurtzite [0001]. Also visible are superlattice fringes, indicating precise layer thickness control of the GaN spacing layers between the GdN regions. From analysis of the superlattice fringes, the GaN spacer thickness can be determined to be 10.98nm which is close to the value determined from STEM. Furthermore, from the diffraction angle, we can determine the lattice parameter of GdN to be 4.97 Å, which is in very good agreement with the value obtained from STEM of the nanoparticles and with values for bulk GdN[5].

Figure 3.4: Magnetic characteristics of GdN-GaN nanocomposites measured by SQUID magnetometry. Adapted from Ref. [3]

The magnetic properties of the sample were analyzed by superconducting quantum interference device (SQUID) magnetometry using a Quantum Design MPMS XL. Results, depicted in Fig. 3.4 clearly show evidence of two distinct ferromagnetic phases in the sample. The dominant phase at low temperature (Fig. 3.4a) can be identified as rocksalt GdN due to a saturation magnetization of nearly exactly $7 \mu_B/\text{Gd}^{3+}$ (158.2 emu/cm³), the expected configuration for GdN. The low remnant magnetization but
correct saturation of $7 \mu_B$ is indicative that a large fraction of Gd is paramagnetic, which is further supported by a temperature dependence containing both a mean field like behavior with a $T_c$ 70 K but an additional $1/T$ contribution. Samples were characterized in both the in-plane ($\vec{B}||$GaN [0001]) and out-of-plane ($\vec{B} \perp$GaN [0001]) configuration. The low temperature phase shows very little anisotropy which is consistent with small particles of a cubic structure, which should be free from the shape anisotropy of a fully coalesced film. The coercive field, $H_c$ is measured to be 363 Oe for the in-plane configuration and 170 Oe in the out-of-plane configuration, respectively.

Past the Curie point of GdN, a second, weaker and anisotropic ferromagnetic phase persists to room temperature. This anomalous phase is hypothesized to be the result of interaction of the Gd with local point defects in the GaN matrix and is of the same type as observed by Dhar, et. al.[13]. It was previously reported[23] that ferromagnetic films of dilutely doped Gd:GaN exhibit anisotropy in their saturation magnetization between the in-plane and out of plane orientations of the film. As observed in Fig 3.4b, the room temperature phase exhibits anisotropy with $M_s=6.84$ emu/cm$^3$ and $H_c = 100$ Oe for the out-of-plane configuration and $M_s = 2.8$ emu/cm$^3$, $H_c = 30.6$ Oe for the in-plane orientation of the film.

Measurement of the magnetization behavior with temperature, after cooling in a 5 T field, is shown in Fig 3.4c. These data reveal a sharp decrease in the magnetization with temperature up to 70 K, the reported Curie point of GdN[45]. After 70 K and up to the highest temperature measured, 350 K, a residual amount of magnetization persists, again pointing to the possibility of an anomalous room temperature phase. In the $M$ vs. $T$ data, anisotropy is observed at low temperatures, which is consistent
with the low field anisotropy present in the 5 K hysteresis scan. For the out-of-plane configuration, a distinct knee is visible in the M vs. T scan which could be due to error in the orientation of the film as mounted in the magnetometer, causing signal from the in-plane configuration to contribute slightly to the measured magnetization. Due to the sample mounting technique employed, the out-of-plane configuration has a larger uncertainty in the absolute orientation of the film.

In summary, we have extended the growth of embedded rare earth pnictide nanoparticles in III-V semiconductors to the family of the III-nitrides. Samples show clear rocksalt structure in cross sectional TEM above a threshold value of 1.2 ML GdN and x-ray diffractometry indicates epitaxial orientation of the [111] direction of GdN to the wurtzite c-axis. Magnetic characterization shows evidence of two magnetic phases, one due to the rocksalt ferromagnet GdN with Curie temperature of 70 K and a second, anisotropic phase whose magnetization persists past room temperature. The room temperature phase is hypothesized to be the same type of defect mediated ferromagnetism reported in Gd:GaN and shows a prominent out-of plane easy axis[13, 22, 23]. This work established the foundation of growth methods and basic sample characteristics for further investigation of nanocomposites, as described throughout the rest of this chapter.

3.6 Optical characteristics of GdN-GaN nanocomposites

The application of GdN nanoparticles in a number of optoelectronic devices such as tunnel junctions for light emitting diodes makes the optical properties of these
nanocomposites important for study. Toward this end, the optical absorption characteristics of these nanocomposites were measured energy resolved absorption spectroscopy. Despite wide reports of these materials being either a narrow gap semiconductor or semimetal, and bulk GdN films appearing opaque, the relatively small volume fraction of the GdN compared to GaN matrix causes the overall optical properties to strongly resemble that of bulk MBE grown GaN as seen in Fig. 3.5. Some additional near band edge absorption is present, as well as an increased green/yellow band is present. Interestingly, no significant NIR absorption is observed other than characteristic Fabry-Perot thin film interference oscillations. This is in contrast with that of ErAs/GaAs nanocomposites, which typically exhibit plasmon resonances at

Figure 3.5: Optical absorption characteristics of GdN/GaN nanocomposites compared with bulk GaN as well as dilutely doped Gd:GaN in the visible part of the spectrum and NIR.
these energies\cite{43}. Additionally, unlike bulk GdN, which has been shown by Yoshitomi, et. al. to exhibit an absorption feature around 1 eV\cite{40}, GdN/GaN nanocomposites do not show a significant difference from bulk GaN.

### 3.7 Effect and control of the Ga-Adlayer during growth of GdN/GaN Nanocomposites

GaN thin films are typically grown with group III elements in excess of the stoichiometric point. In the case of GaN growth, this causes a liquid layer of Ga to accumulate on the surface of the film, which functions as a surfactant and increases the tendency for formation of a smooth, uniform surface\cite{55}. In the case of electrical devices, however, which often require atomically sharp interfaces, this Ga adlayer is widely known to cause interface delocalization due to formation of a local concentration gradient rather than an abrupt interface. The cause of this is that the Ga adlayer can function as a feedstock for Ga independent of the arriving flux composition. In the case of HEMTs, this results in locally higher Ga concentrations directly after the interface than otherwise intended.

Figure 3.6: Effect of Ga adlayer on GdN nanoisland formation.
In our early studies of GdN/GaN nanocomposites, it was noted that there existed significant paramagnetic and room temperature ferromagnetic phases. The behavior of the room temperature ferromagnetism in these samples was indicative of that previously observed for Gd:GaN bulk doped material. Subsequent investigation of STEM data as well as atom probe tomography indicated a substantial amount of Gd being incorporated dilutely in GaN rather than in stoichiometric GdN particles. It was hypothesized that the surface adlayer of Ga was causing formation of a dilute alloy before the Ga feedstock was exhausted and GdN island nucleation could occur. This is depicted diagrammatically in Fig. 3.6.

From this followed a modification in growth procedure, commonly employed in nitride growth for enhancement of periodic structures which require high interface sharpness, such as GaN/AlN superlattice type structures where the Ga adlayer is removed dynamically during each layer in the growth. There exist two common methods for Ga adlayer removal during GaN growth, each with its benefits and costs. For HEMTs the most common method to remove droplets that accumulate during the growth of the GaN buffer layer is to thermally desorb the droplets without active nitrogen present in the chamber. This technique results in exceptionally smooth surfaces and low oxygen incorporation. Unfortunately, since the temperatures employed must be kept below of the thermal decomposition temperature of GaN (740°C) to avoid surface roughening, this process can be exceptionally time consuming, with desorption times measuring in the tens of minutes per layer. Additionally, the nitrogen plasma must be shutoff, lit and retuned for each desorption event. Obviously, for a periodic structure with twenty or more interfaces this method becomes highly impractical.
Alternatively, if the adlayer is kept at a minimum, i.e. that the III/V ratio and temperature are tuned close to the crossover point from Ga rich into Ga droplet regime, exposure to a pure active nitrogen flux will cause the Ga feedstock to be consumed for formation of a new GaN layer on the surface, as shown in Fig. 3.7. If done excessively, this will lead to rather rough, non-uniform growth due to the lack of the Ga adlayer. However, if controlled such that only a small amount of Ga is present, i.e. growth close to the “cross-over” from Ga-rich to Ga-droplet regimes, this method can be highly successful in maintaining both interface sharpness and uniformity in a periodic structure.

In the case of the nanoparticles, the critical time to recover a clean GaN surface was calibrated using RHEED transient analysis during the growth, as shown in Fig. 3.8. First, the droplets from growth of the GaN buffer are thermally desorbed using the previously described technique. This typically takes 15-30 minutes at 730°C for a 400 nm GaN buffer layer. Once the growth surface is clear of droplets, as indicated by a brightened RHEED intensity, the intensity of the fundamental spot is monitored vs. time while 10 nm of GaN is deposited using Ga-droplet stoichiometry. This causes the RHEED intensity to drop as the surface becomes covered with a liquid layer of Ga,
effectively acting as a neutral density filter for incident electrons. When 10 nm has been deposited, the Ga shutter is closed, but the nitrogen shutter is left open, causing the Ga adlayer on the surface to begin to be consumed to form GaN. This causes the RHEED intensity to begin to brighten back up and the time it takes from the closing of the Ga shutter to the point at which the RHEED intensity has fully recovered is recorded. The calibrated time to dry the surface is incorporated in the master recipe sequence for growth of the heterostructure as a wait time with the nitrogen shutter open after GaN deposition.

Samples grown using the technique of dynamic Ga adlayer control exhibit a striking improvement in magnetic and structural characteristics over earlier samples grown without any control of droplets during growth. It is noticed immediately from Fig. 3.9 that the coercive field and remnant magnetization in films grown with droplet control is significantly improved over uncontrolled samples. This suggests a higher volume fraction of the impinging Gd atoms are being incorporated as ferromagnetic GdN particles rather than dilute paramagnetic Gd:GaN.
Figure 3.9: Influence of Ga adlayer presence on magnetic properties of GdN/GaN nanocomposites.

In addition to improved coercivity and remnant magnetization, samples grown with dynamic adlayer control exhibit measurable orientational anisotropy in the magnetization characteristics. Ferromagnetic thin films typically exhibit easy and hard axis behavior due to their rather extreme dimensional anisotropy. The thin, elongated nature of the film causes the magnetization to preferentially lie in the plane of the film, where domains can coarsen and interfacial energy can be reduced. This causes the magnetization to switch rather abruptly around zero field as indicated in Fig. 3.9 for the case where the field is applied in the c-plane. However, when the field is applied out of plane, smaller domains will develop and strongly resist motion, causing the magnetization to linearly track the applied field below saturation. Since the samples where the adlayer is desorbed exhibit this type of anisotropy, it can be concluded that the particles exist in sufficient density to allow for inter-particle exchange coupling to take place, effectively forming continuous domains throughout the film.
Systematic comparison of absorbance spectra from samples where the Ga adlayer has been dynamically removed before each GdN deposition step was performed. These samples were grown on semi-insulating SiC templates using a HEMT-style buffer to enable longitudinal electrical measurements. As can be observed from Fig. 3.10, the 3.0 eV bandgap of SiC is the dominant feature in the absorbance spectrum. Interestingly, samples where the Ga adlayer was removed prior to GdN deposition exhibit increased absorbance in the NIR region, which is consistent with the predicted indirect bandgap behavior of GdN. Analysis of the Fabry-Perot interference fringes yields an overall film thickness of approximately 1.2 µm. This increased absorption in the NIR region suggest that a higher volume fraction of GdN is being incorporated in materials with no Ga adlayer present, yielding properties that are much closer to bulk GdN thin films.
In summary, epitaxial integration of GdN, a rare earth ferromagnetic material with III-nitride wide bandgap semiconductors enables a number of unique functionalities and potential applications. The lack of symmetry continuity between the GdN and GaN along the growth axis is overcome by growing epitaxial, embedded GdN nanoislands in a continuous, single crystalline GaN matrix, forming a nanocomposite that exhibits magnetic properties characteristic of a continuous magnetic thin film, while inheriting the bulk and transport characteristics of the GaN matrix material. Optimized particle morphology and magnetic characteristics are obtained when GdN nucleation interfaces with GaN are engineered for high degrees of abruptness by dynamically controlling the amount of liquid Ga present on the surface of the film during growth.

With this work, the methods of growth and heterostructure design involving GdN/GaN nanocomposites are well established and studied, however, much work remains to understand the finer characteristics of the nanocomposite. Materials parameters such as band alignment, native conductivity type, magnetotransport characteristics and detailed magneto-optical studies are important future goals. Successful utilization of GdN/GaN nanocomposites in a transport application such as a spin injector material, require for charge carriers to exchange couple to the magnetization of the GdN particles. Prediction of whether charge currents will even flow in any reasonable proximity to the nanoparticles requires understanding of the 3D band diagram of the nanocomposite, which is dependent on band alignment and dominant carrier type of the GdN and GaN. Although there have been a number of reports predicting and measuring supposedly semiconducting behavior of GdN films from optical spectra,
no transport experiments have been conducted which conclusively show interaction of GdN with magnetotransport characteristics of the nanocomposite. Demonstration of this is an important goal for future progress with this material.

Another important goal is exploitation of the possibility that the GdN may be semiconducting. Further optical absorbance studies should be performed at NIR and IR wavelengths to better understand the spectral features outlined in Fig. 3.10. Attempts to dope the matrix and particles should be devised using available materials in the MBE system such as Si and Mg. Development of a closely lattice matched InGaN alloy to GdN may allow for the epitaxial growth of wurtzite GdN and thus strikingly different properties as well as strain engineering.
Chapter 4: Polarization Induced Nanowire Light Emitting Diodes (PINLEDs)

Over the last twenty years, there has been great progress in development of solid state light emitting devices. Particularly, much work has centered on the development of highly efficient blue InGaN light emitting diodes toward development of a solid state substitute for incandescent lighting. Combining decades of development of AlGaN, AlGaAs and InGaAs light emitting diodes for green, red and near infrared light production with highly efficient blue InGaN light emitting diodes lead to the realization of the three primary colors of the visible spectrum as well as important emitters for telecommunications applications.

Over the last century, humans have developed the ability to create and measure photons over the whole range of the electromagnetic spectrum, from microwaves to gamma-rays. In the visible parts of the spectrum, where most work on light emitting diodes has taken place since the advent of the semiconductor, we now have efficient solutions for producing the three primary colors from which all others can be synthesized. This, driven by demand for more efficient light sources has resulted in substantial innovation in solid state lighting as a replacement for street lamps, traffic signals and indoor illumination.
However, there exist significant technological applications which require intense, monochromatic, ultraviolet light. These include water disinfection, photo-induced curing of epoxy, production of pure ozone, chemical agent detection by ultraviolet spectroscopy and photolithography[56]. Current commercial solutions for light sources in these areas involve arc discharge lamps (D, Xe, Hg), which require production of high voltages, contain toxic chemicals and have a tendency to fail catastrophically, and Excimer lasers (KrF, ArF), which use extremely hazardous gases and have large footprint and power budgets. Solid state devices have demonstrated both the ability to generate light energetically efficiently with small device footprint and highly scalable manufacturability. It is therefore highly desirable to consider design of a compound semiconductor based solution for the deep ultraviolet part of the electromagnetic spectrum ($\lambda \leq 300$ nm).

The group III-nitride compound semiconductor family offers the wide gap alloy AlGaN which offer a direct energy gap which is composition tunable from 6.02 eV-3.4 eV, corresponding to wavelengths of 210 nm to 365 nm, respectively. It should be possible in principle, then to fashion a hetero- or homojunction light emitting diode (LED) heterostructure with an AlGaN active region to produce LEDs which function over this wavelength range. Although much effort has been directed towards this goal over the last decade, UVC devices still exhibit substantially reduced efficiencies when compared to their visible counterparts[56]. This can primarily be attributed to a myriad of materials related difficulties associated with AlGaN.

High Al composition AlGaN presents difficulties with growth of high quality material, p-type conductivity and formation of ohmic contacts. Growth of high quality material is hindered by the lack of cost effective native substrates, although great
strides are being made in growth of high quality bulk AlN substrates by several companies (Hexatech, Inc. Crystal IS, Inc.). Additionally, Al containing compound semiconductors are well known to incorporate large amounts of oxygen during growth which function as recombination centers[57]. The most compelling problem in this system, however is rather fundamental to even an idealized material. It has been widely shown that the activation energy, which determines the ratio of dopants added to charge carriers imparted to the semiconductor, increases monotonically with the bandgap of materials. Additionally, for group III-nitrides, the magnitude of this energy is substantially above room temperature, meaning that only a limited fraction of dopants added successfully impart charge carriers to the crystal, the rest forming neutral or compensating deep levels. In AlGaN, this problem is acute for p-type dopants, especially since Mg in large doping amounts results in large optically active defect concentrations which hamper the performance of UV optoelectronics. There have been multiple attempts at developing a solution to this problem, including modulation doping, utilization of the polarization field in III-nitrides and searching for alternative dopant elements.

In this chapter we explore the idea of achieving enhancement of p-type doping in wide gap III-nitrides by artificially engineering gradients in the polarization field of the crystal and apply this concept to the problem of solid state deep UV LEDs. Using the exceptionally strain tolerant nature and high optical quality of of III-nitride self assembled nanowires[58], composition graded heterostructures are prepared which enhance both p-type and n-type doping which have composition tunable active region emission from 250 nm to 550 nm. Electrical devices are fabricated from these heterostructures which exhibit electroluminescence.
The core results of this chapter are published in a number of papers by the author and coworkers\cite{4, 7, 59, 5}. It should be noted that this project was a collaborative effort between the author who performed most of the measurements and spectroscopy and fellow graduate students in the Myers research group Santino Carnevale who grew most of the samples in the first few years of the project and A. T. M. Sarwar who followed on with growth and various tasks for the study of polarity in the nanowires. Patrick Phillips provided all transmission electron microscopy work unless otherwise noted.

4.1 Polarization doping in III-nitride compound semiconductors

The group III-nitride family of compound semiconductors exhibits the crystal structure wurtzite, which can be visualized as two hexagonal close packed (HCP) sublattices translated $3/8$ of a lattice constant vertically from one another. What this means is that Ga atoms at tetrahedrally coordinated with nitrogen atoms. However, in nitrides, the translation is slightly different than $3/8c$ (larger or smaller depending on composition) causing a slight imbalance in the net bondlength between Ga and N atoms along there c-axis. This distortion, coupled with the fact that bonds in nitrides are highly polar due to large differences in electronegativity between N and Ga atoms, results in a spontaneous net dipole moment per unit volume which is composition and strain dependent. Since wurtzite is noncentrosymmetric, a sizable piezoelectric effect is present as well.

Since the magnitude of this dipole moment is composition dependent, if we can create engineered, microscopic variation in composition, we can in effect create a local variation in the dipole moment per unit volume or polarization, denoted $P$. Given
Gauss’ law for dielectrics

\nabla \cdot D = \rho_{\text{enc}}. \quad (4.1)

Where \( \rho \) is the charge density and \( D \) is the electric displacement defined as

\[ D = \varepsilon_0 E + P \quad (4.2) \]

where \( E \) is the electric field and \( P \) is the polarization of the dielectric. Inserting this into Gauss law and considering an electric field free region yields the expression

\[ \nabla \cdot P = \rho_{\text{enc}} \quad (4.3) \]

By convention, we define the charge due to a positive polarization gradient to be negative thus we arrive at the expression

\[ -\nabla \cdot P = \rho_b \quad (4.4) \]

where \( \rho_b \) is the bound charge density. The charge due to polarization gradients cannot be isolated and transferred like free charge can, and thus it denotes a bound charge which is fixed in the lattice, much in the same way an ionized dopant ion behaves as a fixed charge. In the absence of fields and forces, crystals must be charge neutral\([60]\). This is an important theorem of semiconductor physics known as the charge neutrality condition and is mathematically expressed as

\[ p - n + N_D^+ - N_A^- = 0. \quad (4.5) \]

Where \( p \) is the positive free charge due to holes, \( n \) is the negative free charge due to electrons and \( N_D^+ \) and \( N_A^- \) are bound positive and negative charge due to ionized
donor and acceptors, respectively. In the case where we have a gradient in polarization within the material, the charge neutrality condition becomes

\[ p - n + N_D^+ - N_A^- + N_{pol} = 0. \] (4.6)

Where \( N_{pol} \) is the bound charge due to the gradient in polarization throughout the material. This additional term in the charge neutrality condition forces the crystal to drive equilibrium towards production of more free electrons or holes from ionized dopants to compensate this bound charge. In this way, we can think of polarization gradients as producing an additional driving force for dopant activation other than thermal energy alone.

Compound semiconductor heterostructures, grown with the atomic layer precision of MBE allow for the synthesis of artificial dielectrics with engineered polarization gradients of substantial magnitude such that they rival impurity imparted charge density in magnitude. This has enabled much research over the last decade seeking to demonstrate polarization induced charge and doping[61, 62, 63, 64, 65, 4]. Currently, both p and n type polarization enhanced doping have been demonstrated by a number of groups with multiple applications targeted. Notable experimentally demonstrated characteristics of polarization doping include thermal invariance of carrier concentration[61] and composition gradient sign dependence of doping type[62].

### 4.2 Growth of III-nitride nanowire heterostructures

As discussed previously, growth of planar films GaN by PAMBE has been shown to produce the highest quality materials when optimized to provide group III elements in excess (> 2x) of stoichiometry. This is primarily due to the fact that in
these conditions a steady state wetting layer of liquid Ga which functions as a surfactant to lower the effective surface energy of the semiconductor, encouraging Ga and N adatoms to incorporate in a more or less two dimensional step-flow growth mode. If the stoichiometry is inverted, and active nitrogen species are provided in excess, the dominant growth mode for nitrides becomes a three dimension Volmer-Webber or Stranski-Krastanov growth mode, favoring nucleation and growth of nano-columnar morphologies[55]. Although this region of the growth phase diagram was initially avoided for thin film growth, it has been more recently been shown to lend itself extremely well to formation of strongly oriented GaN whiskers or nanowires on a variety of substrates, including Si (111)[66, 58], Si(001)[67], Mo, and c-plane Sapphire[68]. More recent work has led to independent control of nanowire aspect ratio and density during growth as well as heteroepitaxy of AlN on GaN nanowires.

The interest in GaN nanowires from a technological and research standpoint has initially centered on their high crystalline quality compared to bulk films. Due to the lack of affordable and high crystalline quality substrates for GaN based devices, most epitaxial layers of this material suffer from high threading dislocation densities (TDD) exceeding $10^6$ cm$^{-2}$. This high amount of TDD causes reliability and efficiency issues in devices fabricated from these materials[69]. Self assembled GaN nanowires have been widely shown to be largely free of extended defects such as dislocations and stacking faults[66]. Moreover, they exhibit very high internal quantum efficiency (IQE) (>50% reported) and narrow PL linewidth which suggests that the overall optical quality is high[70]. These striking properties have attracted much interest, both toward the further understanding of the properties of high quality single crystalline GaN and the possibility of development of functional devices from these
materials. Additionally, GaN nanowires have attracted interest as optical waveguides and lasers for on-chip photonics due to their high refractive index contrast with air and demonstration of room temperature optically pumped lasing[71].

Another unique property of III-nitride nanowires is that when prepared in certain aspect ratios, they are exceptionally strain tolerant. Glas[72] showed that at certain diameters, the critical thickness (thickness of a film at which the first misfit dislocation will nucleate to relax strain) for rather large lattice mismatches can in fact tend to infinity. What this means is that heterostructures that would otherwise be unfeasible in thin films due to strain considerations can be readily grown with high crystalline quality in nanowires, making more of the bandgap engineering toolbox available to heterostructure designers. This has led to demonstrations of InGaN/GaN light emitting diode structures, both coaxial and vertical, AlN/GaN periodic superlattice structures in vertical and coaxial geometries which have been shown by high resolution scanning transmission electron microscopy to be single crystalline and largely free of extended defects.[66]

4.3 Polarization-Induced pn Diodes in Wide-Band-Gap Nanowires with Ultraviolet Electroluminescence

Following the work of Simon et. al.[62] which showed successful p-type polarization doping of GaN heterostructures graded from AlN to GaN in the Ga-polar direction, the concept of applying polarization doping to a bipolar device became of interest. As of 2011 the only device to be demonstrated was a pol-FET[63] which utilizes the 3D electron slab produced by grading composition from GaN to AlN in the Ga polar direction. At that point, however, no device which requires holes to function, such as a pn junction or LED which utilized polarization enhanced doping
had been demonstrated. This demonstration was an important proof of the model of polarization charge leading to enhanced free charge concentrations.

Toward this end, a heterostructure based on self assembled catalyst free III-nitride nanowires which contained linear grades from 0% to 100% Al in AlGaN abutting the active region of the heterostructure was designed and is shown in Fig. 4.1. Nanowires were chosen due to their inherent strain tolerance, as a grade from GaN to AlN and back to GaN over 200nm would not be possible in thin films, greatly limiting the magnitude of polarization charge which could be generated. As can be observed from the band diagram for this device, calculated using a self consistent Schrödinger-Poisson solver[73], the linear graded regions are predicted to result in n and p type regions abutting the active region of the device, which should form a heterojunction light emitting diode of sorts and thus should emit light with energy equal to the bangap of the quantum well in the active region when forward biased.

Figure 4.1: Polarization induced light emitting diode band diagram and charge density as a function of position. Adapted From Ref. [4]
Heterostructures were grown by PAMBE using typical self assembled nanowire growth conditions on Si (111) substrates. In the earliest set of samples, this grade in composition was accomplished by logarithmically ramping effusion cell temperatures of both Ga and Al cells in order to produce a linear change in flux. In later samples an subsequent generations of the PINLED design, the composition gradient is accomplished by instead pulsing the Ga and Al shutters and varying their relative duty cycle at a constant effusion cell temperature. Initially, samples were grown using continuous nucleation and growth process whereby the nanowire density and morphology constantly evolves during growth at lower temperatures. In the graded regions, Mg and Si were added for p-type grades and n-type grades, respectively. This was done following the reports by Simon et. al.[62] of the requirement of providing the polarization doped region with a source of free charge to activate, and lack of success with UID polarization doped p-type regions.

Figure 4.2: PINLED device schematic and IV characteristic showing rectification.
Devices were produced by evaporating metal contacts directly on the tops of the nanowire film with an angled deposition process (Fig. 4.2), which resulted in a coalesced metal film connecting an ensemble of individual nanowires connected in parallel. Contacts were made to the Si substrate by mechanically removing nanowires with a diamond scribe and depositing high purity indium metal with a soldering iron. Device IV characteristics (Fig 4.2b) show rectification and turn on around 5V, suggesting that a diode was indeed prepared. Rectifying IV curves, however, are not conclusive proof for existence of a bipolar device such as a pn-junction, since non ohmic metal-semiconductor junctions can form rectifying Shottky junction which would yield similar IV behavior. Conclusive proof of bipolar transport in these structures hinges on being able to detect the electron-hole recombination which produces electroluminescence in a light emitting diode.

In order to measure the potential output of light from these devices, a custom sample mount for electrical feedthroughs was desired and fashioned from a repurposed printed circuit board for the cryostat. This allowed for samples to be wired up at a workstation under a stereozoom microscope and then easily transferred and connected in the optical system. The optical system at this point consisted of a 50 mm fused silica lens to collimate the light emitted from the sample which was subsequently free space coupled into a 0.5 m Cznery-Turner spectrograph (Princeton Instruments SP2500i) and dispersed onto a deep depleted scientific grade CCD camera (Princeton Instruments PIXIS BR100). The first set of samples measured for this experiment used a thick 100nm metal layer as the top contact, which resulted in exceptionally low optical throughput. In order to maximize serendipity with this experiment, the sample was aligned with photoluminescence at the contact using a xenon arc lamp.
excitation source. Following alignment of the optical system, broadband, background subtracted spectra were collected for case with the device unbiased and forward biased while using multi-second integration times in order to increase signal to noise ratio (SNR).

Figure 4.3: First observation of electrically driven optical emission from PINLED heterostructure in 2011.

Analysis of these spectra showed a slight increase in detected intensity at 3.7 eV, about 335 nm, as shown in Fig. 4.3. Although this signal was exceptionally small due to high absorption loss in the thick metal top contact, its correlation with device forward bias led to the conclusion that electroluminescence was observed. Following this observation, device fabrication routines were modified to reduce the top transparent contact thickness to a more acceptable 10 nm Ni / 20 nm Au. However, it
should be noted that even stacks of tens of nm will absorb considerable amount of light emitted from the semiconductor.

Another observation made early on in the study of these devices was that devices grown at lower temperature where nucleation and growth were not separated have exceptionally high environmental sensitivity, as shown in Fig. 4.4. In order to explain spurious device performance during cryostat vacuum pumpdown, the voltage across device at a constant current injection was systematically monitored as a function of time during pumpdown. It was observed that as the pressure drops, the devices conductivity increases and EL begins to disappear. It was further found that upon venting of the cryostat, all function of the LED was restored. This is explained by the lack of a coaxial shell of AlN for samples grown at lower temperatures, causing the surface of the nanowire to be unpassivated and therefore have strong sensitivity to ambient species of water and oxygen. These findings suggest that unpassivated nanowires could be used as gas or humidity sensors, and should have rather large sensitivity due to their high surface to volume ratio.

In order to further understand the characteristics of this heterostructure and eliminate environmental sensitivity, a sample was prepared using the recently developed two-step nucleation and growth technique which allows simultaneous and independent control of nanowire density and aspect ratio[58]. Wires were nucleated at 720 C and grown at 790 C. In order to attribute the observed EL in the heterostucture, an active region consisting of a single 5 nm GaN quantum well with 5 nm AlN spacers was chosen. This device was loaded into the optical system and its performance was systematically characterized. When forward biased, the device emits visibly violet
Figure 4.4: Environmental sensitivity of polarization enhanced nanowire LEDs. **a.** First generation, one step devices exhibit poor passivation. **b.** Second generation, two step nanowires.

light, corresponding to the bandgap of the active region of the device (GaN, 3.4 eV, 365 nm), as shown in Fig. 4.5a.

Figure 4.5: Electroluminescence spectra of GaN quantum well polarization induced nanowire light emitting diodes. Adapted From Ref. [4]
Moreover, this system exhibits injection level dependent emission energy, which is characteristic of quantum wells grown along the polar direction in III-nitrides. Since GaN and AlN have different dipole moments per unit volume, at their heterointerface a sheet charge exist which causes the quantum wells to be distorted, known as Stark shifted. This quantum well distortion is a major factor which limits GaN-InGaN LED performance and eliminating it via growth of LEDs on non-polar or semi-polar substrates is an active area of research[74]. The origin of the emission shift with injection level is understood to follow from charge carrier screening of the polarization charge at very high injection levels. As can be observed from Fig. 4.5b, at very low injection levels where the polarization charge at the heterointerface dominates, the emission from the quantum well peaks nearly in the green-blue at 500 nm. When the injection level is increased, the emission wavelength gradually begins to shift toward higher energy, eventually reaching the energy equal to the bandgap of GaN.

After the device is fully turned on around 5V, the emission energy tracks applied voltage in a linear fashion until it reaches the bandgap of GaN, as can be observed from Fig. 4.6. The intensity of the EL peak monotonically increases with injection level for low current densities. At higher current densities, however, devices do exhibit measurable efficiency droop in DC mode, likely due to self-heating effects.

In order to more fully understand the origin of the large emission shift with current in these heterostructures, photoluminescence spectra were systematically collected as a function of excitation power density. This was aided by the construction of a non-absorbing, polarization based, automated variable attenuator for our Ti:Sapphire based spectroscopy system, which is discussed in detail in Appendix A. In principle, photocarrier injection should produce an analogous effect to electrical injection into
the stark shifted quantum well. Since the recombination time is finite, carriers will begin to accumulate in the well, screening the polarization charge and undistorting the well. Although this is readily accomplished with electrical injection at high current

Figure 4.6: EL characteristics as a function of injection level. a. emission energy vs. applied voltage and peak intensity vs. current density. b. peak intensity as a function of current density. Adapted From Ref. [4]

Figure 4.7: Optical injection level dependent emission energy from GaN quantum disk active region in PINLEDs.
densities, achieving such high steady state carrier concentrations via optical excitation requires rather high power densities approaching the MW/cm² level. In order to achieve sufficient power densities, a 36x all metal reflective microscope objective was mounted as the excitation objective, allowing for focus to a diffraction limited spot size of slightly under 1 µm. Spectra were collected for each excitation power using an automated data acquisition routine written in NI-LabView. As can be observed from Fig. 4.7, as the power density of the excitation increases, the emission energy of the quantum well monotonically shifts higher. Eventually, at sufficient power density where the interface charges are completely screened, the emission stops shifting at the bandgap of the active region.

This effect was further investigated using the technique of time correlated single photon counting (TCSPC) which allows for the collection of time domain PL decay curves. Fluorescence light from the PINLED samples was directed into a second
monochromator equipped with a microchannel plate photomultiplier tube (MCP) which exhibit instrument response functions of 20 ps. Photon events are binned by a FPGA based counter and timer as a function of time after the first photon event. Further details of this technique as well as construction of the actual instrument are discussed in Appendix A. PL decay curves were collected as a function of laser input power. PL lifetime was determined by fitting a single exponential decay function to these data and reporting the time constant of the decay. As can be observed from Fig. 4.8, the observed lifetime decays linearly with optical injection level. These data are interpreted as follows. As the higher injection level decreases the quantum well distortion, the electron and hole wavefunctions gradually begin to overlap in an increasing amount, which increases the probability of recombination thereby decreasing the PL lifetime.

Figure 4.9: Temperature dependence of emission characteristics of GaN active region polarization induced nanowire LEDs. Adapted From Ref. [4]
In order to further understand the nature of the polarization charge, temperature dependent experiments were conducted. These efforts consisted of mounting the device in a closed cycle cryostat and collecting EL spectra and IV curves as a function of temperature. The purpose of this study was to ascertain how much of a role polarization doping would play in the conductivity of these structures. Semiconductors whose conductivity is dominated by thermally activated impurity doping exhibit significant decreases (often multiple order of magnitude) in electrical conductivity when cooled to cryogenic temperatures, whereas polarization doped materials tend to exhibit behavior which is largely temperature independent, provided that doping levels are not degenerate[62]. Therefore, analysis of conductivity and optical output as a function of temperature should give some insight into how large of a role polarization plays in the behavior of these structures.

From the evolution of electroluminescence spectra with temperature at various current injection levels (Fig. 4.9), we can see that though there exist a marginal amount of intensity variation with temperature, particularly between 150 K and 300 K; a decrease of order of magnitude does not occur from room temperature to low temperature. Additionally, in this experiment, the current density at constant bias of 10 V was collected during the temperature scan. Interestingly, the magnitude of the current at constant bias follows a very similar temperature dependence to that of the electroluminescent intensity, which functions as a sanity check that the trend in EL intensity was not due to a unaccounted for thermal variation in our measurement system.
Analysis of the devices electrical characteristics as a function of temperature provide a more pure insight into the thermal activation of conductivity in these structures. Toward this end, temperature dependent IV-curves (Fig. 4.10) were collected in a systematic fashion from 10 K to 300 K. From these data it can be observed that the conductivity of these structures at various biases in the IV curve behaves in a very similar fashion to the EL spectra collected in an earlier experiment (Fig. 4.9). The current is thermally invariant below 150 K, for all biases recorded. Beyond 150 K, conductivity becomes somewhat thermally activated, but substantially less than that predicted by the exponential dependence of conductivity on temperature predicted by the ideal diode equation\[60\]

\[
I = I_s \left( e^{(V_D/nV_T)} - 1 \right).
\]  

(4.7)

These data can be interpreted as follows. Thermal activation of conductivity in a pn junction comes from multiple sources. Firstly, the carrier concentrations in
the p and n type regions of the diode will determine the series resistance of each section. Secondly, the presence of the built in voltage of the junction, gives rise to a thermal activation term in the conductivity of the junction. In both of these cases, the conductivity at a given bias should be more or less exponential with temperature. As we can see from Fig. 4.10, there exists no such thermal activation at low temperature, suggesting that transport of carriers into the quantum well and/or depletion region of the diode occurs by a largely temperature invariant process such as weakly thermally activated tunneling. Moreover, the fact that the series resistance of the device is not strongly thermally activated is a strong indicator that the charge due to the polarization gradient in these structures is in excess of that due simply to thermal activation of impurity dopants.

As a further proof of concept and investigation into the magnitude of the polarization enhanced doping in these structures, an experiment was designed to test the requirement for external dopant atoms for these devices to function. Reports in the literature prior to this work demonstrated a requirement for a limited amount of impurity Mg atoms in p-type composition graded regions in order to provide a source of free charge[62]. Three samples were prepared by PAMBE where, in each sample the presence of dopant atoms in the p and n type regions of the diode was manipulated. The sample set consisted of a control sample with acceptor and donor doping (Mg and Si, respectively), a sample where the Si was not deposited during growth of the n-type region and finally a sample where neither Si nor Mg were deposited during growth. Standard LED devices were processed from these samples and their I-V curves and EL spectra were measured, the results of which are shown in Fig. 4.11.
Removal of Si doping from the n-type region of the heterostructure has very limited effect on the gross features of both the device conductivity as well as the electroluminescence spectra. Interestingly, the device formed without intentional addition of donors still exhibits both electroluminescence and rectification, indicating that a bipolar device was successfully fashioned. The function of polarization doping for n-type material without impurities has previously been demonstrated, and this result is therefore consistent with those findings. As can be observed from the I-V characteristic, without the addition of Si doping, the devices series resistance increases slightly from that of the control. Additionally, in the control sample there exists an electroluminescence peak at 3.6 eV which is not present in samples where Si has been removed. This may suggest the elimination of an optically active defect level associated with the presence of Si during growth.
Analysis of the data from the third and final sample, where no impurity dopant was added leads to the conclusion that both rectification and electroluminescence are present, indicating successful bipolar transport in the absence of both Si and Mg impurity dopants. This observation is unique in that previous work was unable to achieve conductive p-type material from polarization gradients alone[62]. Moreover, subsequent analysis of C-V measurements carrier out by A. T. M. Sarwar confirms the presence of free holes in this heterostructure[75]. It is hypothesized that due to the considerably higher surface to volume ratio of nanowires, the free surface of the nanowire provides the requisite surface states which may be ionized to produce free holes in the p-type regions[76]. In the case of thin films, there may simply not be enough available ionizable states in graded regions for the polarization charge to activate.

In the interest of obtaining some calibrated numbers to compare these prototype devices with commercial planar film based UVLEDs, a calibrated measurement of device emission intensity was conducted. The apparatus consisted of a calibrated Si photodiode power meter mounted directly above the active contact of a wired device. The device was driven at constant DC current through the full range of the power supply and the output power was recorded for all currents using a computer control VI written in NI Labview. The results of this study are shown in Fig. 4.12, peak output power is measured to be slightly over 65 µW at 120 mA. The operating voltage for these devices is rather high (around 10 V at 120 mA), likely due to a Shottky junction at the GaN/Si interface and a resistive metal top contact, which is likely not ohmic. This causes the external quantum efficiency (calculated as wallplug efficiency) to be in the µ% regime.
Figure 4.12: GaN QW PINLED performance data.

In conclusion, self assembled III-nitride nanowires provide the necessary strain tolerant properties to fashion prototype bipolar devices based on engineered polarization gradients. These synthetic polarization gradients give rise to regions of free charge whose sign depends on the direction of the composition gradient and the crystal axis which the gradient occurs along. This concept was demonstrated by design and synthesis of ultraviolet light emitting diodes using III-nitride GaN/AlGaN heterostructures with composition gradients along the polar c-axis of the crystal. These devices exhibit current rectification and electroluminescence at the bangap of the active region of the heterostructure. The nature of the polarization charge was investigated by temperature dependent measurements of IV characteristics and electroluminescence spectra. It was observed that these devices do not exhibit substantial thermal activation of conductivity or emission intensity, which is consistent with other reports of polarization enhanced doping in the literature. Due to the large mismatch in polarization moment and bandgap, the GaN quantum well active regions in AlN
barriers exhibit a substantial quantum confined stark effect (QCSE) which is found to be mitigated at high carrier injection levels and experimentally demonstrated optically and electrically. Output power of prototype devices is measured and from these measurements the external quantum efficiency is calculated. Although the concept of polarization enhanced doping is demonstrated here in the III-nitride system, it is emphasized that all alloy families with composition tunable polarization moments (ZnMgO, InGaN, etc.) can take advantage of this effect to supplement or replace necessity for impurity doping in achieving desired conductivity.

4.4 Optical Characteristics of PINLEDs

Over the course of this work, two primary pathways for improvements in device functionality have been investigated. The first being emission wavelength tuning of the devices to higher energies, since in principle, emission at all AlGaN bandgaps should be possible with these heterostructures. The second core priority for further development is improvement of emission intensity and wallplug efficiency. For all device iterations and heterostructure modifications, the primary feedback tool in this project is optical data either collected as electroluminescence or photoluminescence spectra and or TRPL decay curves. In this section, a number of optical measurements of nanowire devices and materials performed by the author are described.

An important metric of material quality is the ratio of electron-hole pairs (known as excitons) to emitted photons, known as the internal quantum efficiency (IQE). This is a rather difficult quantity to measure since many factors effect exciton recombination processes, only some of which result in production of bandgap energy
photons and there is no practical way of discretly counting excitons in a semiconductor. Instead, this quantity is empirically reported by assuming the semiconductor to be 100% quantum efficient at low temperature and report IQE as the ratio of intensity at room temperature to low temperature. This is a rather crude assumption in practice, the validity being strongly dependent on high injection level conditions and the activation energy of the traps involved, but it is the dominant metric for material optical quality nonetheless[77].

Figure 4.13: Determination of Internal quantum efficiency of PINLEDs via Photoluminescence spectroscopy.

To this end, in the interest of establishing the theoretical upper bound for external quantum efficiency (EQE) of the PINLED devices, we measured the IQE over a wide range of quantum well compositions. In principle, the external quantum efficiency
which takes into account efficiencies in electrical injection, series resistance, and radiative recombination efficiencies must always be less than or equal to the internal quantum efficiency. This measurement consisted of mounting a series of samples in a closed cycle cryostat and measuring their photoluminescence spectra at 20 K and 300 K (the base temperature of the cryostat and room temperature, respectively). Three samples with increasing amounts of AlGaN incorporated in the quantum well of the device were studied, the results of which are shown in Fig. 4.13. Although no clear trend exists in peak intensity or FWHM, the following observations can be made from these data. Firstly, the emission wavelength decreases with increasing Al composition in the quantum well, as expected from the increasing bandgap of the quantum well. Moreover, the IQE, seems to be compositionally invariant over the range studied. The high IQE values observed in this experiment of 50% for all samples studied are consistent with the work of other groups researching self assembled III-nitride nanowire heterostructures[70] and are strong indicators of the high optical quality of these materials. This result also suggests that the factors limiting the EQE of PINLEDs are predominantly device related. These factors can involve light extraction difficulties due to top contacts, junction series resistance and current injection efficiency. It therefore should be emphasized that a significant portion of future work should be targeted at improvements in device electrical characteristics and light extraction.

Closely related to the internal quantum efficiency of semiconductor materials is the photoluminescence lifetime, which at cryogenic temperature can be assumed to be approximately equal to the radiative lifetime of the material. Time resolved photoluminescence of nanowires has been explored in the literature over the last decade to
some extent, although most studies have focused on rather large, µm scale nanowires. For nanowires, it has been observed that there exists a measurable dependence of the fluorescence lifetime on nanowire diameter[78], resulting a reported surface recombination velocity of $9 \times 10^3$ cm/s, on the order of lightly doped III-V materials. For smaller diameter nanowires (<0.5 µm) there still exists somewhat of a debate as to whether the surface recombination velocity effect exists[79].

![TRPL of Bulk GaN nanowires](image)

**Figure 4.14:** TRPL of GaN nanowires of differing dimensions.

TRPL measurements were performed on PAMBE grown nanowires at OSU. A wide variety of nanowires have been studied over the course of this work, both heterostructures and single composition wires. A general trend that is observed is that the nanowires exhibit lifetimes which are considerably reduced when compared to bulk MBE grown films. Fluorescence decay curves for two single composition GaN
nanowire samples are shown in Fig. 4.14. These two samples are greater than 1 µm in length but differ in diameters. Both samples exhibit PL lifetimes on the order of 40 ps, which is one to two orders of magnitude lower than bulk films of GaN. Self assembled nanowires grown by the two-step technique have rather severe aspect ratios often greater than 4:1 length to diameter. This causes most nanowires to be below 100nm in diameter, which increases the probability of interaction of the exciton with the free surface of the nanowire, enhancing the probability of non-radiative recombination at the surface.

4.5 Using Bias dependent electroluminescence spectroscopy to understand mixed polarity growth of self assembled III-nitride nanowires

This section is an adapted excerpt from a recent publication by the author and coworkers[5]. As outlined in previous sections, a novel bipolar device which utilizes engineered gradients in the dipole moment per unit volume was demonstrated and developed. All initial devices and heterostructures were fashioned assuming Ga face (\([0001]\)) orientation of the growth direction of the nanowires. This is a particularly important assumption since the sign of the grown normal will determine the sign of the polarization charge present in each compositionally graded region. Ga face polarity was assumed since at the time only one group[80] had conducted a systematic investigation of material polarity and concluded the dominant amount of nanowires to have growth normals along the [0001] direction.

This choice of growth direction led to the choice of an n-Si substrate and a p-n junction oriented with the n-type side, supplementarily doped with Si, closer to the Si and the p-type side, supplementarily doped with Mg as the top contact, as shown
in Fig. 4.15a. However, it should be noted that if this assumption proved incorrect and the nanowires actually preferred N-face [000\bar{1}] polarity, then the doped regions reverse and the band diagram would become that shown in Fig. 4.15b. As can be readily observed, for N-face [000\bar{1}] polarity, the n-Si substrate is no longer suitable for creation of an electrical device due to the large discontinuity at the heterointerface with the p-type region.

Establishing the polarity of a thin film or nanostructure is a particularly challenging task due to the lack of approachable direct inspection methods. One of the few direct methods for establishing polarity is to use high resolution STEM in an imaging mode that can show both the cation and anion sublattices. Imaging of the anion sublattice in III-N compounds is particularly challenging due to the low atomic number of nitrogen and thus its low contrast in HAADF imaging mode. Recently an imaging mode for STEM has been develop denoted annular bright field (ABF) which allows for imaging of both the cation and anion sublattices in nitrides[81]. This technique was applied to various PINLEDs grown on Si by PAMBE. The results of this study indicated that most wires observed grew along the N-polar direction [000\bar{1}]. Due to
the limited sample size of TEM analysis, a set of experiments were devised which would allow macroscale investigation of the polarity of the nanowires with reasonable samples sizes. This was broken into three parts, electron microscopy, selective etching and bias direction dependent electroluminescence spectroscopy.

The authors role in this effort was to provide detailed bias dependent electroluminescence spectroscopy for a number of devices in order to infer nanowire polarity from the optoelectronic characteristics of these devices. In this study, two otherwise identical devices were prepared, one with supplemental impurity doping assuming Ga face polarity and one without any intentional doping. The hypothesis was that devices doped for Ga face polarity would only emit bandgap electroluminescence when positive bias was applied to the top of the nanowire (forward biasing doped Ga face wires). Devices which were undoped would emit quantum well electroluminesce in both biasing direction, if there existed a substantial population of both polarities and EL in only one biasing direction if a particular polarity was dominant. This was made possible by the fact that the PINLED heterostructure allows for formation of UID pn junctions[4], the polarity of which are simply determined by crystal orientation.

Devices were wired up individually and their electroluminescence spectra were collected as a function of biasing direction. The resulting spectra are shown in Fig. 4.16. As can be observed from Fig. 4.16a., the device which is supplementarily doped assuming Ga face directionality preferentially emits bandgap EL for positive bias applied to the top of the nanowire, effectively forward biasing all Ga face wires. When the bias is reversed, two distinct peaks emerge, one at 260 nm and another at the energy of the GaN quantum well. The intensity of these peaks is substantially reduced compared with the positive bias case.
For the device which is grown without intentional addition of impurities (Fig. 4.16b.), a wholly different behavior is observed. In this device, both biasing directions produce energy at the bandgap of the GaN quantum well active region and have intensities which are much closer in magnitude than the doped device. Moreover, the case where negative bias is applied to the top of the device, corresponding to forward bias for PINLEDs grown in the [000\bar{1}] orientation, actually results in more intense EL. These data are a strong indicator that there actually exists measurable amounts of both Ga and N face polarities of nanowires. The case of the Ga-face doped device shows that in reverse bias, the measurement samples N-face wires which are essentially doped to compensate charge due to polarization gradients, resulting in highly resistive wires which emit EL likely by impact excitation process or breakdown.
Further investigation into this question via selective etching and detailed atomic resolution ABF electron microscopy exhibited findings consistent with this study. Using selective etching techniques, which remove only one polarity and measuring nanowire density as a function of etch time as well as ABF analysis of samples exposed to long etches, it was determined that about 90% of nanowires grown using the catalyst free self assembly process on Si (111) grow in the N-polar orientation[5].

The implications of these findings for the project at large were very far reaching. Obviously, all previous samples which were designed and doped assuming [0001] polarity were exhibiting conductivity and rectification from only 10% of the parallel wired nanowire devices. Subsequent devices have been grown on p-Si and doped according to N-face polarity. Interestingly, despite expectations for large increases in device performance, these modifications resulted in devices with more or less unchanged EQE. This suggests that the conductivity of the nanowire device itself is not the prime reason for the low EQE in PINLEDs. One of the more unfortunate consequences of N-face polarity in these devices is that Si is no longer a very ideal substrate as a substantial discontinuity occurs in the valance band at the p-Si/p-GaN heterointerface. This issue has resulted in a number of explorations such as growth of PINLEDs on refractory metal substrates[68].

Mixed polarity of GaN nanowires on Si is inherently due to the mismatch in crystalline symmetries at the interface. This problem has been overcome in other materials systems by forcing a particular surface recombination of the Si due to angle of miscut (vicinality) and or a chemical treatment of the Si prior to growth. Growth kinetics and thermodynamics of the nanowires may also play a role. It has been widely reported that growth of an AlN seed layer on Si prior to GaN nanowire growth
established a dominant Ga-face ([0001]) polarity\cite{66}. For device applications it is obviously desirable to have a single polarity present. Patterned growth via selective area epitaxy would allow for enhanced control over kinetic variables such as island size and nanowire aspect ratio, allowing for systematic analysis of the effects of various variables on polarity.
Chapter 5: Atomically sharp 318 nm Gd:AlGaN ultraviolet light emitting diodes on Si

In the previous chapters of this thesis we have primarily covered two topics, integration of rare-earth ferromagnetic materials with wide bandgap semiconductors and development of nanowire based polarization enhanced light emitting diodes for deep ultraviolet applications. Separately, these projects have yielded materials and devices with unique structures, properties and functionalities. This section describes an effort to integrate GdN as the active region of polarization induced nanowire light emitting diodes. It is shown that addition of GdN between AlN barriers in the active region of a PINLED results in a novel optoelectronic device which allows for electrical modulation of rare earth 4f shell luminescence lines. Although a rich literature exists for a related device structure, thin film electroluminescent devices, which utilize high voltage bias to drive impact excitation of 4f centers, PINLEDs with GdN active regions produce narrow linewidth 318 nm emission at biases as low as 5V. The core results of this chapter are described in a prior publication by the author[7]
5.1 Rare earth phosphors: physics and properties

Following the realization of the ruby (Cr:Al₂O₃) laser over half a century ago[82], many materials have been developed as hosts for elements with optically-active energetic transitions to produce lasers and electroluminescent devices with emission in the visible and infrared part of the electromagnetic spectrum. Host materials typically have consisted of insulators with wide bandgaps such as Al₂O₃, YVO₄ and YAG, which can be prepared as high quality bulk synthetic crystals. Phosphor elements typically consist of elements with $d$ and $f$ orbitals, because the crystal field interacts with the energy level scheme of these in such a way that energetic transitions from the ground to excited state produce photons with energies ranging from the near-infrared to mid-UV regions of the electromagnetic spectrum. Most notable of these have been Nd, Ti, Er and Cr. Historically, fluorescent centers in these materials have been optically excited using a high intensity, high energy laser beam or flash lamp. More recently, Er-doped fiber amplifier (EDFA) based lasers have made an extremely large impact in the manufacturing, telecom and research fields. In the last twenty years, electrically driven devices utilizing rare earth phosphors in wide or medium gap semiconductors have begun to make an appearance[6]. These thin film electroluminescent devices (TFED) have found applications as visible and IR emitters, and will be discussed in detail in further sections of this chapter.

Design of optoelectronic devices which utilize atomic transitions in the rare earths can offer a number of advantages over traditional band-to-band based devices such as LED’s. First, the transition energy is dictated by the energy level scheme of the $4f$ orbital, which is relatively unperturbed by the crystalline environment due to the fact that the $5d$ and $5s,5p$ orbitals extend to further radial distances, and fill before the
shell of lower principal quantum number[33]. This shielding by the earlier filled 5d and 5s orbitals causes the the energies of the 4f transitions to be relatively insensitive to crystalline imperfections, unlike transitions based on band-to-band transitions in semiconductors. Band-to-band optical transitions are well known[83] to be extremely sensitive to deep levels, point defects, and disorder in the crystal structure, leading to broadening of emission or parasitic emission at an unintended energy.

When an atom with d or f orbitals is placed in a solid state system, the local symmetry of the crystalline environment forms a periodic electrostatic potential, known as a “coordination sphere” which causes a perturbation to the energies of each sub-orbital. Depending on the interactions of the coordination sphere and the orbital symmetry, the suborbital may rise or fall in energy. Suborbitals of given l and m_l quantum numbers (e.g. d_{xz}, d_{xy}, d_{yz}, d_{z^2} and d_{x^2-y^2}) are degenerate when subjected to no external coulombic potential. However, when the symmetry of the coulombic potential becomes non-spherical, as in a crystalline environment, the degeneracy is lifted and the suborbital will assume an energy which is influenced by the local coulombic environment.

Although for 4f electrons the influence of the crystal field on orbital energies is relatively insignificant, it has important effects on the optical properties of intra-f shell optical transitions. The influence of the crystal field is crucial to the function of devices utilizing intra-orbital transitions in f shells, as they are otherwise forbidden by the Laporte selection rule for electronic energy transitions which is stated as \( \Delta l = \pm 1[6] \). This can be understood to mean that electronic transitions between quantum states in the same electronic shell are highly unlikely. The Laporte selection rule follows from a computation of the oscillator strength, f, which is directly proportional
to the measured intensity of a given transition[84]. The oscillator strength is given by[85]

\[ f = \frac{8\pi^2mc}{3he}G\nu M^2, \]  

(5.1)

where \( c \) is the speed of light, \( m \) is the electron mass, \( h \) is Planck’s constant, \( e \) is the electric charge, \( G \) is the degeneracy parameter, \( \nu \) is the frequency of light emitted from a radiative relaxation event and \( M \) is the transition moment, given by

\[ M^2 = M^2_x + M^2_y + M^2_z. \]  

(5.2)

Each of the components of the transition moment can be calculated separately by the inner product

\[ M_i = \int \overline{\psi_m} \hat{D}_i \psi_n d\tau. \]  

(5.3)

In this equation, the integral is over all space, \( \overline{\psi_m} \) is the final state wavefunction, and \( \psi_n \) is the initial state wavefunction for the electron and the transition dipole moment operator is denoted \( \hat{D}_i \). Although the mathematical details of \( \hat{D}_i \) are beyond the scope of our discussion, it is important to note that it has the property that its elements can be nonzero only if the initial and final quantum states do not have the same parity[86]. The symmetry of atomic orbitals is such that a unit change in the \( l \) quantum number leads to a switch of the parity of the orbital. Thus, for the case of a free ion, only transitions satisfying the condition \( \Delta l = \pm 1 \) will have nonzero transition moment and thus nonzero oscillator strength. Since all intraorbital transitions involve no change in \( l \) between initial and final quantum states, they are deemed “forbidden” and are not observed in spectra of free or gaseous atoms.
In the case of a rare earth ion in a crystalline environment, however, the Laporte
selection rule can be relaxed. As discussed previously, the periodic electrostatic po-
tential of a crystal causes a perturbation to the structure of quantum states in a given
atomic orbital. If the local crystal symmetry around a rare earth atom lacks inver-
sion symmetry, as in the case of tetrahedral coordination, previously forbidden intra
$f$-shell transitions become allowed and are often observed[86]. Thus, when designing
a rare earth phosphor device, the crystal symmetry and manner by which the rare
earth incorporates in the lattice is worthy of careful analysis.

5.2 Thin film electroluminescent devices

Thin film electroluminescent devices traditionally have consisted of a double het-

erojunction between an insulator a semiconductor doped with a phosphor atom and

an insulator, with electrical contacts being deposited on the insulating layers. When a

sufficiently large bias is applied to the device, hot electrons at interface states between
the insulator and semiconductor will begin to tunnel into the conduction band of the
semiconductor, where they will be accelerated by the very high electric field. These

hot electrons may then interact with the lattice by inelastic scattering processes. If
a hot electron happens to collide with a rare earth ion, the energy transfer resulting

from the collision may be sufficient to excite a $4f$ electron of the ion to an excited
state. Because of the weak coupling of the $4f$ shell with the lattice, the probability
that this excitation will result in radiative relaxation by generation of a photon char-
acteristic of the energy difference between the excited and ground state of the ion is

high.
The previously described process is known in the literature as *impact excitation* and is fundamentally different than the mechanism of band-to-band recombination by which conventional semiconductor light emitting diodes function. It is also very important to distinguish the process of impact excitation with that of impact ionization. As shown in Fig. 5.1, in the impact excitation process, the kinetic energy transferred from the hot electron to the rare earth ion results in $4f$ electrons gaining energy, but not a sufficient amount of energy to become delocalized in the conduction band.

![Figure 5.1: Illustration of distinction between mechanisms of impact excitation and impact ionization. From Rack[6].](image)

In the process of impact ionization, the energy transferred from hot electrons to a lattice atom is sufficient to ionize the lattice atom, causing the highest energy electron to become delocalized in the conduction band. This process is commonly known as the mechanism by which carrier generation in avalanche breakdown takes place. The process of relaxation from the conduction band back into the localized $4f$
state is highly unlikely, since once the electron enters the conduction band, it is swept away by the large applied electric field. Thus, design of optoelectronic devices around impact ionization processes is unfavorable. Furthermore, in selection of a host for the rare earth phosphor, the bandgap of the material and alignment of $4f$ energy levels in the bandgap must be chosen such that the excited state is multiple thermal energies ($k_B T$) below the conduction band to avoid impact ionization. It should be noted that impact excitation is by nature a relatively inefficient process, due to short mean free path of hot electrons in a condensed system and the dilute nature of phosphor centers. Through derivation of an analytical expression of the quantum yield of RE phosphors, Bringuier[87] showed that quantum yield of RE in II-VI compound semiconductors is less than 1%, which suggest that structures need to be carefully designed to maximize electron energy before scattering events take place and maximize the interaction cross section of hot carriers with phosphor centers.

5.3 Integration of Gd phosphors with PINLED heterostructure

This chapter is a modified version of a previous publication by the author[7]. In this section we report on ultraviolet light emitting diodes based on self-assembled Al-GaN nanowire heterojunctions doped with Gd, which emit ultraviolet (UV) radiation at 318 nm and operate at lower device bias compared with existing Gd electroluminescent technology. Following the realization of the ruby laser over half a century ago[82], many materials have been developed as hosts for elements with optically-active energetic transitions to produce lasers and electroluminescent devices with emission in the visible and infrared part of the electromagnetic spectrum.
Design of optoelectronic devices which utilize atomic transitions in the rare earths for EL can offer a number of advantages over EL produced from band-to-band recombination. First, the transition energy is dictated by the energy level scheme of the 4f orbital, which is relatively unperturbed by the crystalline environment due to the fact that the 5d and 5s,5p orbitals extend to further radial distances, and fill before the f shell of lower principal quantum number[33]. This shielding by the earlier filled 5d and 5s orbitals causes the energies of the 4f transitions to be relatively insensitive to crystalline imperfections, unlike transitions based on band-to-band transitions in semiconductors. Band-to-band optical transitions are well known[83] to be sensitive to deep levels, exciton-phonon interaction, and crystalline disorder which can lead to broadening of emission or parasitic emission at an unintended energy. Additionally, due to the decoupling of the 4f orbital with the lattice, emission from rare earth centers is spectrally pure with common FWHM of less than 30 meV.

In recent years, the family of III-nitrides, particularly the pseudobinary Al\(_x\)Ga\(_{1-x}\)N, has become attractive as a potential host for rare earth elemental phosphors[88]. This material system offers a high breakdown field (1.2MV/cm for AlN) and sufficiently wide bandgaps (3.4 to 6.1 eV) to accommodate phosphors with emission from the UV to IR. Equally significant is the way in which rare earths incorporate in the wurtzite structure of GaN and AlN alloys. Rare earth (RE) ions commonly exhibit the RE\(^{3+}\) ionization state, which makes them isovalent with the Al\(^{3+}\) and Ga\(^{3+}\) cations of Al\(_x\)Ga\(_{1-x}\)N. RE atoms exhibit high solubility (in excess of 1at% has been reported[89]) and regularly incorporate at the cation site. Due to the wide range of energy level schemes of the lanthanides, EL from RE centers in AlN and GaN have been reported for Er\(^{3+}\) (IR, green)[90], Tm\(^{3+}\)(blue)[90], Eu\(^{3+}\)(Red)[88], and
Gd$^{3+}$(UV)[91]. Additionally, room temperature optically pumped lasing in Eu-doped GaN[92] has been successfully demonstrated.

Although most RE phosphors have been developed for optical transitions in the visible and infrared parts of the electromagnetic spectrum, the energy scheme of Gd$^{3+}$ in wurtzite AlN offers an energy difference between ground and first excited state of 3.90 eV (318 nm). The spectrally-narrow and energetically-stable nature of the Gd$^{3+}$ fluorescence emission make it a potential candidate for spectroscopic and lithographic applications in the UV. This led to exploration of dilutely Gd doped Al$_x$Ga$_{1-x}$N in the form of fluorescence[93] and cathodoluminescence experiments[94, 53, 91]. Although the 4f levels in the RE$^{3+}$ are typically thought not to interact with the surrounding lattice, cathodoluminescence data for Gd:AlN thin films shows phonon replica satellite peaks of the Gd$^{3+}$ $^6P_{7/2}\rightarrow^8S_{7/2}$ (318nm) transitions[94]. These data suggests that the 4f electrons in Gd$^{3+}$ in AlN are not completely decoupled from the host lattice.

Although there have been a number of reports[91, 93, 94, 53] on the spectroscopy of Gd:AlGaN compounds, less work has has focused on development of active opto-electronic devices that utilize Gd$^{3+}$ 4f transitions. This is likely due to the difficulty of achieving electrical contact to uid-AlN. Reports[91, 95] have been made of a “field emission device” consisting of a reactive ion sputtered Al$_x$Gd$_{1-x}$N film with metal contacts, forming a MIS structure whereby a high voltage 270 V to >1 kV driven across the device produces fluorescence of the Gd$^{3+}$ ions, likely by the process of impact excitation.
Figure 5.2: Optically active Gd$^{3+}$ 4f levels in the active region of a III-N nanowire polarization induced light emitting diode. **a.** Calculated device band diagram showing location of optically active Gd ions. Insert shows device schematic as measured. **b.** Device IV exhibiting turn on in forward bias at 5 V. Adapted from Ref. [7]

In this work, we study two separate heterostructures which are designed to generate EL under low electric field conditions (pn-diode) and high electric field conditions (Gd:AlGaN MIS structure). Self-assembled III-nitride nanowire heterostructures grown by plasma assisted molecular beam epitaxy have recently gained popularity for applications requiring high crystalline quality and largely mismatched, complex heterostructures that would otherwise be difficult to form in thin films due to strain considerations[58, 4, 59]. In addition, they have been shown to function at high current densities[59]. Additionally, UV-LEDs based on III-nitride nanowire heterostructures have been demonstrated to accommodate active regions spanning from high %Al AlGaN to GaN[59].
Polarization-induced nanowire diodes (PINLEDs), as discussed in previous chapters, containing Gd doping in their active region are prepared by plasma-assisted molecular beam epitaxy on n-Si(111) in the III-limited growth regime, the details of which are discussed in a publication by a coworker[4]. These devices consist of a GaN nucleation layer followed by a linear grade in composition from GaN to AlN over 100 nm. This is followed by an active region consisting of 2.4 ML of GdN deposited between two 5nm uid-AlN spacers. The structure is then linearly graded in composition from AlN back to GaN. This structure forms a pn-diode as shown in Fig. 5.2a, the band diagram of which is calculated with a self consistent Schrödinger-Poisson solver[73], as described in the previous chapter. The spontaneous polarization present in wurtzite Al$_x$Ga$_{1-x}$N combined with a gradient in composition give rise to polarization-induced hole and electron doping, respectively[62]. In addition to the built in polarization doping, wires are supplementary doped with Mg and Si in p and n regions, assuming c-axis,Ga-polar orientation of the nanowires.

From these heterostructures, electrical devices are fashioned by depositing semi-transparent 10nm/20nm Ni/Au contacts with an electron beam evaporator for the top contact, which connect the vertical ensemble in parallel. The back contact is fashioned by mechanically removing the nanowires adjacent to the top contact with a diamond scribe and thermally diffusing In metal directly to the n-Si with a soldering iron. Current-Voltage (IV) behavior of the devices are measured with a probe station and an Agilent B1500 semiconductor parameter analyzer. Device IV’s show rectifying behavior with device turn on at 5V, as shown in Fig. 5.2b.

After the IV behavior of the devices are characterized, they are transferred to a variable temperature UV-VIS-NIR spectroscopy system consisting of a closed cycle
ARS DMX20-OM cryostat and a Princeton instruments SP2500i 0.5m spectrometer equipped with a Princeton instruments PIXIS100 UV-VIS-NIR CCD. Devices are connected to a Yokogawa DC constant current source and Keithley 2700 data acquisition system. Prior to the collection of any spectra, a background spectrum is collected with no current injection in the device. Constant currents from 10mA to 120mA, corresponding to device current densities from 1.32A/cm$^2$ to 14.5A/cm$^2$ (the current density through any given nanowire is unknown since not all individual nanowires give EL[96]) are sourced at room temperature and the resulting EL is collected through a 50mm, f/2 uv-fused silica singlet lens, collimated and subsequently focused onto the entrance slit of the 0.5m spectrometer.

Room temperature EL spectra, shown for multiple current densities in Fig. 5.3a., exhibit multiple emission peaks from the UV through the visible parts of the spectrum. The sharp peak at 318nm (Fig. 5.3b.), corresponds to the $^{6}P_{7/2} \rightarrow ^{8}S_{7/2}$ first excited
state to ground state transition of the Gd$^{3+}$ ion$^{[53]}$. More careful inspection of spectra around the Gd atomic line region reveals an additional peak at the correct energy for the $^6\text{P}_{5/2} \rightarrow ^8\text{S}_{7/2}$ second excited state to ground state transition$^{[53]}$. In addition, the intensity of these peaks scale linearly with current density, within the range of currents investigated. The Gd emission exhibits FWHM of 23.1meV. Additional broad EL peaks in the 400nm-700nm range are attributed to below band gap defects in AlGaN, due to observation of identical emission spectra in non-Gd containing devices (Fig. 5.4), though the graded nature of structure prevents precise identification of the deep levels responsible.

![Evidence for 350-700nm peak as defect band in AlN/Graded region](image)

Figure 5.4: Comparison of spectra from PINLED with GdN active region and control sample with no GdN and an otherwise identical heterostructure
In order to further investigate the mechanism by which the UV emission occurs, variable temperature EL measurements are conducted from room temperature to 30K, the results of which are shown in Fig. 5.3c. Spectral intensity of the main $^6P_{7/2} \rightarrow ^8S_{7/2}$ Gd 4f peak is observed to be invariant at temperatures above 75 K, below which the intensity increases dramatically (Fig. 5.3c., insert). Similar behavior has been previously observed in Eu-doped GaN[97] as well as Er-doped InGaP[98] which is attributed to thermal quenching of the multi-step excitation mechanism of the RE$^{3+}$ ion. At low temperature another peak becomes distinct at 324 nm. This peak has been previously identified as a phonon replica of the primary 318 nm peak in cathodoluminescence experiments[94]. From analysis of the peak positions, a phonon mode energy of 72.2 meV is measured, which is smaller than the LO phonon energy of the surrounding AlN matrix (110 meV[99]) as well as GaN (92 meV[100]). This phonon energy agrees within the resolution of the spectrometer used with results from cathodoluminescence experiments, which report 72.9 meV[94].

Many RE electroluminescent devices rely on the impact excitation mechanism to drive intra-f-shell EL. In the interest of investigating EL under these conditions in nanowire based devices, a structure consisting of an n-type nanowire graded from GaN to AlN, with a 200 nm uid-AlN layer doped with Gd ions (1E18 cm$^{-3}$) and capped with a small amount of n$^{++}$ AlN for a top contact is prepared. An identical device contact scheme to that of the heterojunction diode is used and is shown in Fig. 5.5a. This device is again rectifying, as shown in Fig. 5.5b., but is less conductive than the PINLED device, producing 5.9A/cm$^2$ compared to 11.2 A/cm$^2$ when forward biased to 15V. This additional resistance can be attributed to the uid-AlN center region as well as a large Schottky barrier between the n$^{++}$ AlN and the Ti/Au top
Figure 5.5: Optically active Gd ions in a purely unipolar metal-insulator-semiconductor heterostructure. 

**a.** Device heterostructure and calculated band diagram. Insert shows device schematic. 

**b.** Device IV curve exhibiting rectification and a turn on voltage above 10V. 

**c.** EL spectra showing weak EL of the Gd 4f $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition. Insert shows detail of the 4f EL peak with an overlay of the more intense spectrum from the PINLED device under comparable conditions. Adapted from Ref. [7]

Electroluminescence spectroscopy (Fig. 5.5c.) reveals a weak, but detectable peak at 318nm among a large background of defect luminescence, indicating that some Gd ions are being excited by hot electrons passing through the structure as well as impact excitation of band to defect luminescence. Comparison of emission from PINLED devices and Gd:AlGaN MIS structures (Fig. 5.5c., insert) shows a 372% enhancement of intensity of the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition in the PINLED devices over the Gd:AlGaN MIS devices at 15 V bias. Additionally, no peak corresponding to the $^6P_{5/2} \rightarrow ^8S_{7/2}$ higher order transition is present in the emission spectra from the Gd:AlGaN MIS structure.
5.4 Attempt at resonantly exciting Gd:AlGaN active regions via bandgap tuning and PL

Understanding the process by which the Gd ions are excited in these structure is an important goal for further development. Toward this end, both resonant optical excitation and bandgap resonance of LED heterostructures were tested. Samples for Bandgap resonance were grown with the target quantum well composition to give rise to EL at 318 nm. This, in principle should allow direct excitation of of the Gd 4f $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition. In this study, two samples were grown, one with no Gd doping in the active region and the other with concentrated Gd doping of 1E18 cm$^{-3}$. Light emitting diode devices were processed on these structures and their EL spectra were measured. Despite emission of radiation at 320 nm, no sign of the Gd 4f luminescence is present in these structures. This suggests that excitation of the Gd ion in AlGaN may occur instead by a multi-step process likely involving higher order excited states. Recent reports from another group[101] suggest that indeed this is the case, a resonant transition occurs from the AlN band edge to high order excited states of the Gd ion, which decay non-radiatively to the $^6\text{P}_{7/2}$ first excited state and then relax radiatively to the $^8\text{S}_{7/2}$ ground state. Further investigations involving optical excitation of the Gd ions using a frequency tripled 800nm Ti:sapphire oscillator (266 nm) similarly did not result in observation of the 318nm emission line.

5.5 Summary and outlook for Gd:PINLEDs

In conclusion, polarization induced light emitting diodes (PINLEDS) doped with Gd in an AlN active region are prepared by plasma assisted molecular beam epitaxy on n-Si substrates. These devices produce narrow band UVB electroluminescence at
one to two orders of magnitude lower biases than previously reported Gd:AlN electroluminescent devices, making them an attractive candidate for low power, UV EL applications, particularly portable devices requiring narrow-band line sources. When forward biased, devices emit sharp peaks at 318 nm and 313 nm, which correspond to the Gd intra-f-shell $^6P_{7/2}\rightarrow^8S_{7/2}$ and $^6P_{5/2}\rightarrow^8S_{7/2}$ transitions, respectively and scale linearly with current density. Emission intensity is shown to be temperature independent above 75 K, below which it increases strongly. By studying two different devices, designed to produced Gd 4f EL under both low and high electric field conditions, we observe a significant improvement in emission intensity for PINLED devices which function under low-field operation conditions over hot electron MIS devices. Although this device has been applied to Gd, it would be possible in principle to dope with any of the 4f phosphor rare earths to achieve spectrally stable electrically driven emission at a variety of wavelengths.

Further work must be done to systematically engineer the resonant excitation of this transition in order to achieve higher excitation efficiencies. The preferred method would be to grow a number of composition active regions with compositions very close to AlN. At a certain point the energy transfer from band to band recombination should become resonant with the higher order excited state which allows efficient excitation of the Gd$^{3+}$ ions. The observation would be an appearance of the peak at 318 nm. The composition could then be tuned locally and the emission intensity analyzed. This project would also benefit from outfitting the Ti:Sapphire oscillator with a fourth harmonic generation path, which would allow for excitation of the AlN host to study energy transfer from the host to the Gd ion.
Chapter 6: Engineering Deep Ultraviolet Emission in PINLEDs

The field of optoelectronic devices operating in the deep ultraviolet or UVC spectral range has recently drawn considerable interest among researchers[102, 56, 103, 104]. This has been driven in part by successes in development of commercial ultraviolet light emitting diodes which operate at sub 270 nm wavelengths. Much of the effort in this area has been centered on thin film growth techniques for improving material quality of high composition AlGaN. Important technological applications such as chemical agent detection, biological disinfection and ultraviolet curing of adhesives, however require more efficient emitters at shorter wavelengths than are currently available[56]. Pushing emission deeper into the ultraviolet has resulted in a number of materials related problems associated with high Al composition AlGaN. First and foremost is the difficulty of achieving efficient hole doping in high Al content AlGaN layers[105]. This is primarily due to the large ionization energy of Mg acceptors in this material. Second, it is well known that AlGaN which is tensely strained (as is the case when grown on sapphire and most common planar substrates) exhibits a switch from TE polarized emission with propagation vector along the c-axis to TM polarization with propagation vector perpendicular to the c-axis[106, 107]. This transition
from TE to TM emission greatly reduces light extraction efficiency for c-axis oriented devices.

In this chapter efforts are described to tune emission from PINLED devices systematically to shorter wavelengths in the deep ultraviolet by controlling the composition and optical quality of AlGaN quantum wells. We have previously demonstrated that the intrinsically polar nature of the III-Nitrides can be exploited to enhance or even substitute impurity doping of compound semiconductors in compositionally graded AlGaN nanowire heterostructures, called PINLEDs[4, 7, 5]. In our original report, this technique was used to fashion GaN active region light emitting diodes with bright emission at 365 nm[4]. We have subsequently investigated the potential for using the PINLED heterostructure as a host for rare earth (Gd) phosphor devices which has led to devices with narrow emission lines at 318 nm[7] as described in Chapter 5. In this study, we explore a wide composition range of AlGaN active regions to yield deep ultraviolet light. The technique of polarization doping has much promise for overcoming the poor hole conductivity in high composition AlGaN. Since the gradient in polarization gives rise to a secondary driving force for activation of impurity dopants, polarization graded layers make a good candidate for enhancing hole concentration in AlGaN layers while potentially reducing the amount of Mg impurity atoms required to achieve a sufficiently high conductivity[61, 62, 108, 64, 65]. High Mg concentrations currently required for even marginally conductive AlGaN present a major roadblock toward developing electrically driven deep ultraviolet laser diodes, since Mg gives rise to an optically active absorption band in the blue-visible, which causes significant optical loss. In recent years, multiple groups have demonstrated the promise for using polarization graded heterostructures to improve hole conductivity
in p-AlGaN layers with the application of deep UV LEDs in mind[4, 109, 110]. Most of these efforts are focused on thin film heterostructures, which contain the benefit of planar, uniform samples, but come with an inherent limit to the magnitude and range of composition gradients due to strain considerations, which therefore limits the magnitude of polarization doping possible.

Figure 6.1: Polarization Induced nanowire Light Emitting diodes for DUV emission. a. HAADF mode STEM micrograph showing individual heterostructure nanowire. Insert shows heterostructure schematic b. band diagram showing n and p type regions as well as AlGaN QW active region. c. device schematic on Si.

Toward this end, the polarization induced light emitting diode heterostructure (PINLED) has been increasingly investigated for use in deep ultraviolet applications. The as grown heterostructure (Fig. 6.1a), calculated band diagram, using a self consistent poisson-Schrödinger solver[73], (Fig. 6.1b) and device schematic (Fig. 6.1c) is shown. Which consist of a linear grade from GaN to AlN over 100 nm to form a p-type region in N-polar wires, active regions consisting of one or more quantum
wells and a linear grade from AlN to GaN over 100 nm to form an n-type region in N-polar wires. The benefits of such a heterostructure for deep ultraviolet light emitting diodes are manifold. Firstly, low resistance contacts can be made to the conductive p-Si substrate and the very thin layer of n-GaN at the top of the device. This removes the difficulty of fashioning ohmic contacts to p-AlGaN or using large lossy regions of p-GaN as the contact layer, which is currently the industry standard for DUV LEDs. Secondly, p-conductive graded AlGaN layers readily provide holes to the active region of the device (Fig. 6.1b), allowing for reduced Mg concentrations and low reflective losses. Thirdly, the graded regions terminate at AlN cladding layers (6.4 eV band gap), meaning that any composition in the AlInGaN system can be used as the quantum well active region, provided it can be grown with sufficient optical quality and radiative efficiency. It is likely that the decreased strain in the crystal structure of the nanowire would give rise to a higher onset of the TE to TM emission polarization transition in these devices, enhancing their vertically directed optical output power. Lastly, the ability to arbitrarily tune the nanowire composition without concern for strain relaxation (at least in the AlGaN nanowire heterostructures) would allow polarization and band gap tuning of the active region potential, recently suggested as a method to reduce non-radiative Auger processes in nitride LEDs[111].

6.1 Wavelength tuning of PINLEDs over the UVC

As part of this study, we have explored the composition/emission space for this heterostructure by growing a wide variety of AlGaN composition active regions in these devices, the results of which are shown in Fig. 6.2. As expected, increasing
%Al in the active region of the PINLED causes the electroluminescence (EL) to blue shift and does so in a monotonic fashion from 365 nm to 300 nm. In this composition region, the EL intensity stays relatively constant indicating that the external quantum efficiency of the devices is relatively composition independent. However, as %Al exceeds 40%, EL intensity begins to drop and becomes pinned at 290 nm.

To further elucidate the cause of this pinning, we performed photoluminescence (PL) spectroscopy on unprocessed samples, the results of which are shown in Fig. 6.4. All devices exhibit similar PL spectra, with the emission dominated by two peaks, a high energy emission that initially shifts with composition and a lower energy composition invariant peak at 3 eV. Analysis of the peak position with increasing Al
Figure 6.3: Pinning of emission at 300nm in high Al composition Active regions. Photoluminescence Spectra with 250nm Excitation showing initial shift in emission of active region at low %Al and a clear decrease in intensity and pinning of emission at 300nm as %Al exceeds 50.

composition (Fig. 3b) shows a saturating behavior toward 4 eV for the highest energy peak and a rather composition invariant behavior for the broad emission at 3eV. Moreover, the intensity of the photoluminescence signal from the high energy peak is strongly quenched as the composition is increased (Fig. 3c). This behavior is indicative of the presence of a deep level in the active region of the device which is dominating over radiative band to band recombination processes.
6.2 Photoluminescence spectroscopy of AlGaN nanowires

In order to study the optical properties of the active region without simultaneously exciting PL in the rest of the structure, two-step AlGaN nanowires were prepared under identical nucleation and growth conditions to the PINLED heterostructures. The two step method of Carnevale, et al. [58]. allows for identical nucleation conditions, which are important for maintaining nanowire density and morphology, across samples with varying heterostructures and active region growth conditions. An array of GaN/AlGaN nanowire samples are prepared with varying %Al and growth temperatures. We observe that when the temperature is held constant and the Al composition is varied, similar behavior to what was observed in the PINLEDs with varying active regions, that is dominant emission occurs around 290 nm as shown in Fig. 6.5. The
slight blue shift in emission can be explained by a change in the overall band gap of the material, shifting the deep level energy slightly.

Figure 6.5: Photoluminescence of bulk AlGaN Nanowires. **a.** Experimental PL spectra for multiple compositions. **b.** Mismatch between expected and observed PL spectra based on Measured Composition.

Similar behavior has been recently observed in other III-Nitride nanowires studied by Daudin and coworkers[112], who examined catalyst-free nanowires grown by PAMBE over a large portion of the composition range of AlGaN. AlN and AlGaN are well known to have a very high affinity for oxygen incorporation during thin film growth, leading to below bandgap optically active defect levels[113] at similar energies to what is observed. Additionally, the low mobility of Al adatoms on the nanowire surface at typical growth temperatures can lead to composition fluctuations and reduction of crystalline quality.
6.3 Achieving higher energy emission by increasing growth temperature

In principle, increased substrate temperatures should limit the incorporation of oxygen and other high vapor pressure impurities[114]. The use of increased substrate temperature to reduce oxygen incorporation was well established in AlGaAs grown by MBE and essential in the development of the first bright red LEDs[115]. Since catalyst-free nanowires are grown in the nitrogen rich regime, far above the decomposition temperature of GaN, we should note that increasing the substrate temperature during growth will also decrease the GaN growth rate and therefore increase the effective composition of Al in AlGaN. Toward exploring this hypothesis, a series of three samples of fixed composition but varying temperature were prepared. Micrographs of these samples are shown in Fig. 6.6. Samples grown at all three temperatures exhibit similar morphology, indicating that growth at higher temperatures did not induce a change in growth mode.

![Cross section SEM images of samples showing that nanowire morphology is maintained despite higher temperatures](image)

Figure 6.6: Cross section SEM images of samples showing that nanowire morphology is maintained despite higher temperatures

PL spectra for samples grown at a fixed target composition of 80% Al and increasing substrate temperature are shown in Fig. 6.7. It can be readily observed that as the substrate temperature increases the once dominant emission peak is readily
Reduced and dominant emission shifts to 260 nm, which is closer to the expected emission for the targeted composition. This could suggest that higher temperature growth suppresses formation of impurity related deep levels, for example by increased oxygen desorption rate (effectively reducing the sticking coefficient for oxygen) at high temperatures.

Figure 6.7: Recovery of DUV emission and reduction of 300nm defect emission with increasing growth temperature
6.4 Observation of composition fluctuations in AlGaN nanowires with atomic resolution STEM

Additionally, recent studies by atomic resolution STEM of the nanowires from this sample set by colleagues at the center for electron microscopy and analysis (CE-MAS) have shown marked indications of composition fluctuation on the monolayer scale, as shown in Fig. 6.8. This oscillation in contrast is observed to track growth facets of the nanowires, indicating that what is being observed is true composition contrast and not an interference pattern caused by overlapping wires. Moreover, the periodic nature of the contrast allows for measurement of spatial period, and is shown to monotonically decrease with increasing growth temperature, as shown in Fig. 6.9. Although composition ordering such as Spinodal Decomposition is not expected for AlGaN given the fact that the equilibrium phase diagram predicts full miscibility between the elements, it is emphasized that growth under highly non-equilibrium,
kinetically limited conditions could in fact lead to production of compositional instability. This observation presents a possible secondary explanation to the presence of spurious peaks from high composition AlGaN nanowires. The period of these periodic structures is such that it may present a digital alloy potential to electrons and thus give rise to a effective composition which is some what less than expected from flux ratios. It should be noted, however that the nanometer length scales of these variations could also be due to periodic fluctuation in composition of adatoms or fluxes arriving at the surface with time. It is possible that this may be due to an intrinsic kinetic effect during growth or extrinsic system related periodicity. Further investigation into the effect of substrate rotation and sample uniformity is suggested to elucidate this question further.

Figure 6.9: Observation of Composition fluctuations in self assembled AlGaN nanowires grown by PAMBE
6.5 Application of high temperature growth to PINLEDs

Using this higher substrate temperature growth (840 C) for the active region only, a new high %Al PINLED device heterostructure is prepared. The substrate temperature is ramped toward the end of the p-type graded layer, removing the necessity of a growth interruption around the active region of the device. A three period 5 nm Al$_{0.8}$Ga$_{0.2}$N multiple quantum well with 5 nm UID AlN inserts is deposited at 840 C. The rest of the structure is grown normally at 790C with the temperature ramp down occurring at the end of the active region without a growth interruption. Contacts are made to the p-Si substrate and 350 µm x 350 µm gridded pads are deposited on the tops of the nanowires via photolithography. Device IVs (Fig. 5a) show rectification and turn on at 6 V, approximately the bandgap of AlN, as expected from the PINLED band diagram shown in Fig. 6.1b. EL is collected by a collimating lens and passed to an imaging spectrometer equipped with a UV-CCD.

Unlike previous PINLED devices with AlGaN active regions, which exhibited emission pinned at 290 nm at similar compositions, the device with high temperature grown active regions exhibits EL peaks at 250 nm as shown in Fig. 6.10. As current density increases, the output power increases initially linearly and then levels off in a similar fashion to AlGaN LEDs in planar devices. This is likely due to thermal effects and has been shown to be mitigated by pulsed current excitation. Peak power was measured to be 90 nW @ 400 mA in DC, yielding an EQE of approximately 2µ% at DC. Although this is a very small efficiency, it is emphasized that the device geometry for such devices is far from optimized, causing a low percentage of nanowires to be contacted and requiring thick, absorbing contact layers to form coalesced tops that contact all nanowires in parallel, suggesting that significant improvements can be
made with future development. Additionally, it is noted that fully optimized commercial devices emitting in this spectral range are around 0.2% efficient[116]. In pulsed mode which offers the ability to neglect self-heating effects in the measurement, (5% duty cycle, 15 ms period) a peak power of 0.22 µW is measured at 400 mA. This is to our knowledge the shortest operating wavelength nanowire LED to be reported to date.

6.6 Outlook and Future Directions for PINLEDs project

The PINLEDs technology has a number of key characteristics which make it a candidate for future development and potential commercial success. First and foremost is the success of growing and fabricating UV-VIS optoelectronic devices which are

Figure 6.10: Deep Ultraviolet emission from PINLED grown with high temperature active region. a. Device I-V curve showing 6 V turn on and rectification. Insert shows image of active device taken with an ultraviolet microscope. b. Electroluminescence spectra of high temperature active region device showing evolution of EL with increasing current density. Insert shows peak power vs. current density.
monolithically integrated with Si wafers. Epitaxy of active nanowire optoelectronic devices on Si offers new possibilities for light sources for integrated optics, photonic integrated circuits and lower cost solid state lighting. It is widely accepted that the majority of cost in compound semiconductor manufacturing are the exotic wafers which must be used to grow high quality III-nitride devices. Although much progress has been made in developing high brightness solid state UV emitters in the last 5 years, dependence on exotic substrates such as bulk AlN and sapphire will continue to keep costs high for the foreseeable future.

In summary, the PINLED heterostructure takes advantage of a number of unique properties of nitride semiconductors and nanowires which work in concert to house wide bandgap AlGaN active regions for production of deep ultraviolet light. In PINLEDs it is possible to reproducibly control AlGaN compositions and resulting EL across a wide range of emission wavelengths. Furthermore, when growing high composition AlGaN regions in nanowire devices, a substantial increase in substrate temperature is required in order to produce material with band to band optical characteristics. Using both control of AlGaN composition and high temperature growth conditions, we are able to demonstrate a nanowire light emitting diode operating in the technologically important UV-C band.

Regardless of the success of the PINLEDs technology, it is likely that polarization enhanced doping will play an increasingly important role in enhancing p-type doping in UV-LEDs. Since the publication of the first PINLEDs paper in 2011, multiple other research groups have begun to fashion UVLED devices which include composition gradients to form polarization doped regions and have observed enhancements of functionality[110, 65]. Unless progress is made with selecting a lower activation energy
p-type dopant to replace Mg for wide bandgap AlGaN, series resistance in p-type regions will continue to be an issue in UVC devices. Polarization doping is therefore a sound method of mitigating this difficulty.

Despite much progress being made with this project, much work remains to be done. This work saw the genesis of the concept, successful fabrication of prototype devices, work to understand various aspects of polarization doping and successful tuning of the emission from these devices from 365 nm to 250 nm, which spans the commercially important wavelengths for UV curing and water disinfection. Future work should focus considerable effort in attempting to solve the question of low quantum efficiency in these devices and output power. Preliminary work done by A. T. M. Sarwar in 2014 shows that droop occurs at very low thresholds, indicating that high amounts of loss are occurring which are proportional to carrier densities to high order exponents.

Much progress in this area can be made simply by improving the device fabrication routine. Already, switching from a single step 10 nm Ti / 20 nm Au metalization to a two step 10 nm Ti / 20 nm Au with 500 nm Au grid process have substantially improved device performance and output power. Regardless, it is well known that for high composition AlGaN, the emission direction becomes largely in the plane of the film. This has a number of important implications, firstly that detection normal to the film and through a metal contact is less than ideal because of losses in the metal contact as well as reduction of photons produced which have wavevectors normal to the semiconductor surface. Secondly, it may be possible to fashion an efficient cleaved edge laser diode or high brightness LED which takes advantage of this propagation direction normal to the c-axis. Although the nanowire film is not fully dense, the
spacing between nanowires is $\leq 1/10\lambda$ at 250 nm. This suggests that choice of the correct nanowire spacing may make the film behave electromagnetically continuous, leading to gain in the medium and reflection at the ends. It is therefore an important goal to develop a test routine for nanowire devices which effectively couples the light out from the side of the device. Although the free surface of the nanowire gives rise to large strain tolerance and likely functions as the source for free charges in polarization doped regions, it may also play a strong role in the reduced efficiency in these devices. Though the axial band diagram exhibits very strong confinement in the quantum well for these devices, high %Al composition AlGaN is not effectively confined in the radial direction, due to the low bandgap difference with the coaxial AlN shell of these structures. This could allow for a pathway for non-radiative recombination of charge carriers in the quantum well of the structure at the surface.

One possible method for mitigation of this phenomena is passivation of the free surface via growth or coating of a wider bandgap material in between the nanowires. One possible method, available during growth would be to coat the nanowires with Al, thereby creating a widebandgap oxide upon removal from the vacuum chamber. Complete formation of the oxide would require the correct amount of Al to be deposited and calibration of this would likely require growth of multiple samples and feedback via high resolution transmission electron microscopy. Methods which are popular for visible nanowire LEDs such as pyroline and spin on glass (SOG) will not work for UV devices because of the lack of transparency and therefore high loss in these materials. When the oxide system (MBECS M7) comes online, it may be possible to deposit Al and oxidize in a controlled manner using an oxygen plasma.
Progress in understanding the presence of and mitigating unintended recombination pathways in these devices requires application of a number of experimental methods. The primary feedback tools in the study of these devices will continue to be device electrical and optical characteristics. These data can be collected from IV curves, electroluminescence spectra on the UV protestation (described in appendix B). Studies involving optical excitation of the active regions of these devices in the form of photoluminescence experiments are equally important, however, since they allow study of unprocessed devices under more controlled conditions. Toward this end, an effort should be made to construct a 195 nm fourth harmonic generator. This would allow for excitation above the bandgap of AlN, allowing observation of all optically active deep levels in this heterostructure. These data would aid in understanding the origin of output spectra from PINLEDs and likely lead to enhanced feedback into growths.

Current device designs which utilize pads and grids developed for planar LEDs operating at rather low current densities and with more ideal surface morphologies have been shown to fail at typically PINLED operating conditions, typically directly under probe tips. This suggests that deposition of thicker probe landing pads or utilization of probes with a larger contact area should be investigated. It is also likely that current spreading in the metal layer is rather poor due to rough morphology and thickness inhomogeneity. Toward this end, four point measurements of the metal contacts should be made to establish their resistivity and efforts should be made to improve these contacts. Growth of a fully coalesced n-AlGaN layer on top of the nanowires may aid current spreading as well as uniformity and quality of the semi-transparent metal layers, although some growths have been done to prototype
this idea, further development is necessary to achieve optimal thickness and surface morphology.

Finally, the ultimate in control of these structure is patterned growth. At this point, most major groups researching catalyst free nanowires, as well as companies attempting to commercialize lighting solutions based on nanowires, have switched to some form of patterned growth[117, 118]. The benefits of this technique are manifold, leading to higher control over density, morphology as well as uniformity. Development of this technique in the Myers group would allow for new directions for research with self assembled nanowires, such as patterned photonic crystals and optical frequency selective surfaces. In early 2014, efforts were started by the author using the technique of nanoimprint lithography, using an EVG 520HE hot embosser at the Nanotech West laboratory. This tool was a sort of predecessor to modern NIL tools, and although some success was made in fashioning a die from Si and transferring the pattern to a GaN wafer, the project fell victim to wrapping up other studies. It should be an important goal to continue development of this technique, either by purchasing a commercial die and simply using the hot embosser to transfer the pattern or doing the whole process in house.

In summary, future research with these devices should target output power solely to demonstrate technological relevance over existing technologies. Once this has been clearly established, concerted efforts need to be made to mitigate loss pathways and thereby improve device efficiency and reliability.
Chapter 7: Collaborative spectroscopy work

Over the course of the last four years, the author has been fortunate to be able to take part in a number of collaborative studies where he contributed semiconductor spectroscopy work. This section outlines the versatility of the Myers group optical spectroscopy system for various optical spectroscopy experiments involving a wide variety samples. Each subsection of this chapter will briefly describe the scientific goal of each project as a whole as well as my contribution to it. Due to the wide spectrum of solid state work actively being pursued at Ohio State, the author has been able to measure spectral data for almost all of the important semiconductor materials families, from GaAs/P, GaN, ZnO to novel 2D materials such as MoS$_2$. Experimental studies have ranged from simple photoluminescence experiments to determine alloy composition to complex, multi sample growth condition mapping of spectral properties in the time domain and frequency domains.

7.1 Spectroscopic determination of non-radiative and radiative lifetimes in InGaN thin films

InGaN is an exceptionally technologically important compound semiconductor alloy. It forms the backbone of the modern solid state illumination and lighting industry, primarily for blue emission\cite{8}. Currently, most green LEDs are grown with
GaP/AlGaP alloys. In principle, it should be possible to cover this spectral region with high efficiency, high power InGaN based LEDs which would allow production of multiple colors using identical process equipment, leading to significant cost reductions and expansion of existing capabilities for the solid state lighting industry. However, there exists a number of challenges associated with growth of high quantum efficiency InGaN alloys with bandgaps spanning the green region. One of the possible pathways towards growth of high quality, high In composition InGaN is a modification of growth regime from group III rich growth stoichiometry to III-limited stoichiometry which has been shown to reduce InGaN thermal decomposition and allow for higher In incorporation. Toward this end, Fatih Akyol working in the group of Prof. Siddharth Rajan (ECE/OSU) prepared a number of InGaN films on commercial GaN/Sapphire templates by MBE under various growth conditions with In compositions ranging from 20%-30%. In order to understand the effect of growth conditions on In incorporation and optical quality of the films, as measured by their photoluminescence spectrum, temperature dependent, time resolved photoluminescence experiments on a number of samples were conducted. These measurements allow for calibrated reports of radiative and non-radiative lifetimes in these films. Determination of these parameters gives insight into the presence of unintended recombination centers in these films which effect overall external quantum efficiency of the light emitters. This work supported a manuscript[119] which is currently in review.

Measurement of non-radiative and radiative lifetimes requires combination of measuring steady state PL spectra with measurement of PL decay curves, both as a function of temperature. The measurement consists of cooling samples down to the base
temperature of the cryostat, in this case 10 K, and then collecting spectra and decay
curves at regular temperature intervals to room temperature. First, internal quantum
efficiency (IQE) is determined by taking the ratio of the PL peak intensity to the low
temperature peak intensity. Next, the PL decay time is collected by fitting the TRPL
decay curve according to the equation

\[ I = I_0 e^{-\frac{t}{\tau \beta}}, \]  

(7.1)

where \( I_0 \) represents PL intensity at \( t=0 \) sec, \( \tau \) is the PL lifetime and \( \beta \) is a parameter
representing compositional disorder in the system. This type of decay law (rather
than the typical single exponential observed in most semiconductors) is common for
InGaN, especially in the intermediate, high composition regimes[120]. Radiative and
non-radiative lifetimes are calculated by combining the equations

\[ \eta = \frac{1}{1 + \frac{\tau_R}{\tau_{NR}}}, \]  

(7.2)

and

\[ \frac{1}{\tau_{PL}} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}, \]  

(7.3)

to determine \( \tau_R \) and \( \tau_{NR} \), where \( \eta \) is the IQE, \( \tau_{PL} \), \( \tau_R \) and \( \tau_{NR} \) are the measured PL
decay time, the radiative and non-radiative lifetimes, respectively.

Samples were co-loaded in a closed cycle He cryostat equipped with a translation
stage allowing for analysis of multiple samples without modification of optical sys-
tem alignment. Room temperature photoluminescence (RT PL) measurements were
performed using a mode-locked Ti:sapphire oscillator (Coherent Chameleon Ultra II)
operating at 900 nm, a repetition rate of 40 MHz, pulse width of 150 fs. The laser
output was then frequency tripled yielding an excitation wavelength of 300 nm, and
average power of 10 mW focused onto the sample through a 36, 0.5 numerical aperture
(NA) reflective objective. Using this same objective, the PL was collected, passed through a 300 nm long pass filter, and focused onto the slit of a 0.5 m monochromator (SP2500i) with a 1200 g/mm grading blazed at 300 nm, and dispersed onto a PI PIXIS 100 CCD camera yielding a spectral resolution of 0.06 nm. Time resolved photoluminescence (TR-PL) measurements utilized the same reflective objective described above for excitation and collection, while the Ti:sapphire laser was tuned to 740 nm, a 40 MHz repetition rate, frequency doubled to an excitation wavelength of 370 nm, and finally focused to a 10 m spot size on the sample at an average power density of 764 kW/cm$^2$. The collected PL photons passed through a 300 nm long pass filter, and were focused on to the entrance slit of a 150 mm f/4 spectrometer and then counted using a Hamamatsu R38009U-51 micro channel plate photomultiplier tube. The photocurrent pulses were pre-amplified then input to an SPC-130 time correlated single photon counting system (Becker& Hickl) where the individual photon events were correlated with the repetition rate of the laser ultimately providing a histogram of photons events as a function of time, i.e. the TRPL decay trace. The instrument response function (IRF) of the system with full width half maximum (FWHM) < 60 ps was measured by collecting the back scattered laser light from the sample at the excitation wavelength. Samples were mounted in a closed cycle cryostat with a base temperature of 9 K and TRPL decay curves were collected at temperatures of 10 K and 300 K with the spectrometer set to the peak center of the PL emission at 552 nm, the slit width at 1000 µm yielding a spectral bandwidth of 5.55 nm.

Measurement of IQE values by ratios of high temperature to low temperature photoluminescence, although common in the literature and used in this study suffers from a number of shortcomings. Most notably is the significant dependence on
measured IQE on excitation power density, fluence and excitation energy. Due to these factors, IQE is better written as $\eta(P, E, \lambda)$, emphasizing the effect of each of these parameters on the lifetime[77] and comparison between IQE measurements in the literature is inherently a slippery manner. However, comparison between samples measured in single controlled experiment, as was performed in this study allow for valid insight into the relative optical quality of the samples measured. In order to investigate the dependence of PL lifetime on power density, and to choose an excitation condition which would be similar to the high level injection conditions experienced by light emitting diodes during normal operation, a measurement of PL lifetime was made as a function of excitation power, shown in Fig. 7.1 From these data, it can be readily observed from this plot that the measured lifetime is largely dependent on excitation condition. It is possible that at higher power densities, many body (Auger)
relaxation pathways become accessible, thereby limiting lifetimes. In the case of this measurement, a power density of 764 kW/cm$^2$ was chosen.

Initially, steady state PL spectra were collected for the samples in order to determine appropriate peak wavelength for TRPL collection. Most samples exhibit luminescence in the form of two broad peaks in the green-yellow, as shown in Fig. 7.2.

![Figure 7.2: Temperature Dependence of photoluminescence from high %In InGaN thin film. Calculation of internal quantum efficiency.](image)

For each sample at each temperature, the peak wavelength was selected from the spectrum and a TRPL decay curve was measured with the center wavelength of the TRPL system monochromator set to peak wavelength, a characteristic curve is shown in Fig. 7.3. Target compositions for these films indicated that the intended emission should be in the green, around 550 nm. The emergence of a second peak at 675 nm could be due to indium segregation or an optically active deep level.
For the three samples measured, the data for IQE and PL lifetime were plotted according to the total group III (In+Ga) flux and PL peak energy energy (Fig 7.4). The most clear trend exists in the dependence of IQE on total group III flux, with increasing total fluxes resulting in lower IQE values. This could possibly be the result of less uniform incorporation of InGaN at these fluxes. Interestingly, although there is a strong linear dependence of IQE on total group (III) flux observed, the trend is less clear with PL emission energy or realized composition. Moreover, no clear trend exists between the PL lifetimes of these samples, suggesting that it is dominated by an uncontrolled parameter during growth.

In summary, non-radiative and radiative lifetimes were systematically measured from temperature dependent IQE and TRPL measurements of MBE grown InGaN thin films. Within this sample set, a clear trend of measured internal quantum efficiency on total group III flux was observed. No clear trend was observed for radiative
Figure 7.4: Effect of total group III flux and composition on measured IQE and PL lifetime.

and non-radiative lifetimes, although all measured values fall in a range consistent with other reports of TRPL on InGaN in the literature[120]. This measurement established the experimental methods for this technique and it could be readily applied to any systematically created sample set with a bandgap that falls in the range of the spectroscopy system (250 nm-900 nm).

7.2 Optical properties of PVD grown Yittrium Iron Garnet (YIG) thin films on Gadolinium Gallium Garnet (GGG)

Yittrium Iron Garnet (YIG) is a room temperature ferromagnetic material with common applications in microwave resonators. It combines room temperature ferromagnetism, low coercivity and narrow ferromagnetic resonance (FMR) linewidth[121]. In the Myers group, this material has become the material of choice for prototyping a magneto-opto-thermal experiment being directed by Brandon Giles. Interestingly, despite the fact that YIG is so widely studied and discussed in the literature, there exists a significant lack of information regarding its optical properties and bandstructure. Typically regarded as an “insulator” by the physics community[122], YIG was
actually the subject of attempts at producing a wide bandgap material in the 70’s and 80’s[123, 124]. It was therefore of interest to the various studies being undertaken in the Myers group regarding YIG to conclusively know what the optical properties of the YIG which was being grown in house by reactive ion sputtering on GGG substrates were.

Two experiments were performed in order to deduce the bandgap as well as absorption features of our PVD grown YIG. The first to be performed was an absorption spectroscopy experiment to understand the magnitude of the bandgap in this material. In this experiment, white light from a 190 nm - 2500 nm Deuterium-tungsten halogen source is collimated and focused through the sample under test which consists of an epilayer and transparent, optically polished, substrate. The transmitted light is then free space coupled into a spectrometer and analyzed. Using a translation stage, an identical substrate with no epilayer deposited is measured. This second measurement allows for correction of the spectral response of the instrument as well as the substrate. The absorbance spectrum, $A(\lambda)$, is calculated as

$$A(\lambda) = -\log_{10} \left( \frac{I(\lambda)}{I_0(\lambda)} \right),$$  

(7.4)

where $I(\lambda)$ is the measured transmission spectrum of the substrate and epilayer and $I_0(\lambda)$ is the measured transmission spectrum of the substrate.

The experimentally measured absorption for a 22 nm YIG thin film is shown in Fig. 7.5. From these data a clear observation of an absorption edge at 2.9 eV (427 nm) as well as multiple higher energy excitonic peaks are observed. These results are consistent with the few existing previous reports of the bandgap of YIG[125]. Measurement of the bandgap of the films which were employed in this study allowed for
calibration of excitation wavelengths for opto-magneto-thermal measurements with the excitation both above and below the bandgap of the material.

Figure 7.5: Optical spectra of measured absorbance of YIG thin films grown on GGG substrates by reactive ion sputtering.

Further interest in the optical properties of YIG lead to the desire for a measurement of any possible photoluminescence of the YIG. If the bandgap was indeed around 2.9 eV and the samples were of sufficient optical quality, PL should be observed near this energy. This measurement consisted of exciting samples mounted in the cryostat with a frequency tripled Ti:Sapphire oscillator (800 nm fundamental, 266 nm output) and coupling any luminescence into a UV-VIS spectrometer. Initial measurements revealed a complicated broadband luminescence with various narrow lines throughout. It was hypothesized and experimentally verified that the GGG substrate was giving rise to a large portion of this luminescence signal. Toward this
Figure 7.6: Experimental optical spectra of photoluminescence of YIG thin films grown on GGG substrates by reactive ion sputtering.

In summary, optical characteristics of PVD grown YIG thin films were studied by absorption and photoluminescence spectroscopy. Experimentally measured spectra indicate an optical bandgap between 2.5-2.9 eV in this material. Observation of excitonic peaks indicate that this sample is largely insulating, which is consistent with measurements of transport properties. These measurements support further efforts to
understand the interaction between heat, charge and spin in this material. Detection of photoluminescence from this material opens the doors to further investigation of spin polarized band structure via polarization resolved PL.

7.3 p-type doping in MoS2: Optical Spectra of 2D Compound Semiconductors

Two dimensional (2D) conducting materials have attracted much attention and been the subject of intense research over the last decade. This interest is driven by demonstration of extraordinary properties such as enhanced thermal conductivity, mobility and strength over the current staples of synthetic materials[126]. To a large extent many of these materials occur in nature as minerals with lamellar habits such as MoS$_2$ or graphite. Recent advances in synthesis of single monolayers of various 2D compounds and elemental forms of group IV elements have led to intense study of engineered devices and materials.

Particularly interesting for study are a family of compounds known as the transition metal dichacogenides (MoS$_2$, WS$_2$, SnSe$_2$, etc.). These compounds all share identical crystal structures and may offer the ability to translate the vast literature of bandgap engineering developed for III-V compound semiconductors into 2D materials[127]. Moreover, they show promise for optical devices which take advantage of direct bandgaps.

An important aspect of development for this materials system is achieving control over conductivity in these materials. For a material to be accepted as a “semiconductor”, its conductivity must be controllable by introduction of impurity elements giving rise to electron (n-type) or hole (p-type) conductivity. The group of Prof.
Siddharth Rajan in ECE (OSU) has recently demonstrated a controllable, straightforward method of synthesizing these compounds[128]. The author was fortunate enough to be involved in a study[129] which demonstrated successful p-type doping of these materials using Nb. This section contains spectroscopic data of these materials in the form of absorption experiments performed by the author.

Figure 7.7: Absorbance spectra of MoS$_2$. Detail of absorption edge showing excitonic peaks in undoped samples.

Thin film samples of MoS$_2$ grown by CVD of sulfur with of electron beam deposited Mo metal on sapphire substrates were prepared and provided. Three samples were studied, two samples were doped using a modulated e-beam deposition of Mo and Nb (p-type) and Mo and Mo/Re (attempted n-type) prior to CVD growth. The final sample being a pristine undoped MoS$_2$ control. Absorption measurements were performed in a method similar to the one discussed in the previous section, using a double side optically polished sapphire wafer as the reference sample. As a calibration,
absorbance spectra were collected for the undoped MoS$_2$ control sample, the results of which are shown in Fig. 7.7. The absorbance spectrum of pristine MoS$_2$ shows an approximately 1.7 eV absorption edge accompanied by multiple excitonic peaks in the direct vicinity. The location of these peaks as well as the magnitude of absorbance agrees very well with previous reports of optical characteristics of MoS$_2$ films.

![Absorbance Spectra Comparison of Doped MoS$_2$](image)

Figure 7.8: Comparison of absorbance spectra for p-type dopant Nb as well as attempted n-type dopant Re.

Further investigation of the optical properties of the doped films via measurement of their absorption spectra is shown in Fig. 7.8. As can be readily observed, the spectra for the MoS$_2$ control and Nb:MoS$_2$ are remarkably similar, with the Nb:MoS$_2$ spectrum exhibits slight enhanced near band edge absorption, as expected for a degenerately doped semiconductor material. The high quality optical spectra for this
sample is consistent with measurements of high hole mobilities[129]. In contrast, although the high energy features of the spectrum for Re:MoS$_2$, which according to electron configuration should be a good n-type dopant candidate, match well with UID MoS$_2$ and Nb:MoS$_2$ the region around the bandgap is starkly different, showing instead enhanced absorption. This behavior indicates the presence of a mid gap deep level which is rather optically prominent. This observation is consistent with poor conductivity observed in Re:MoS$_2$ films.

In summary, optical absorbance spectra of the 2D compound semiconductor MoS$_2$, in UID and doped form, were collected and analyzed. UID samples exhibit strong excitonic peaks and an absorption edge at 1.7 eV which is consisted with the reported bandgap. Nb doped samples exhibit high optical quality, with similar absorption features to UID films and a slight enhancement of near band edge absorption. Doping films with Re appears to result in a prominent midgap state which is consistent with observation of insulating behavior.
7.4 Catalyst-free ZnO nanowires on silicon by pulsed laser deposition with tunable density and aspect ratio

ZnO has attracted a great deal of attention as a wide gap, radiation hard compound semiconductor of the II-VI family. As a member of the transparent conductive oxide family of semiconductors it has shown promise for applications involving high power and harsh environments[130]. Although this material shows much promise, synthetic growth of high quality crystals has proven to be a challenging task[131]. Additionally, control of p-type doping remains elusive[132]. In many respects, ZnO shares many characteristics with GaN such as crystal structure, band gap as well as similar lattice constants. It was therefore proposed that the ZnO/ZnMgO system would be an ideal candidate for demonstration of the PINLEDs concept in another polar materials system. This project was conducted largely by Santino Carnevale and Micheal Susner during the summer of 2013 with the author providing optical studies of the samples grown, and lead to a subsequent publication[133]. Using the technique of pulsed laser deposition (PLD) whereby an KrF excimer laser ablates a target and the ablation plume is deposited on a heated substrate in an oxygen ambient partial vacuum environment, ZnO self assembled catalyst free nanowires were grown on Si substrates.

Samples grown were investigated by a number of characterization methods such as SEM, STEM, and high resolution XRD. Key observations into the semiconducting quality of these materials was, however necessary. Optical characteristics provide a keen insight into the electronic quality of these materials, allowing identification of trap states and band to band recombination intensity. The growth study produced a wide array of sample prepared under different substrate temperatures and oxygen
partial pressures. By systematically studying this array by photoluminescence spectroscopy, insight can be gained into the effect of growth conditions on the optical quality of these materials. Using a frequency tripled Ti:sapphire oscillator (Coherent Chameleon ultra II) for excitation and a PIXIS BR100 CCD coupled to a SP2150 0.5 monochromator for collection, PL spectra were collected and analyzed. Spectra

![Photoluminescence spectra of PLD grown ZnO nanowires.](image)

Figure 7.9: Photoluminescence spectra of PLD grown ZnO nanowires.

from these samples, a characteristic of which is shown in Fig. 7.9 exhibit two dominant emission peaks, a ZnO near band edge peak at 3.2 eV and a broad defect band centered at 2.3 eV. These spectra are largely consistent with existing reports of ZnO optical characteristics[130]. The origin of the 2.3 eV “green band” has been attributed to oxygen deficiency during crystal growth and therefore the ratio of this peak to the NBE peak can be considered a metric of stoichiometric ideality. In the case of some
samples measured, this ratio is as high as 136:1 in favor of the NBE peak, which is substantially better than many reports for thin films and bulk crystals of ZnO[130]. Keeping this in mind, this ratio was chosen as the figure of merit for comparison of the relative optical quality of samples grown in a wide variety of temperatures and oxygen partial pressures. In this part of the study, an array of nine samples were co-loaded into the optical cryostat and systematically investigated under identical excitation and collection conditions.

![Figure 7.10: Using photoluminescence spectroscopy to map optical quality vs growth condition.](image)

As can be observed from Fig. 7.10, samples grown at higher temperatures exhibit ratios near unity, suggesting that defect content is high, perhaps due to poor oxygen incorporation. Higher quality samples seem to have been grown below a substrate temperature of 700 C. The highest ratio of 136:1 is observed at 650 C, 340 mTorr. In
future studies, samples should be developed which explore the 600 C-650 C substrate temperature and above 300 mTorr oxygen partial pressure range to further elucidate these findings. This method can be applied to a wide variety of samples, only limited by the excitation and collection ranges of the spectroscopy system.

7.5 Using NIR photoluminescence to map the Optical quality of MBE grown InN nanostructures

InN, the smallest bandgap member of the III-nitrides materials family has attracted much interest over the last two decades for potential uses in nitride based NIR optoelectronics as well as high mobility electrical devices. With a direct bandgap of 0.7 eV, InN offers the ability to fashion IR photodiodes and novel heterostructures such as HBTs from nitrides. Unfortunately, InN has proven notoriously difficult to grow in high crystalline quality and dope p-type. Currently, only InN self assembled nanowires have demonstrated p-type conductivity[134] with thin films being naively n-type, suggesting that realization is possible, but growth conditions will need to be further developed to improve crystalline quality. Recently, the Myers group has demonstrated successful growth of InN nanowires on Si (111) using a similar growth regime to that of GaN nanowires.

Optimization of growth conditions is a major goal for these nanowires and toward this end, A. T. M. Sarwar recently embarked on a task of establishing a growth phase diagram for these materials. This study involving growing InN nanowires under systematically varied conditions of substrate temperature and III/V (In/N) flux ratios. Primary characterization was accomplished by phase analysis by SEM. Methods involving true identification of stoichiometric InN were necessary, however. It was decided to perform a photoluminescence mapping routine similar to that undertaken
in the previous section. This experiment was conducted by the author and A. T. M. Sarwar, the results of which are discussed in this section.

![Figure 7.11: Spectra of MBE grown InN nanowires for various substrate temperatures and stoichiometries.](image)

The subject of the bandgap of InN is a storied one, with early reports suggesting a much larger bandgap than was ultimately observed, due to poor quality and stoichiometry of early material[135]. Today, the widely accepted bandgap of InN is 0.69 eV which converted to wavelength is about 1800 nm, in the near infrared. Detection of light of this wavelength involves use of InGaAs photodiode arrays with sensitivity from 1.2-2.5 µm. Photoluminescence experiments were carried out at room temperature using the fundamental of a Ti:Sapphire oscillator tuned to 800 nm excitation.
Detection was provided by a Princeton Instruments OMA-V-2.2 InGaAs diode array detector attached to a SP2500i 0.5 m spectrometer.

Twelve samples, cleaved into roughly 3 mm equilateral triangles were co-loaded into the optical system in a gridded manner. In-situ microscopy (discussed in appendix A) was used to translate between samples. Once the optical system was aligned and focused and the PL signal optimized from the first sample, no parameters were adjusted other than sample position between samples. This technique allows for rigorous comparison of peak intensities between individual samples, a task that is typically difficult in spectroscopy. The resulting observed spectra are shown in Fig. 7.11, as expected, a single peak at 1800 nm (0.69eV) is observed, despite the far above gap excitation of 800 nm, indicating that the material being investigated is indeed InN. Moreover, a significant variation in peak intensity, energy and full width half max (FWHM) is observed as a function of growth conditions, which are plotted separately, in Fig. 7.12.

Figure 7.12: Spectra of MBE grown InN nanowires for various substrate temperatures and stoichiometries.
From these data we can conclude that samples with the highest optical quality seem to be grown in the 425°C temperature range with high III/V ratios approaching one half. There seems to be a rough trend of higher emission energies with increasing III/V ratios indicating a higher likelihood of band-to-band recombination. For low temperature growth and low III/V no PL was observed indicating that either an insufficient amount of InN was present or what was present was too defective to be optically active.

In summary, InN nanostructures were analyzed by combinatorial microphotoluminescence spectroscopy. This method allowed for systematic mapping of optical spectra over a wide array of growth condition, as well as valid comparison of peak intensity, FWHM, emission energy between co-loaded samples. It was determined that the highest optical quality material was produced when III/V ratio approached 0.5, the upper limit studied and a substrate temperature of 425°C, in the intermediate range studied.

7.6 Summary

This chapter functions as an outline of the breadth of materials investigated using the techniques of optical spectroscopy implemented by the author in the Myers group spectroscopy laboratory. Optical characteristics of samples were investigated over wide spectral ranges from 200 nm - 2500 nm. Using a variety of light sources such as pulsed lasers, arc lamps and broadband halogen lamps and a suite of detectors including Si CCD cameras, InGaAs NIR diode arrays and micro channel plate photomultiplier tube single photon counting detectors. Study of such a broad range of
samples and experiments allowed development of a flexible, robust measurement tool for the dynamic demands and challenges of future research.
Chapter 8: Conclusions and closing remarks

Throughout the course of this dissertation, a wide range of topics have been investigated. The common thread between studies being the materials family, synthesis methods and characterization techniques. It was part of the nature of being one of the first students in a young lab that the author was involved with many collaborative projects as well as spending considerable efforts to develop techniques and instrumentation, which are the topics of multiple appendices of this document to which the interested reader is directed to.

In this dissertation, the growth and characterization of III-nitride based nanostructures for principally two areas: magnetic functionalities and optical functionalities were designed, synthesized, characterizes and developed. Epitaxial ferromagnetic GdN/GaN nanocomposites show promise for use in III-nitride based magnetic devices and tunnel junctions. The allow for more or less seamless integration of a ferromagnetic material into a compound semiconductor host, without causing extreme levels of defective interfaces or morphology. In this work their growth by molecular beam epitaxy was developed and optimized and their magnetic and structural characteristics were investigated. Much work, however, remains to understand their transport properties and subsequently investigate the possibility of fabricating useful devices from these nanocomposite materials.
Exploration of polarization enhanced doping and development of the PINLED prototype heterostructure led to many interesting devices and observations. This project was particularly enjoyable for the author due to the wide variety of heterostructure design iterations and rapid feedback from optical characterization into subsequent growths due to a well functioning research team. The concept of a bipolar polarization doped device in the form of a light emitting diode was demonstrated, even in the absence of intentional doping. More recent results by the authors coworkers suggest that these devices can in fact produce sizable amounts of optical power using GaN active regions. Further work to engineer the PINLED heterostructure as a solid state emitter for deep ultraviolet applications resulted in pushing emission to 250 nm, the shortest reported operating wavelength for a III-nitride nanowire based LED to date. As discussed in Chapter 6, the question remains, how can devices with high Al composition quantum wells be synthesized with high quantum efficiency. Within the chapters dedicated to PINLEDs, many suggestions are made for further development towards these goals.

Using the concepts learned working on both nanocomposites and nanowire LEDs enabled demonstration of a unique optical device which facilitated electrical modulation of ultra narrow linewidth intra-\( f \)-shell optical transitions in Gd atoms. These devices otherwise function very similarly to bulk III-nitride quantum well active region nanowire light emitting diodes, but instead contain spectral lines that are more familiar to high voltage atomic spectroscopy of plasmas. Further development of this concept could lead to a novel device for compact UVB spectroscopy applications.

Over the course of performing the core experiments which make up this dissertation, a number of useful tools for optical characterization were designed, implemented
and developed. These tools continue to be used in the Myers group daily by other students and likely will for the foreseeable future. Among these are an Ultrafast laser optical spectroscopy system (Appendix A), a spectroscopic DUV probestation (Appendix B) and a modified magneto-optical cryostat (Appendix C).
Bibliography


[101] Yuta Ishizu, Kazuma Tsuji, Yukihiro Harada, Takashi Kita, Yoshitaka Chigi, Tetsuro Nishimoto, Hiroyuki Tanaka, Mikihiro Kobayashi, Tsuguo Ishihara,


Appendix A: Design and Construction of a wide band ultrafast fluorescence spectroscopy system

Over the last four years, my primary experimental expertise has been in semiconductor optical spectroscopy. This has involved construction and development of an in-house test and measurement capability for optical characteristics of compound semiconductor materials. Construction of the system in MQ462 began initially by Roberto Myers in 2009, it then consisted of a broadband excitation source (monochromated 300W Xe arc lamp), free space coupled fused silica optical system and a 0.5 m czerny turner spectrograph equipped with an scientific grade CCD array detector.

In early 2010, the system was outfitted with a closed cycle He cryostat manufactured by ARS, Inc. This optical cryostat (DMX-20-OM) consisted of a vibrationally decoupled two piece expander and sample space, accomplished by using He as an exchange gas between the expander cold finger and the sample space. Although this design worked as intended when the cryostat was constructed in a stationary application, the design of our optical system required it to translate in xyz space in order to perform comparison measurements between samples while keeping the optical system invariant. This caused problems with expander/sample space interference which lead to large amounts of vibrational coupling and measurement drift. In order to mitigate this, a xy translatable mount for the expander was designed which allowed
simultaneous alignment of the sample stage of the cryostat and the expander. This allowed full translation of the sample space in the cryostat while keeping the expander cold finger properly centered in the center of the exchange bore, enabling large multi-sample measurements and growth maps to be developed. Although this system was functional, it suffered from a number of issues associated with the monochromated broadband illumination source, such as a low UV throughput below 300 nm, spurious peaks from the monochromator and poor collimation characteristics.

Figure A.1: Fluorescence system in 2012 before $\mu$-PL upgrades

In July 2011, Roberto received notice that he had won a defense university research instrumentation program (DURIP) grant through ONR to support our efforts in spectroscopy of compound semiconductor nanostructures. This grant enabled purchase of
a tunable Ti:Sapphire Coherent Chameleon Ultra II femtosecond oscillator equipped with an auto tracking SHG/THG non-linear optical system for second harmonic generation and sum frequency generation. Installation of a coherent, high power light source capable of UV excitation greatly enhanced the capabilities and efficiency of operation within the lab. What were once exceptionally difficult spectroscopy measurements to perform due to low SNR or spurious excitation peaks, became routine characterization work. This instrumentation grant allowed, in addition, a time correlated single photon counting (TCSPC) system based on a Hamamatsu R3809U micro channel plate photomultiplier tube (MCP-PMT) and B&H SPC130-EM TCSPC electronics.

One of the major challenges presented to the designer of an optical system using a Ti:Sapphire oscillator based light sources is efficiently dealing with the large amount of average output power (in the case of our Chameleon Ultra II, 4 W at 800 nm). Because of the high output power and short pulse duration, absorptive methods such as variable neutral density (ND) filters are highly ineffective as they are readily damaged by the light source. Toward this end, a variable power attenuator based on non-absorbing crossed polarizers (Fig. A.2) was designed and implemented. The optical system consists of an achromatic zero order half waveplate on an automated rotation stage and a fixed mount linear polarizer. Since our optical system employs a Pockels cell electro-optical modulator to modify the repetition rate of the laser oscillator, the output polarization past the variable attenuator must be vertical. The Pockels cell then turns pulses that it passes horizontal polarization before the beam enters the nonlinear optical system. This system is shown schematically in Fig. A.2
Figure A.2: Ti:Sapphire output conditioning system controlling pulse amplitude and repetition rate. Concept

and in hardware in Fig. A.3. NIR photons enter the half waveplate horizontally polarized from the laser oscillator. The half waveplate rotates the polarization between horizontal and vertical. This light is then passed through a Glan Laser polarizer which is oriented to pass vertical polarization and direct horizontal polarization into a beam dump. This results in an attenuation according to the Law of Malus,

\[ I = I_0 \cos^2(\theta) \]  \hspace{2cm} (A.1)

where \( \theta \) is the angle between the fast axis of the half waveplate and the s-direction of the Glan Laser polarizer. The benefit of this system is that all rejected power is directed into a high power beam dump, preventing damage to optics or substantial thermal drift from occurring in the excitation system.
In the summer of 2013, it became clear that we were interested in obtaining better focusing of our excitation laser beam. Up until that time we had been using a glancing incidence PL excitation path, which has certain advantages for dealing with reflected light, but is unable to accommodate short working distance objectives for microphotoluminescence type measurements. Measurements of small processed devices as well as spatially inhomogeneous samples required use of a high numerical aperture microscope objective. Toward this end, a 0.5NA 36x Schwartzchild Castlegrain reflective objective was purchased from Newport Corporation. This objective uses all metal optics, resulting in very low dispersion in its optical properties over the full range of the optical system. In order to accommodate the objective, the excitation path needed to be modified for through lens parallel illumination and collection. The optical path
of a fluorescence microscope was decided upon and implemented. This upgrade involved creating a single straight and parallel excitation path that aligns directly to the objective. To collect the fluorescence photons, a 50/50 beamsplitter was placed at 45 degrees to the excitation beam which allows the excitation to pass through but directs collimated fluorescence photons toward the spectrometer paths. This setup offers a number of important advantages over more common glancing incidence excitation/normal collection. First, it allows for a rigid system of optical alignment for the main excitation beam to be put in place. This system consists of using the -20 threaded holes on the optical table to mount two adjustable apertures whose heights are calibrated to be identical within 0.005, through which the input beam is adjusted until maximum optical power is obtained after the aperture pair. Second, it readily accommodates in situ sample imaging. The ability to resolve small features on samples or locally illuminate a particular device greatly expands the usability and throughput of the optical system.

The imaging system implemented in the Myers group spectroscopy system went through a number of evolutionary steps before converging on the final design shown in Fig. A.4. The design constraints for this imaging system were that it be able to image samples while illuminated with the excitation laser (or a visible laser on a co-linear path), have sufficient imaging resolution to resolve small devices and patterned features and not interfere with or attenuate the signals present in the fluorescence system. The solution to these constraints involved developing an optical system based on commercial off the shelf (COTS) c-mount optomechanics and lens tubes which would be located in between the objective and the PL collection path on a flip mount allowing the imaging system to be inserted and removed from the path without
The major challenge with design of a microscopy system is choosing and effectively implementing an illumination method. Over the evolution of the system, multiple illumination methods were experimented with, the simplest being direct side illumination of the sample, which provides adequate brightness, but is extremely difficult to align and has poor contrast. Based on my observation of the way most commercial light microscopes illuminate samples (coaxial, through objective) and experience its implementation in the design of a spectroscopic probe station (Appendix B), a coaxial illumination system for imaging was designed and implemented on the main table. This system involved adding a second c-mount cube beamsplitter, oriented to reflect light down the optical path toward the sample from
a side illumination provided by a collimated fiber illuminator. After turning the cube, the light is linearly polarized by an adjustable plate polarizer. The illumination then passes through the imaging cube beamsplitter and is focused on the sample by the microscope objective. Reflected light is passed backward and collimated by the objective, it then reflects on the imaging cube beamsplitter and passes through a second linear polarizer whose angle can be adjusted. The purpose of the crossed polarizers is to reject the directly scattered (low angle) illumination rays, allowing for better brightness/contrast images. This system has thus far proven to be robust to regular use and has enabled regular positioning of the laser spot on very small features on samples, as shown in Fig. A.5.

![Image of sample and laser excitation with imaging system and 36x, 0.5NA objective lens showing excellent resolution of small features and laser position.](image)

In the summer of 2012, shortly after the main laser system was setup, calibrated and in use, construction of a time correlated single photon counting system for collection of time resolved PL decay curves was constructed and refined. Over the
last two years the basic functions of the systems have remained unmodified, save for the addition of an output collimator for the spectrometer. The TCSPC system added a whole new time domain aspect to our measurements, enabling analysis of the time decay of fluorescence signals, from which exciton as well as radiative and non-radiative lifetimes can be estimated, as outlined in Chapter 7, section 1. The extreme sensitivity to light of the MCP-PMT necessitated design and construction of a light tight enclosure and interlock system for the detector and spectrometer, shown in Fig 43. In order to give the TCSPC system some wavelength selectivity, a 0.150m spectrometer (PI-SP2150i) equipped with entrance and exit slits was installed in the optical path in front of the MCP-PMT housing. An entrance shutter with remote control was installed on the spectrometer to protect the MCP-PMT from ambient light. The design of the thermoelectrically cooled MCP-PMT housing necessitated that the PMT be recessed 2 into the housing behind a sapphire window, which initially caused large light throughput issues, since light exciting the spectrometer is not collimated and in fact diverges according to the f# of the spectrometer. In order to correct this issue, a c-mount adapter for the SP2150i was designed and machined in the physics student shop. This allowed rigid, light tight alignment of a collimation lens for the spectrometer such that the 11mm photocathode of the MCP-PMT could be uniformly illuminated with reasonable signal intensity (a key aspect due to the low QE of MCP-PMTs) to achieving high counting rates. Although the main table optical system in MQ462 is a stable tool for fluorescence and photoluminescence, among a host of other less common measurements, there will always be room for future improvements. It was my design philosophy to keep all components modular.
and minimally interconnected/dependent on the alignment of other optics in the system. It is my hope that future students preserve this philosophy when modifying or expanding the instrument. There are a number of modifications and upgrades which, if given more time, I would have made to the system. Firstly, automated, motorized positioning of the cryostat would enable a host of new scanning based experiments and well as make day to day operation less painful. This would be accomplished by setting up a system controlling 5 stepper motors (2 for x-y of the expander, 3 for x-y-z of the cryostat) that could be accessed and controlled through labview. I spent some time playing around with a single axis stepper motor, and actually got things to work, but did not have enough time to see the full implementation through. Second, I would greatly encourage writing a VI to control the laser and the non-linear optics hardware. Although both of these component systems are highly sophisticated and automated, we tend to use them more or less manually when tuning between wavelengths. If experiments are designed later on that require scanning of the excitation energy in a systematic fashion then these VIs could be useful. Moreover from a safety standpoint, remote control of the laser for shutter operation and wavelength selection would eliminate the need to kneel below the plane of the optical table when performing experiments.
Appendix B: Design and Construction of a Spectroscopic Probe Station for High Throughput measurements of DUV LEDs

Device research requires an efficient, reproducible measurement routine to provide feedback on permutations and iterations in design. Through the first two years of the PINLEDs project, all devices EL spectra (a key device characteristic since the goal of the project was to develop LEDs with a specific emission wavelength) were collected using the full analytical main table spectroscopy system in the MQ462 laboratory. This involved a laborious procedure of manually wire bonding using indium solder, a process that requires an exceptional amount of skill and patience to perform efficiently. This measurement protocol prevented any reasonable amount of device statistics or spatial variation data to be collected, because it was simply too time consuming.

It became clear that a superior solution in the form of a dedicated test instrument for optoelectronic devices was needed. This instrument would add key capabilities that our laboratory was currently lacking such as rapid device I-V characteristics collection, optical inspection, and rapid electroluminescence spectra collection. Although most groups would simply purchase a semiconductor probe station, our application required sophisticated, DUV transparent optics and the ability to integrate a high
power source measure unit (SMU). To the knowledge of the author, at the time no satisfactory commercial solution existed that fulfilled these design criteria.

The initial design exercises for this instrument began in May 2013 with the design of the optical system for sample illumination and collection of EL spectra. This was largely accomplished using an educational version of Autodesk Inventor Professional and solid models for COTS components from Edmund Optics, thor labs and Newport corporation (Fig. B.1). Edmund Optics has done a tremendous job of making 3D solid models of most of their optomechanics available freely online. This allowed for the design, visualization and measurement of the entire optical system as well as design of various adapter plates for the microscope body and spectrometer prior to actual construction of the system.

Figure B.1: Spectroscopic probe station optical system, concept

The optical system was designed to facilitate simultaneous sample imaging and spectroscopy with the accommodation for illumination by an external light source,
either for photoluminescence spectroscopy experiments, photoconductivity or illumination with a broadband light source for imagining or reflectometery measurements. Light is coupled into the system via an optical fiber which is then passed through a collimating lens and into a micro patterned polkadot beam splitter to divert the light down towards a focusing objective onto the sample. Light for spectral analysis is either produced at the sample from fluorescence or reflection at the sample surface is collected by the objective lens, collimated directed up the path which diverts 50% of the light via a micopatterened polkadot beamsplitter to an imaging spectrometer. The remaining 50% of the light passes through another micro patterned all metal beam splitter and is focused onto a 1024x768 imaging CCD camera. This allows for

Figure B.2: spectroscopic probe station partial components

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simultaneous sample imaging and spectral collection. Moreover, since the system is equipped both with an imaging spectrometer as well as a wide area 1340x400 pixel CCD (Princeton Instruments PIXIS BR400), high resolution images can be collected with the spectrometer, although the field of view is substantially reduced compared with the dedicated imaging CCD due to increased path length and high f# of the spectrometer.

Figure B.3: Completed spectroscopic probe station

Physical construction of the instrument post design phase involved procurement and assembly of COTS optomechanics from Edmund optics, Thor labs and Newport Corporation for the main optical system. For the most part, these components
(optical cage system and lens tubes from Edmund optics) worked as advertised and required minimal modification during implementation. The exception to this is the 45 degree kinematic mirror mount from Edmund optics which uses a typical two spring + three screw kinematic system. In these mounts the springs are far too weak and required substitution. The body of the microscope was constructed from a surplus Zeiss inspection microscope from university surplus. This provided a rigid platform

![Image](image.png)

Figure B.4: Imaging through the spectrometer with PIXISBR400

with an x-y, focus stage and an objective turret. Adapter brackets were designed in CAD to convert the proprietary Zeiss lens tube connector to a c-mount 1-32 thread and were fabricated in the Physics student machine shop by the author. The sample stage was designed as a three piece part with the sample platen fabricated from
aluminum to mate to the slide holder of the microscope, yielding x-y positioning. Magnetic base probe positioners were acquired from Prof. Siddharth Rajans research group in semi-functional order. These were refurbished by the author. In order to accommodate magnetic base probes, two arms for the sample table were designed out of mild steel, which is ferromagnetic. These arms consist of precision flat surfaces prepared with a surface grinder. Since mild steel on its own has poor corrosion resistance, these parts were finished with a gun bluing black oxide coating process which converts the outer layer of the part to Fe$_3$O$_4$ which has substantially better corrosion and abrasion resistance.

![Image](image.png)

Figure B.5: Imaging of samples and probes with SPS multiple objectives showing wide area imaging through achromatic doublets and high resolution imaging with a 36x microscope objective.

Due to the nature of incorporating the microscope body and turret, which is equipped with RMS objective threads, a number of lenses and objectives can be simultaneously employed. In the current configuration of the instrument, two 18mm
focal length objectives are employed, one is a VIS achromatic doublet for imaging and the other is a fused silica singlet for DUV spectroscopy. For higher resolution work, a 36x reflective objective can be rapidly installed. Since the system was designed for low loss in the UVC region of the spectrum, samples must be imaged through two polkadot beam splitters which results in some ghosting and artifacts during imaging (Fig. B.5), although these are relatively minor.

![Figure B.6: Custom LabView interface for control of the SPS.](image)

Computer control and development of a monolithic control system was accomplished using the LabView Software package from National Instruments (Fig. B.6). The LabView programming language allows rapid interfacing of computer connected instrumentation and development of standard, automated measurement protocols. In the case of this instrument, the software integrates control of the PIXIS spectroscopy CCD, SP2150i spectrograph and Keithley 2604B two channel SMU. Due to a number
of considerations, it was chosen to write all of the code for the SPS in 64-bit in order to take full advantage of memory for rapid spectra collection and processing. This resulted, however in the need to develop a hardware interface layer with labview for the PIXIS camera, since a reasonably priced solution for control of the instrument via an application programming interface (API) did not exist. The details of this LabView/PICAM API interface library are outlines in a subsequent appendix.

Physical calibration of the instrument was accomplished in a number of stages. Initially, the optical systems mirrors and lenses were aligned and installed using a mounted HeNe (633 nm) laser. Once the light was correctly coupled into the spectrometer and imaging CCDs the spectral calibrations were performed. Though the microcontroller on the Princeton Instruments spectrometer takes most of the guesswork of doing wavelength/grating angle calibrations, some finer points of the system must be addressed before high spectral resolution may be achieved. First and foremost, since we are using an array detector on a Czerny-Turner spectrograph, there are certain known optical aberrations that occur at varying distances from the central wavelength for a given grating angle. These aberrations lead to substantial broadening of sharp features when local spectra from multiple grating angles are stitched together to form a broadband spectrum.

If the error of the system is known and systematic, its output can be modified with a calibration factor to produce correct results given a known standard. This calibration was performed initially for only a single wavelength, using a HeNe laser frequency standard. It was determined that to first order, the error in wavelength position is linear with the distance in wavelength between the source frequency and the center wavelength of the imaging array as shown in Fig. B.7. Fitting of the data
yields a correction coefficient that can be implemented in the instrumentation control software. This technique worked exceptionally well for the wavelength calibrated, as shown in Fig. B.8. However, at shorter wavelengths, significant error was found to be present. It was hypothesized that there exist some dispersion to the correction factors being employed.

This was accomplished by coupling a broadband white light source (deuterium-tungsten-halogen) through a monochromator and into the SPS collection path. The monochromators output slit was set to provide the minimum output FWHM and the output wavelength was systematically stepped through the entire wavelength range of the spectrometer (200nm-1000nm) while exposure were collected on the PIXIS CCD. Using an automated data processing routine in MATLAB, for each wavelength, a linear fit was performed, all of which resulted in R2 values >0.9 and the slope and intercept of this fit were returned as a lookup table of fitting parameters. Interestingly,
Figure B.8: Spectrum collected with SPS of HeNe laser post empirical calibration and correction of dispersion error of the array-spectrograph combination.

Figure B.9: Dispersion of error parameters for SPS PIXIS array detector and spectrograph.
a substantial dispersion in the error parameters (Fig. B.9) appears and is more or less quadratic in nature. The results of this study were incorporated into the SPS control software in LabView as an empirical, wavelength dependent correction factor for spectral position. In order to fully test the quality of this calibration, the light from a broadband deuterium-tungsten-halogen light source was coupled into the optical system of the SPS and a broadband spectrum was collected with the spectrometer. The resulting spectrum showed exceptional detail of the fine D-line features such as the D-line and Fulcher bands (Fig. B.10).

Figure B.10: Verification of broadband calibration of SPS using the spectrum of a deuterium tungsten halogen light source.

At this level of functionality the SPS entered service as the workhorse characterization tool of the UV-LED project in November 2013, allowing for rapid characterization
of device IV characteristics and EL spectral output to users with minimal training in optical system. Further work and development with this system over the last year has centered around developing more sophisticated automated measurement routines to measure EL intensity and spectra for multiple injection levels as well as incorporation of pulsed current excitation, a technique popular for characterization of LEDs since it eliminates many self-heating effects, allowing for exploration of device characteristics at high peak current density. Examples of data collected with the system can be found in the EL spectra of chapter 6. The calibration seems to be holding over a long course of 8 months as well as through significant temperature swings in the lab due to HVAC issues, which suggests that it is relatively insensitive to environmental conditions and will continue to hold validity for the foreseeable future.
Appendix C: Modification of a closed cycle He cryostat for low level magneto-optoelectronic experiments

Research in the Myers group over the last few years can be divided into two fields of study, magnetic phenomena of materials and semiconductor optoelectronics. Through most of 2012, the optical system in the group was exclusively devoted to measurements for various optoelectronics related projects. In order to bridge the magnetism projects into the rich area of magneto-optical phenomena, an apparatus was required which integrated a magnetic field with the existing sophisticated spectroscopy system in MQ462. In the fall of 2012 I worked with Brandon Giles to set up an electromagnet on the table and get a rudimentary room temperature experiment involving a laser (thermal) induced voltage in uniformly magnetized samples of yttrium iron garnet (YIG). This project grew substantially over the next year, eventually adding two other full time students (Zihao Yang and John Jamison). Eventually, it became clear that in order to take full advantage of the tunable nature of the spectroscopy system (laser wavelength tuning, power attenuation, variable temperature) we desired to integrate a magnetic field with our ARS-DMX-20OM closed cycle He cryostat. Most experiments of interest required Voigt geometry (Magnetic field parallel to surface and perpendicular to direction of light polarization). This orientation conflicted with the geometry of the existing optical cryostat (Fig. C.1) which had a large circular
vacuum space around the sample radiation shield and cold finger. This prevented incorporation of any sizable or uniform magnetic field in the Voigt geometry at the sample.

In order to enable these measurements, the author and Brandon Giles worked together to design and construct a modification to the existing cryostat that would enable samples to be mounted in a magnetic field at low temperature. Although a number of commercial solutions, including a kit from the manufacture to accomplish this feat existed, they were prohibitively expensive and did not offer as much functionality as the custom designed modification. Our design requirements stipulated that we be able to mount samples in a 0.1T transverse magnetic field on a 0.5 diameter circular mount equipped with semi-rigid coaxial cables in order to provide both high frequency performance and excellent shielding from electromagnetic interference. These parameters must be met while preserving cryostat functionality in terms of vacuum and base temperatures (<1E-6Torr and <20K respectively).
This modification involved a large number of design considerations such as how to efficiently insert/remove samples without disturbing the optical system, how to route coaxial cables without creating a large thermal short and how to ensure high enough thermal conductivity in the sample mount to maintain low base temperatures. The final design consisted of four custom parts which mount on existing cryostat hardware, shown schematically in Fig. C.2. The design approach was to model the sample holder first and then create the mounting hardware to the cold finger, a radiation shield to encapsulate it and a set of vacuum shrouds to encapsulate it while providing optical transparency.

The sample holder consists of a solid rod machined from a billet of low oxygen copper. The rod has a smaller diameter center section to reduce weight, thermal mass and to accommodate signal cables. At either end of the rod the diameter becomes larger, the front to 0.6 and the rear to 0.75. In order to mount the rod in a rigid manner, the rear diameter of the rod is threaded 3/4-20 and threads into a mounting
block attached rigidly to the cryostats cold finger. In order to remove any slop from
the threaded joint in the sample mount during mounting, a right angle mounting
block to the cold finger was designed with a smaller diameter step after the threaded
portion in order to seat the threaded portion. The diameter is specified so that
the sample ends diameter clears but the threaded end does not. Most of the parts
for this project were constructed by the Physics Dept. Machine shop by the skilled
instrument makers Josh Gueth and Jon Shoever. The Physics machine shop has many
high quality CNC machining centers and lathes and most of the parts for this project
were too intricate and delicate to be constructed by the author in the student shop.

With the right angle mount and the sample rod designed and machined, the
new front radiation shield, consisting of a low oxygen copper tube brazed to a copper
flange was designed and constructed. The tolerances on this part were rather delicate,
since it must not interfere with the sample rod or the vacuum housing and be able to
connect to the existing mounting points for the front radiation shield. The purpose of
this part is to shield the cryostat cold finger from radiative heating from the outside
wall of the vacuum housing. Due to the design on the DMX-200M, the radiation
shields mounting is rather delicate and lacks rigidity. During assembly, substantial
care was necessary to ensure that the shield did not interfere with the sample rod.

Finally, the outside vacuum housing (Fig. C.3) was designed and constructed.
Initial designs stipulated machining two separate parts (the flange and the tube) and
then joining them with a weld. Unfortunately, due to the nature of Al weld distortion
and difficulty in creating vacuum tight Al welds, this design was abandoned at the
prototype phase. Instead, we settled on a monothic design turned out of a solid
8 diameter billet of Al alloy. Although this yielded a substantial amount of waste
material, it ensured a square flange/tube relationship and vacuum tight seal. The main design constraints on this component were the interference with the radiation shield (favoring maximization of inner diameter) and maximization of magnetic field magnitude and uniformity at the sample (favoring minimization of outer diameter in order to reduce pole gap to the electromagnet).

In order to get light into the cryostat, a transparent window needed to be furnished and integrated with the vacuum housing. In the early design stages a number of methods were explored for mounting the window while ensuring a vacuum tight seal, involving mechanical joints with o-ring seals. With the convergence on a design involving sample rod insertion and removal from the rear of the cryostat we settled on a fixed high vacuum epoxied window. The window is SpectraSil UV-grade fused silica. For epoxy, we chose the same product that the cryostats manufacturer uses in the original equipment windows, STYCAST 1266, which is a low thermal conductivity, low thermal expansion epoxy designed for vacuum and cryogenic applications. The window sits on a step machined in the vacuum housing and is epoxied in place.
Vacuum tests of the assembled system showed that this joint holds vacuum levels of 1E-6 Torr with turbo pump running, which is comparable with operation pre-modification.

With the physical cryostat hardware designed and validated (Fig. C.5), we turned our focus to the outfitting of the cryostat with high frequency semi-rigid coaxial cables. The purpose of this was twofold. First, we desired to achieve the maximum possible isolation and shielding of the signal cables, since most of the experiments conducted in the cryostat require sensitivity to low levels. Second, for future projects, we desired to introduce high frequency signals to the sample. Semi-rigid cable was chosen since it combined the most acceptable balance of ease of manipulation with high frequency behavior. In order to ensure thermal isolation, the semi-rigid cable was wound around the main body of the expander (Fig. C.6). Semi-rigid cable can be bent a single time, so we had only one shot to do this correctly. In order to connect
the cables to outside equipment, a tee connector was purchased from ARS cryo to extend the DC breakout connector and allow for mounting of a custom designed SMA breakout connector. Hermetically sealed (glass for center conductor and o-ring for ground) SMA connectors were procured from Pasternack corporation (Fig. C.6b).

Prior to putting the cryostat back in service, the RF properties of the semi-rigid coaxial cables were characterized using a HP/Agilent 8510 vector network analyzer from DC-20GhZ. In the interest of future experiments, we were interested in knowing to what frequency the wires are good for. The specification from the supplier stated acceptable operation to 27 GHz. Since we added numerous bends and connectors, it was important to know the performance for the assembled system. Using the VNA transmission loss ($S_{21}$) was measured versus frequency for each of the two semi-rigid coaxial cables (Fig. C.7). In order to compare to a physical object, a flexible SMA
cable was tested. Both semi rigid runs exhibited similar transmission loss over all wavelengths tested and agree very well with the specification from the manufacturer. Furthermore, the high frequency characteristics are superior to that of the flexible coaxial cables.

Since completion of construction, this system has been widely used for Opto-Thermal Spin Seebeck experiments, photoluminescence spectroscopy and a temperature dependent circular polarization resolved electroluminescence study of GdN nanoparticle tunnel junctions. It has proven to be robust, although there are some areas where improvement can be made. The male SMA connectors between the sample rod and the inner cryostat run are very delicate and easy to break solder connections.
Figure C.7: High frequency performance of coaxial cabling as installed in cryostat compared to regular flexible SMA coax cable.

if mishandled. There seems to be an issue developing with the vacuum integrity of the system, causing pressure to rise gradually if the turbo pump is disconnected, though the manufacturer does not recommend doing so. This could be diagnosed by connecting an RGA to the system via the KF pumping line. Although only tangentially related, the addition of stepper motors to the cryostat should be made a priority since it would eliminate the possibility of expander/exchanger contact which cases the cold finger to migrate out of alignment.
Appendix D: PAMBE Growth Details

All III-nitride compound semiconductor samples in this dissertation were grown using a Veeco GEN 930 Molecular beam epitaxy system. This system is a modern commercial MBE based on the venerable GEN II originally developed by Varian, Applied EPI and later Veeco. The system consists of three separate vacuum chambers, illustrated in Fig. D.2.

![VEECO GEN930 System Schematic](image)

Figure D.1: Schematic of GEN930 MBE system operated by SEAL at OSU

Samples are loaded in a backable loadlock which is pumped by a scroll pump and a turbomolecular pump down to base pressures around $1 \times 10^{-8}$ Torr. This chamber
linearly connects to a UHV buffer chamber pumped by an ion/titanium sputtering pump and is capable of base pressures in the low $1 \times 10^{-10}$ Torr range. The buffer chamber is outfitted with a sample bake out station capable of temperatures up to 800 C, which is used to pre-bake samples prior to loading them into the growth chamber to desorb all volatile species from the substrate and thereby maintain the purity of the chamber. Samples can be transferred into the growth chamber, which is pumped with a combined closed cycle cryopump, LN2 cryoshroud and ion pump and commonly exhibits base pressures in the $5 \times 10^{-11}$ Torr range.

Figure D.2: GEN930 MBE system operated by SEAL at OSU

In the main growth chamber samples are mounted on a continuous azimuthal rotation mount (CAR) equipped with a shielded ion gauge for flux measurement and
a sample heater capable of temperatures from 25 C -1100 C. Fluxes are provided by elemental solid source effusion cells with the exception of nitrogen which is supplied as a gas and cracked into reactive species with a microwave plasma. The view of the source flange of the system is shown in Fig. D.2.

It is beyond the scope of this document to discuss the fundamentals of the technique of molecular beam epitaxy as a number of excellent references have been written[136, 137, 138]. This section mainly concerns the particular procedural details of operation of a GEN930 PAMBE system for growth of III-Nitrides.

D.1 Growth Procedure

This section describes normal operation of the N2 PAMBE system. Although written as an OPSPEC, it should not be used word for word, as all users of the system must know the procedure from memory. It is however instructive during training for new users to have access to such a document so it is included here for reference. Since the system is constantly being upgraded and modified, some details may become different over the years.

D.1.1 Sample preparation and loading

The day before your growth, typically toward the end of the day, coordinate with whoever is growing on that system that day to load and bake your samples in the load-lock chamber. This involves physical preparation of the growth substrates as well as mounting and insertion into the MBE system. Finally the samples must be baked in high vacuum to bring the pressure in the loadlock chamber low enough that it can be transferred to the buffer chamber without causing damage to the ion-pump or causing contamination.
Sample Preparation

All samples are prepared by a standard organic solvent cleaning procedure. Substrates are removed from packaging and transferred (using pre-clean or "DIRTY" sample handling tweezers" and clean gloves) to the beaker marked "N2 MBE SOLVENT CLEAN" and sonicated in acetone, methanol and isopropanol for 10 minutes each. This decreasing polarity solvent regiment removes organic particulates and moisture from the sample surface. Waste solvent is poured into the container in the hood after each wash step. After the IPA step is complete, handling samples with "CLEAN SAMPLE HANDLING" tweezers and new outer gloves, quickly dry samples completely with N2 to remove residual solvent. Once samples are dry, transfer them to sample prep bench and place them epi-surface up on a clean texswipe, then cover with a petri dish cover.

Removing the Trolley

The trolley is typically in the buffer chamber because the current grower just loaded their sample off of it into the growth chamber. Before moving the trolley into the loadlock chamber, check that all baked samples are removed from it and placed either on the heater station in the buffer chamber or on the transfer arms. Next, check the pressures in each chamber. The buffer chamber and loadlock pressures should be \(9\times10^{-8}\) Torr before even thinking about opening the gate valve between the two. To prevent pressure waves from unseating samples, the two chambers should not be at a pressure differential of more than \(5\times10^{-8}\)Torr between the two chambers. Next, verify that the gate valve to the growth chamber is closed (check valve visually and see that the pressures are different).
Finally, the gate valve between the buffer and loadlock can be opened, pay attention to the pressures in the buffer and loadlock as the gate valve is opened and be ready to close quickly if pressure spikes. Once open, use the magnet on the top of the chamber to move the trolley into the loadlock. Close the gate valve between the two chambers, observe the "closed" mark on the valve and watch the pressures become different. Next, begin to prepare to vent the loadlock. Make sure that the loadlock Ion Gauge is shut off at the controller and the locking screw on the loadlock door is loose. Again verify that the gate valve between the loadlock and the buffer chamber is closed. Turn off the loadlock turbo pump on the E-rack by hitting "START/STOP" on the Varian control panel. Watch the pressure in the buffer to verify that it remains unchanged.

While the loadlock is venting, prepare to handle the trolley by putting down new texswipes on the sample prep bench and putting new out gloves on. The loadlock will vent and then purge with dry nitrogen, reaching 790Torr. Once the loadlock is at atmosphere, the door should be carefully opened, preferably with the side or back of your hand to avoid contaminating the new gloves you just put on. Note that the o-ring that seals the door tends to stick to the loadlock flange, rather than the door, leave it there for now.

Remove the trolley by sliding it to the end of the rail and picking up the magnet and moving it to the buffer chamber so that it does not interact with the trolley. Place one hand on the top post of the trolley and the other hand on the bottom. Pull out until the rollers have cleared the track, try not and over anticipate the amount of torque the trolley will put on your hands, doing so will result in violent motion of the trolley after it clears the track. rotate the trolley such that the blocks and pins are
pointed toward the ceiling and walk it over to and place it on the sample preparation bench.

**Mounting Samples**

Now, a sample holder or "block" must be prepared and mounted to the trolley. The blocks are unlocked to three pins on the trolley by a block handling tweezer in two of the unused mounting locations and rotating CCW. Pull the block directly upwards to remove. Working over the sample mounting jig, invert the block and mount face down in the jig. Next, take the clean sample tweezers and remove the circlip by compressing the eyelets with the tip of the tweezers. Transfer the circlip to the texswipes.

Depending on your growth substrates, there are two different paths to take. The blocks are designed to hold 3” wafers, so if you are growing on 3” Si or have In-bonded samples to a 3” Si wafer, load the substrate episurface down. If you are growing on a 1/4 of a 2” wafer, as many of our GaN and AlN templates come, you must first put down a molybdenum faceplate, which is stored in the N2 dry box with the templates. Place the faceplate growth side (duller of the two) down and place the substrate epiface down on top of it. Carefully line up the faceplate with the substrate and place a quartz backing plate on top of the stack, taking care not to slide the template when the plate is placed. While compressing with clean sample handling tweezers, place the circlip back in the block, indexing the wafer flat to the matching thicker part of the circlip if and Si wafer is used. The circlip holds the stack in place and therefore it is imperative to ensure its correct seating and function. Using the blunt block handling tweezers, apply lateral force to the circlip to check that it is seated at its lowest possible point in the block and is fully expanded, little to no play
should be observed. Now, run the tweezers in a circle to check that it is at the lowest possible position and free of play. As a final check, while using tweezers to handle the assembled block and sample, tap the block perpendicular to the table to ensure that the sample is positively mounted to the block.

Remount the block to the trolley by orienting the pins to the more CCW set of three mounting holes, placing the block down through the pins and rotating CW to lock in place. If possible (it always should be) place prepared blocks on separate and vacant trolley locations. Verify that the block is locked in place by gently pulling back with tweezers. Repeat these steps for all samples and record sample positions on the trolley clipboard.

**Baking the loadlock**

Transfer trolley to loadlock, inserting such that the epifaces of the substrates point away from the growth chamber. Transfer the o-ring from the loadlock flange to the door. Turn on turbo pump by pressing START/STOP on the Varian controller. Hold door closed until vacuum is sufficient to hold it closed. The ion gauge will come on once pressure reaches the 5E-5Torr.

After the Ion gauge has turned back on, and pressure is less than E-7, begin the loadlock bake to remove moisture and absorbed gases from the substrates. Check that the bake temperature is set to 200C in MOLLY. Set the bake time to 4 hours on the loadlock bake controller in the bottom left corner of the e-rack. Flip the RESET switch and depress the switch to start the bake. You should see that heating coils in the loadlock become active.
Transferring and Baking the Sample

Before growth, samples are taken up to high temperature to completely outgas all remaining contaminants on the surface and sample mounts. This is accomplished on a heater station located in the buffer chamber. First, the trolley must be transferred from the loadlock to the buffer chamber. The same rules for pressures outlined in section IIIb apply, i.e. make sure that the loadlock bake has finished and that the pressure in the loadlock is in the high 8s or lower and that the pressure differential between the loadlock and buffer is \( \leq 5 \times 10^{-8} \). If the pressures check out, check that the gate valve to the growth chamber is closed. Then open the gate valve between the buffer chamber and the loadlock. Watch pressures. Move the trolley into the buffer. Close the gate valve.

Now, with the samples on the trolley in the buffer chamber, the first substrate for growth needs to be transferred to the heater station. Align the trolley with the short transfer arm. Transferring samples consists of three steps, alignment, insertion and simultaneous unlocking and locking. The transfer arm should be aligned with the center of the slot on the sample that is CW from the occupied slot on the trolley. Move the transfer arm forward until the pin touches the narrow part of the slot. Rotate CW and press inward lightly to position the pin in larger diameter part of the slot, where the locks can pass freely. Insert the transfer arm until the spring touches the block. Now in a fluid motion, rotate CCW until the rotation ends. This should simultaneously lock the block on the transfer arm and unlock the block from the trolley.

With the block locked on the transfer arm, pull straight back without rotating the transfer arm. Move the trolley out of the way (toward the other end of the buffer...
tube). Make sure that adequate lighting is present to clearly see the heater station. Now, with only CCW rotations to ensure that the block does not loosen from the transfer arm, align the pins from the heater station with the slot CCW from the occupied slot. Center the pins just CCW of the larger diameter hole closest to the occupied position. Gently press inwards and rotate CCW to align the pin in the larger diameter slot. Insert the transfer arm until travel stops. Rotate CW to lock the block onto the heater station and unlock from the transfer arm. Gently pull the transfer arm back from the heater station.

Now that the sample is loaded on the heater station, begin the sample bake recipe, which will gradually take the sample up to 800C in multiple steps (add details of sample bake recipe here). Make sure that buffer pressures do not rise above the mid 6s. If they do, then slow the ramp down in the buffer bake recipe. This takes about 2 hours to complete and is typically done by the grower the night before you grow or during your first growth of the day for your second sample. When the buffer bake is complete, the sample can be transferred back onto the trolley using identical procedure to transferring from the trolley to the heater station.

D.1.2 Growth Procedure

Transferring sample to growth chamber

Now we must transfer the sample from the trolley to the growth chamber. The procedure for removing the sample from the trolley is identical to that outlined in IIIe: align the pins CW of the occupied position, insert the transfer arm and unlock from the trolley and lock to the transfer arm in one concerted CCW motion. Pull backward to free the sample from the alignment pins. Move the trolley out of the way (towards the loadlock).
Now that we have our sample on the long transfer arm we are ready to open to the growth chamber and mount the sample on the CAR. As with all interchamber transfers, pressures must be checked carefully before proceeding with opening a gate valve. The Growth chamber should be in the mid-low 10s. the buffer should be in the mid-low 9s before transferring can occur. Verify that the gate valve to the loadlock is closed. Make sure that the CAR is indexed to the 90deg (sample loading) position, which it should be as that is the park position. Open the gate valve to the chamber. Watch the pressures and be ready to close if a spike occurs.

Move the transfer arm forward without rotation in two steps one until the view from the buffer tube is blocked and then open the viewport into the growth chamber, turn on the fiberlight and gooseneck lamp to view the CAR. At this point, make sure that rotation is enabled on the CAR. It is vital that there is some resistance to motion, which will be provided by the internal resistance of the CARs stepper motor. The procedure for attaching the sample block to the CAR is identical to loading the sample on the heater station: Align to the CCW slot from the engaged slot with only CCW motions, then press inward and gently rotate CCW to align the pin with the large diameter part of the slot. Press inward without rotation until travel ends and rotate CW to lock the block on the CAR and unlock the block from the transfer arm. Pull back on the transfer arm without rotation. Close the gate valve to the growth chamber. Close the viewport above the CAR.

**Walk up - System in idle state**

When you walk up to the system in the morning, your sample for growth will typically be already baked and either mounted in the growth chamber or located on a transfer arm in the buffer chamber. If the sample is not in the growth chamber,
then transfer it following the procedure outlined in IVa. The remainder of the growth procedure involves starting up system ancillary components and executing the recipie. The first things to set up are to initiate the cell cooling and liquid nitrogen flow to the cryo shroud.

During operation, the chamber is surrounded on all sides except for the effusion cell manifold by an insulating jacket of liquid nitrogen, the purpose of which is to keep chamber pressures low by immobilizing molecules that hit the chamber walls and thermally isolate the chamber from the outside environment. Open the LN2 valve above and right of the cryopump (the out flowing valve is always open), note open time in the LN2 log file. The effusion cells are thermally isolated from each other by a coolant jacket through which a chilled solution of 50%ethylene glycol (e.g. antifreeze) and 50%DI water flows through. This solution is maintained at -25C during normal operation and must be set from its idle temperature of -5C. Currently, the chiller tends to leak, so check the coolant level when you set the temperature, if the chiller still says Add then mix a 50/50 solution of ethylene glycol(from the flammables cabinet) and water and add it to the chiller until it stops displaying add.

**Warming up cells and initial setup**

When the system is idle, the effusion cells are set to values that minimize material consumption and thermal wear to the crucible. See the master table in 095DL above the control console for current idle temperatures. Depending on the strustructure to be grown, set cells to the ramp rate and required temperature based upon the flux calibration. Note that Ga cell is a SUMO cell and requires two heater zones. The tip is set to 200C+Base temperature. Wait until the cells are around 3/4 of the target
temperature before changing the PID setting from the IDLE PID settings to the HOT PID settings.

Measure Fluxes

Once cells are warm and thermally stable (usually after 1h), prepare to measure fluxes. Open the flux calculation excel spreadsheet template. The flux from an effusion cell is exponential in temperature. The fitting parameters A and B are determined from the flux calibration. For each flux that you will using during growth, i.e. each cell temperature, a flux must be measured. Before measuring fluxes or opening shutters ever, verify that all viewports are closed and if fluxes greater than 1E-7 are going to be employed, shut the gate valve to the growth chamber ion pump. Rotate the CAR to 180 so that no material is deposited on the substrate during flux measuring. Now is a good time to measure the ion gauge temperature with the pyrometer to get an idea how much the viewport is being coated over time. Use the Si emissivity calibration (0.67).

Verify that all cells are at the desired temperature. Measure the flux by opening the shutter on a given cell for 1min and recording the BEP reading at the end of 1min. Close the shutter. Record the background chamber pressure with the shutter closed. Input the target, measured flux and cell temperature into the spreadsheet. Set the cell temperature to the corrected value. Repeat for all relevant cells (Ga,Al,Gd). It is not nessasary to measure fluxes for dopant cells. Repeat measurements in 5 minute intervals until the flux for each cell is stable for 3-4 intervals.
Pump out N2 line

In between growths, a residual pressure will develop in the N2 line between the RF plasma source and the ultra high purity N2 cylinder. It is necessary to pump this line to avoid a pressure spike when the N2 cyl is opened. When the valve is opened, the chamber will spike slightly, so close the growth chamber ion pump gate valve. The CAR should still be located at 180 from the flux measurement, so keep it there, because you dont want whatever particulate is coming out of the N2 line sticking to the sample. Open the conflate valve on the RF plasma source until you just see the first thread. It is imperative that you do not open it further, doing so could vent the chamber. After opening, chamber pressure will rise slightly and then go back to equilibrium. Next, set the MFC to some low flow rate, around 1sccm to allow for pumping from the MFC back to the N2 cylinder.

Power up the RHEED

While the system is pumping on the N2 line, now is a good opportunity to power up the RHEED. Slowly ramp the voltage to 10kV in 2kV/10s steps. Then ramp the current to 1.4A in 0.1A/5s increments. By the time you are done setting up the RHEED, the line should be almost done pumping.

Prepare the Growth Surface

Depending on the substrate employed, the surface preparation is different. For Si and AlN, which both form a native oxide in air, this oxide must be thermally desorbed. GaN, which does not form a substantial native oxide is polished with a strong flux (3x stoich. Of GaN) of Ga. Rotate the substrate to the growth position and engage substrate rotation at 3rpm. Use the surface prep procedure relevant to
Table D.1: Surface preparation conditions for different substrates and pyrometer emissivity calibrations

<table>
<thead>
<tr>
<th>Substrate</th>
<th>GaN</th>
<th>AlN</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Car Temperature</td>
<td>600°C/20min + 760°C/5min</td>
<td>600°C/20min 1000°C/5min</td>
<td>600°C/20min 1000°C/5min</td>
</tr>
<tr>
<td>Flux Polish</td>
<td>Ga 2x stoich</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Emissivity Cal</td>
<td>0.53</td>
<td>0.53</td>
<td>0.67</td>
</tr>
</tbody>
</table>

your substrate from the following table. All temperatures are as recorded with the pyrometer. Now is a good time to heat up the dopant cells. These cells are small and will be used up quickly if heated up first thing with the source cells.

During the surface cleaning, you can monitor the progress with the RHEED. First you must align and focus the beam on the sample. To do this, find the direct reflection and then tilt it slightly away. Add more details of RHEED operation here. When GaN and AlN are clean, a clear 1x1 reconstruction should be visible. Si (111) should give a 7x7. Note that GaN and AlN quarter wafers will go in and out of brightness because of shadowing of the faceplate.

After the surface has been prepared and the reconstruction is clearly visible in RHEED, close all shutters and set the substrate to growth temperature, note that the temperature setpoint and the actual temperature as recorded with the pyrometer are different, and the pyrometer must be set to the correct emissivity for the substrate being measured. Adjust the CAR heater setpoint as required to get the temperature to the desired value. Wait for the temperature to equilibrate.
Open the N2 source

Now we are ready to begin flowing nitrogen into the chamber. First, make sure that the growth chamber ion pump gate valve is closed. Because this step may dislodge debris in the N2 line, you should rotate CAR to 180 such that the substrate is facing the back of the chamber and debris will have a lower probability of interacting with the growth surface. Next, set the MFC to the flowrate from the previous growth (assuming that the person before you was using the standard N2 pressures and power). Watch the pressure in the growth chamber for a spike and be ready to set the MFC to zero. When the chamber pressure has equilibrated, open valve #2 on the N2 manifold to begin flowing N2 gas into the chamber. Carefully watch the chamber pressure to ensure that it does not exceed 2.5E-5torr. Once pressure has come to equilibrium, adjust MFC up or down to reach 2.5E-5+/0.1E-5torr. Wait for equilibrium.

Light the plasma

Once the nitrogen is flowing at the correct rate, we must begin production of reactive nitrogen species. This is accomplished by creating a 350W RF plasma. Once the plasma is lit, growth should take place as soon as possible thereafter. First, we must rotate the CAR back to the growth position of 0. The RF cavity that the plasma is generated in is cooled by city water. Check that the flow rate of the plasma source is correct, the float should be at or above the mark on the gauge, located below the turbopump for the loadlock. Next, set the setpoint of the plasma power to 60W. Turn the power On in MOLLY. It will ask you to check the water, which you just did. Since there is a great impedance mismatch between a plasma and the RF source, a good amount of the radiation incident on the gas will be reflected when it comes
to the interface. This reflected power can damage the RF power supply and must be
minimized. The RF source is equipped with a manual impedance matching network.
Once the source is powered on, adjust the impedance matching network, rotating B
first and A second, in small increments to minimize the reflected power to zero. Make
sure that it is stable before continuing.

Now, set the plasma to full power, 350W. Adjust matching network again to
minimize reflected power. Note that the plasma will not immediately light in entirety.
A non-equilibrium change in the chamber pressure or the flow rate typically allows
the plasma to light fully. This is accomplished by temporarily lowering the flow
rate of N2 into the chamber, set the MFC to the current setpoint -1sccm. Working
quickly, adjust the matching network to minimize the reflected power. When the
reflected power is stable at zero, set the MFC back to the original setpoint and adjust
impedance matching network to be stable at zero. This is a good opportunity to
carefully find the minimum of the reflected power with respect to the impedance
matching network by rotating the knob in one direction and finding the point at
which reflected power increases, then rotate backward to the point where it increases
from zero in the opposite direction. The halfway point between these positions is
where the reflected power is minimized. During growth, it is imperative that the
reflected power is monitored throughout using the graphing tool of MOLLY. If the
reflected power jumps to 1W, reduce it to zero.

**Execute the growth**

Depending on the structure to be grown, the amount of user interaction with the
system during growth will vary. MOLLY has a scripting language where one can
control growth parameters from a very high level GUI based script to a low level
visual c# type language. This low level scripting has been employed in the growth of graded structures.

The first layer to be grown, called the buffer layer, is typically an undoped homoepitaxial layer with the substrate. It is grown to isolate defects at the interface and provide a high quality layer on which the heterostructure of interest is grown. This layer can be grown manually by opening the relevant shutters, making sure to start a timer so that the thickness of the layer can be known. The RHEED pattern should initially be spotty, then transition to a clean, streaky pattern indicating a smooth surface. Once the desired thickness has been reached, the shutters can be closed and the recipe can be started. While the recipe is running, monitor reflected power and adjust the impedance network if necessary. Monitor shutter open and close times to make sure the recipe is running as expected.

End of Growth

When you write your growth script, it should include commands to end the growth. The plasma power should be automatically set to zero. The cell temperatures should be ramped to the next temperature required. If you still have another growth left for the day, the cell temperature should be set to the value required for the next growth. If this is the last growth of the day, cell temperatures should be ramped to their idle values. The CAR temperature should be ramped automatically to 50C in the script. When the recipe is done, the power for the nitrogen plasma must be turned to OFF in MOLLY, even though the setpoint is at 0W.

Next, follow the startup procedure in reverse; close valve #2 on the nitrogen manifold and let the system pump on the line. Stop sample rotation. Once the chamber pressure has fallen below the 5E-7torr, it is safe to open the gate valve to
the growth chamber ion pump. This will allow the chamber pressure to fall a bit faster and the N2 line to pump out more completely. Once the chamber pressure is stably falling into the low 1E-8s, close the conflat valve on the N2 plasma source. The handle to the valve is actually a 1/4 socket T-wrench and pulls out once tight. Use the torque wrench to torque the valve to 20lb-ft.

Once the substrate temperature has fallen below 250C and the pressure has fallen into the low 8s/mid-high 9s, begin the procedure to transfer the sample out of the growth chamber. Check that the gate valve between the loadlock and the buffer is closed. Rotate the CAR to 90. Open the growth chamber gate valve. Transfer the sample to the trolley as outlined above. Load your next sample for growth (assuming that is has been baked). Close the gate valve. At this point, you will either begin growth procedure again starting with heating of the substrate or continue on to the next section which covers system idling.

D.1.3 End of Day Idling the System.

After the end of the final growth of the day, the script will have set the plasma power to zero, set the CAR temperature to 50C and set the cells to their idle temperatures. Since the Ga effusion cell is a SUMO cell and has two separate heater zones, the tip tends to cool faster than the base. You must monitor the cooling rate of the tip and the base and adjust the ramp rate of the tip to keep it cooling linearly with the base. The target temperature differential at the beginning of the ramp is 200C between the tip and the base but will decrease to 100C towards the end of the ramp.

Manually turn off the plasma power, close the #2 valve on the nitrogen manifold and let the system pump on the line. While the system is pumping down, set the
chiller back to the idle setting of -5C and check the level, since it leaks. Add more coolant solution if required. Stop sample rotation. Once chamber pressure has fallen below 5E-7, open growth chamber ion pump gate valve, the chamber should start pumping down faster. Close the LN2 valve above the cryopump, pressure in the chamber will drop slightly. Now is a good time to shutdown the RHEED. Ramp the current down to 0A in 0.1A/5s steps, then ramp the voltage down to 0V in 2kV/10s steps. Switch the RHEED power supply off.

Close the conflat valve on the RF plasma source, torque to 25in.lb with torque wrench. Once chamber pressure is below 5E-8 and the substrate temperature is below 250C to transfer out of the growth chamber. Once the above conditions are met, run through the sample transfer procedure. Rotate the CAR to 90 in load/unload position/ Check that the LL/buffer chamber gate valve is closed. Open buffer chamber/growth chamber loadlock. Transfer sample from CAR to trolley in the usual fashion. Align transfer arm with block pins CW of engauged slot. Push transfer arm in and rotate CW slightly to align pin. Insert transfer arm until end of travel. Rotate CCW to unlock sample from car and lock onto transfer arm. Pull transfer arm and block out of growth chamber. Close gate valve. Transfer sample to trolley.

At this point you are ready to unload your sample. Prepare to transfer trolley from buffer to loadlock. Verify that pressures are compatible (ie. There is less than a 5E-8Torr difference between the chambers). Verify that growth chamber gate valve is closed. Open the gate valve between the loadlock and the buffer chamber. Move the trolley to the loadlock. Close the gate valve between the loadlock and the buffer chamber. Prepare to vent the loadlock: turn the ion gauge off. Turn the turbopump
off. Remove the trolley as described above. Remove samples from trolley as described above. Replace trolley and pumpdown and bake the loadlock as described above.

Before leaving, make sure that the Ga cell is cooling correctly and fill out the growth log and the filemaker sheet.
Appendix E: A C++ library for 64bit PICAM API-NI
Labview interfacing

This section is to function as a permanent record for an alternative to the costly implementation of 64 bit commercial software for control of Princeton Instruments cameras. Princeton Instruments provides support to OEMs for their spectroscopy detectors via an application programming interface for windows which essentially is a software layer that facilitates communication between programs and low level device driver communication. Although this package works quite well, its data types are not compatible with the way that NI-LabView can call dynamic link libraries. The solution to this problem is to write a wrapper library in C++ interface communication between PICAM and LabView via standard datatypes. The following appendix contains this code to interface between LabView 2010 DLL reference function and PICAM set up to control a PIXIS BR400 on a windows 7 64bit system with LabView 2010 64 bit. Note that some care must be taken in how pointers and datatypes are handled in labview. For more details on this check out the labview code on the group drive code repository for the SPS. Also, be careful copy-pasting from this document as MS word will auto-wrap text. Unfortunately, I was rather in a hurry when I wrote this so the code isnt very well commented, but it is rather self-explanatory if you
know some C++. This was compiled using the minigw implementation of 64bit gcc
g++ open source C++ compiler.
//get_set_temp.h
//header file for PICAM-Labview API wrapper to define functions in DLL
//Author - Thomas Kent (The Ohio State University)
//R4 11/21/13
#ifndef GET_SET_TEMP_H
#define GET_SET_TEMP_H
#if defined __cplusplus
extern "C"
{
#endif
#if defined _DBUILDING_GET_SET_TEMP_H
#define GET_SET_TEMP __declspec(dllexport)
#else
#define GET_SET_TEMP __declspec(dllimport)
#endif

float __stdcall GET_SET_TEMP get_CCD_temp(PicamHandle camera);
int __stdcall GET_SET_TEMP read_temp_status(PicamHandle camera);
char* __stdcall GET_SET_TEMP get_cam_serial(PicamHandle camera);
char* __stdcall GET_SET_TEMP get_cam_type(PicamHandle camera);

void __stdcall GET_SET_TEMP set_ccd_temp(PicamHandle camera, piflt setpoint);

int __stdcall GET_SET_TEMP get_pixel_count(PicamHandle camera);
int __stdcall GET_SET_TEMP get_acquire_array_elem(PicamHandle camera, void* available, int element, int readout);

int* __stdcall GET_SET_TEMP get_acquire_array(PicamHandle camera, void* available, int rnumber);

void __stdcall GET_SET_TEMP expose_one_frame(PicamHandle camera, void* &out);

void __stdcall GET_SET_TEMP set_exposure_time(PicamHandle camera, int time);

#endif //GET_SET_TEMP_H

//get_set_temp.cpp
//PICAM-Labview API wrapper DLL
//Author - Thomas Kent (The Ohio State University)
//Some sample code adapted from PICAM coding example
//R4 11/21/13
//
//Requires princeton instruments PICAM API to be installed on the computer which this code is compiled on.
//
//complier commands with g++:
g++ -c -DBUILDING_GET_SET_TEMP_H get_set_temp.cpp
g++ -shared -o get_set_temp.dll get_set_temp.o "c:\Program Files\Princeton Instruments\Picam\Runtime\picam.dll" -Wl,--out-implib, getserial_dll.a
g++ acquire2.cpp get_set_temp.dll "c:\Program Files\Princeton Instruments\Picam\Runtime\picam.dll" -o acquire2.exe
//
//sorry there are no comments to the code. I wanted data when I wrote this, clearly.

#include "stdio.h"
#include "picam.h"
#include "get_set_temp.h"
#include <string.h>
#include <iostream>
#include <string>
#include <stdlib.h>

// - prints any picam enum
void PrintEnumString( PicamEnumeratedType type, piint value )
{
    const pichar* string;
    Picam_GetEnumerationString( type, value, &string );
    std::cout << string;
    Picam_DestroyString( string );
}

__stdcall float get_CCD_temp(PicamHandle camera) //get current ccd temperature
{
    // read camera temperature
    PicamCameraID id;
    PicamAcquisitionErrorsMask errors;

    piint readoutstride = 0;

    Picam_GetCameraID( camera, &id );

    piflt temperature;
    Picam_ReadParameterFloatingPointValue(
        camera,
        PicamParameter_SensorTemperatureReading,
        &temperature );
    // printf("SN%s",id.serial_number);
    return temperature;
}

__stdcall int read_temp_status(PicamHandle camera) //read temperature status (e.g. locked/ unlocked)
{
// - return temperature status of camera
// value 2 is locked value 1 is unlocked.
PicamCameraID id;
int isstable;
PicamAcquisitionErrorsMask errors;
PicamSensorTemperatureStatus status;
uint readoutstride = 0;
Picam_GetCameraID( camera, &id);

    Picam_ReadParameterIntegerValue(
        camera,
        PicamParameter_SensorTemperatureStatus,
        reinterpret_cast<
            uint*>( &status ));

std::cout << "    Status is ";
PrintEnumString( PicamEnumeratedType_SensorTemperatureStatus,
    status );
std::cout << std::endl;
// printf("SN%s",id.serial_number);

// transform value into a status byte e.g. 1 or zero.
if (status == 2){
    isstable =1;
} else {
    isstable = 0;
} 
return isstable;
}
__stdcall char* get_cam_serial(PicamHandle camera) //get open camera serial number string
{
    PicamCameraID id;
    Picam_GetCameraID( camera, &id);
    pchar camID [50];
    int n = sprintf(camID, "%s",id.serial_number);
    printf("%s\n",camID);
    return camID;
}
__stdcall char* get_cam_type(PicamHandle camera) //get open camera type string
{
    PicamCameraID id;
    const pchar* string;
    Picam_GetCameraID( camera, &id);
    Picam_GetEnumerationString( PicamEnumeratedType_Model, id.model, &string );
    pchar camID [50];
    int n = sprintf(camID, "%s",string);
    printf("%s\n",camID);
    return camID;
}

__stdcall void set_ccd_temp(PicamHandle camera,piflt setpoint) //set CCD temperature setpoint
PicamCameraID id;
printf("setpoint=%f\n",setpoint);
Picam_GetCameraID( camera, &id);
Picam_SetParameterFloatingPointValue( camera,
    PicamParameter_SensorTemperatureSetPoint,setpoint);
//commit changes to hardware setting
const PicamParameter* failed_parameters;
piint failed_parameters_count;
Picam_CommitParameters( camera,
    &failed_parameters,
    &failed_parameters_count);
}

__stdcall int get_pixel_count(PicamHandle camera)
{
    piint bit_depth;
    Picam_GetParameterIntegerValue( camera,
        PicamParameter_PixelBitDepth,
        &bit_depth );

    piint frame_size;
    Picam_GetParameterIntegerValue( camera,
        PicamParameter_FrameSize,
        &frame_size );
    return frame_size/ sizeof( pi16u );
}

__stdcall int get_acquire_array_elem(PicamHandle camera, void* available, int element, int rnumber)
{
    PicamError error;
    printf("got to here\n");
    piint readout_stride;
    Picam_GetParameterIntegerValue( camera,
        PicamParameter_ReadoutStride,
        &readout_stride );

    piint frame_size;
    Picam_GetParameterIntegerValue( camera,
        PicamParameter_FrameSize,
        &frame_size );

    const piint pixel_count = frame_size / sizeof( pi16u );
    const pi16u* pixel = reinterpret_cast<const pi16u*>(
        static_cast<const pibyte*>(available) +
        rnumber*readout_stride );

    int intensity = *(pixel+element);
    // printf("got to here\n");
    // printf("intensity=%i\n",intensity);
    // printf("got to here\n");
}
__stdcall int* get_acquire_array(PicamHandle camera, void* available, int rnumber)
{
    PicamError error;
    printf("got to here\n");
    piint readout_stride;
    Picam_GetParameterIntegerValue(
        camera,
        PicamParameter_ReadoutStride,
        &readout_stride);

    piint frame_size;
    Picam_GetParameterIntegerValue(
        camera,
        PicamParameter_FrameSize,
        &frame_size);

    const piint pixel_count = frame_size / sizeof(pi16u);
    const pi16u* pixel = reinterpret_cast<const pi16u*>(static_cast<const pibyte*>(available) + rnumber*readout_stride);

    // printf("got to here\n");
    // printf("intensity=%i\n",intensity);
    // printf("got to here\n");
    // Picam_StopAcquisition(camera);

    int* array = (int*) malloc(pixel_count * sizeof(int));
    for (int i = 0; i < pixel_count; i++)
    {
        array[i] = *(pixel+i);
    }

    return array;
}

__stdcall void expose_one_frame(PicamHandle camera, void* &out)
{
    PicamError error;
    PicamAvailableData available;

    const pi64s readout_count = 1;
    const piint readout_time_out = -1; // infinite
;
    PicamAcquisitionErrorsMask errors;
    PicamAvailableData available;

    error =
        Picam_Acquire(
            camera,
            readout_count,
            readout_time_out,
            &data,
            &errors);
//data = available;
out = data.initial_readout;
}
__stdcall void set_exposure_time(PicamHandle camera, int time)
{
    PicamError error;
    // - set exposure time (in milliseconds)
    std::cout << "Set 500 ms exposure time: ";
    error =
        Picam_SetParameterFloatingPointValue(
            camera,
            PicamParameter_ExposureTime,
            time);

    // - commit
    std::cout << "Commit to hardware: ";
    const PicamParameter* failed_parameters;
    puint failed_parameters_count;
    error =
        Picam_CommitParameters(
            camera,
            &failed_parameters,
            &failed_parameters_count);
        Picam_DestroyParameters( failed_parameters );
}

//__stdcall void post_exposure_cleanup(void* available, int* array)
//{
//    free(available);
//    free(array);
//}
__stdcall void post_exposure_cleanup(int* array)
{
    free(array);
}
Appendix F: MATLAB Code for QD SQUID data processing

This section is to function as a permanent record for a MATLAB script that was written by the author to process and calibrate data from a Quantum Design SQUID magnetometer. It is specifically written to calibrate the output magnitude (emu) into Bohr Magneton per formula units. The code expects two datafiles, a hysteresis scan (MvsH) for low and high temperature. The diamagnetic background is corrected by fitting a line to the high temperature data and then all data is corrected for this. Depending on the input flags, the code will normalize the data, write ASCII output files, etc. note that to plot, it requires the subroutine ERRORBAR,TICK available online through the Mathworks. This code is widely used in our group to rapidly process data from the instruments, an otherwise tedious task. The script will also process and background correct temperature dependent (MvsT) scans, if the input flag and target files are changed. Note that the directory plots must be created in the folder where this code is run before being able to write output files.
clear all
close all

%INPUT PARAMETERS

%INPUT OPTIONS
variabletemp = 0; %variable temp data (1) or normal mag vs. field (0)?
saveplots = 0; %save plots (1)?
normalizedata = 0; %normalize data to mu_B/Gd^{3+} (1) or leave in emu (0)?
seperatebgfile = 1; %use separate bg file (1) or just high field points (0)
ploterror = 1; %plot errorbars (1) or just data (0)?
writeoutputfile = 1; %write output file for data processed to plots folder (1) or not? (0)
isbulkdoped = 1;
datatype = 'multimeasure'; %options are 'scandc' or 'multimeasure' use scandc with *.dc.dat files
%and multimeasure with *.dc.ndat files (all data collected after 7/20/11 utilizes
%the multimeasure format)

%INPUT SAMPLE DATA
lotnumber = '130319A';
samplearea = .380*.539; %units of cm^2
gd_Areal_density = 2.3E14; %units of N_dopant/cm^2
gd_volume_density = 3.9749E22; %units of N_Gd/cm^3
layerthickness = 34.4160/2; %in nm
sampledesc = '25x [2.4ML GdN/10nm GaN] Superlattice IP';
datafolderpath = 'F:\Group\Sample Characterization Data\SQUID\130319A';
datafilename = '130319A_IP_hyst5T_5K_rev2.rso.ndat';
bgfilename = '130319A_IP_hyst5T_300K_rev2.rso.ndat';
plotoutputfolder = 'F:\Group\Sample Characterization Data\SQUID\130319A\plots';
% definition of constants
emu2muB = 9.274E-21;
layersThickness = layersThickness*(1E-7);

% read data files, write data to arrays
% Open datafile for reading
datafid = fopen(strcat(datafolderpath,'\',datafilename),'r'); % file identifiers
bgfid = fopen(strcat(datafolderpath,'\',bgfilename),'r');

% read entire file, input into cell structure
rawdata = textscan(datafid,'%s
','Delimiter','');
rawbg = textscan(bgfid,'%s
','Delimiter','');
data_headers = textscan(rawdata{1,1}(24,1),'%s','Delimiter',''); % get the header file info (unused)

% convert data from cell arrays to arrays
switch datatype 
 case 'scandc' 
 j=1;
 for i=25:length(rawdata{1,1}) %convert data from cell arrays to arrays
 sampledata(j) = textscan(rawdata{1,1}{i,1},'\s','Delimiter',''); 
 if i<= length(rawdata{1,1}) 
 bgdata(j) = textscan(rawbg{1,1}{i,1},'\s','Delimiter',''); 
 end 
 j=j+1; 
 end 
 case 'multimeasure'
 j=1;
 for i=21:length(rawdata{1,1}) %convert data from cell arrays to arrays
 rawdata{1,1}{i,1} = regexp prep(rawdata{1,1}{i,1},'\.*\s\s','
');
 sampledata(j) = textscan(rawdata{1,1}{i,1},'\s','Delimiter','
'); 
 if i<= length(rawbg{1,1}) 
 rawbg{1,1}{i,1} = regexp prep(rawbg{1,1}{i,1},'\.*\s\s','
');
 bgdata(j) = textscan(rawbg{1,1}{i,1},'\s','Delimiter','
'); 
 end 
 j=j+1; 
 end 
 end 
 if normalizedata == 1 
 datafilename = [datafilename,'NORM']; %rename the datafile to reflect units 
 end 

% create individual variables for data
samplefield = zeros(1,length(sampledata));
samplelongmoment = zeros(1,length(sampledata));
samplelongstdev = zeros(1,length(sampledata));
sampletemperature = zeros(1,length(sampledata));

switch datatype 
 case 'scandc'
 for i=1:length(sampledata)
 samplefield(i) = str2double(sampledata{1,i}{3,1});
 samplelongmoment(i) = str2double(sampledata{1,i}{5,1});

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samplelongstdev(i) = str2double(sampledata{1,i}{6,1});
sampletemperature(i) = str2double(sampledata{1,i}{4,1});
end

for i=1:length(sampledata) %convert emu to Bohr magneton/Gd atom
    samplemagdata(i) = samplelongmoment(i)/
        (samplelongstdev(i));
end

for i=1:length(sampledata) %convert emu to Bohr magneton/Gd atom
    samplefield(i) = str2double(sampledata{1,i}{3,1});
    samplelongmoment(i) = str2double(sampledata{1,i}{5,1});
    samplelongstdev(i) = str2double(sampledata{1,i}{7,1});
    sampletemperature(i) = str2double(sampledata{1,i}{4,1});
end

bgfield = zeros(1,length(bgdata));
blongmoment = zeros(1,length(bgdata));
blongstdev = zeros(1,length(bgdata));
bgtemperature = zeros(1,length(bgdata));

% create individual variables for background
switch datatype
    case 'scandc'
        bgfield(i) = str2double(bgdata{1,i}{3,1});
        blongmoment(i) = str2double(bgdata{1,i}{5,1});
        blongstdev(i) = str2double(bgdata{1,i}{6,1});
        bgtemperature(i) = str2double(bgdata{1,i}{4,1});
    end
end

% convert long moment data to magnetization data
samplemagdata = zeros(1,length(sampledata));
samplemagstdev = zeros(1,length(sampledata));

if normalizedata == 1
    switch isbulkdoped
        case 0 % 2D doped
            for i=1:length(sampledata) % convert emu to Bohr magneton/Gd atom
                samplemagdata(i) = samplelongmoment(i)/
                    (gd_areal_density*samplearea*emu2muB);
                samplemagstdev(i) = samplelongstdev(i)/
                    (gd_areal_density*samplearea*emu2muB);
            end
        case 1 % 3D doped
            for i=1:length(sampledata) % convert emu to Bohr magneton/Gd atom
                samplemagdata(i) = samplelongmoment(i)/
                    (gd_areal_density*samplearea*emu2muB);
            end
        end
    end
end

for i=1:length(bgdata) % convert emu to Bohr magneton/Gd atom for background
    bgmagdata(i) = blongmoment(i)/(gd_areal_density*samplearea*emu2muB);
    bgmagstdev(i) = blongstdev(i)/(gd_areal_density*samplearea*emu2muB);
end
(gd_volume_density*samplearea*layerthickness*emu2muB);

samplemagstdev(i) = samplelongstdev(i)/
(gd_volume_density*samplearea*layerthickness*emu2muB);
end

bgmagdata = zeros(1,length(bgdata));
bmgstdev  = zeros(1,length(bgdata));

for i=1:length(bgdata)  %convert emu to Bohr magneton/Gd atom for background
    bgmagdata(i) = bglongmoment(i)/
(gd_volume_density*samplearea*layerthickness*emu2muB);
bmgstdev(i) = bglongstdev(i)/
(gd_volume_density*samplearea*layerthickness*emu2muB);
end
else  %if we dont convert, just rename variables
    samplemagdata = samplelongmoment;
samplemagstdev = samplelongstdev;
bmgdata = bglongmoment;
bmgstdev = bglongstdev;
end

%perform linear regression on background data to determine diamagnetic correction factor
%if separatebgfile == 1
[cfun,gof] = fit(bgfield',bgmagdata','poly1'); %fit line to background file
elseif separatebgfile == 0  %no separate background file, just use high field points
%select out only field points above +/-1T to include in linear regression
j=1;
for i=1:length(bgfield)
    if bgfield(i) > 3E4
        bghighfield(j) = bgfield(i);
bghighmagdata(j) = bgmagdata(i);
j=j+1;
    end
end
[cfun,gof] = fit(bghighfield',bghighmagdata','poly1');
end

%perform background correction
bgcorrectedmag = zeros(1,length(sampledata));

for i=1:length(sampledata)
    bgcorrectedmag(i) = samplemagdata(i) - (cfun(samplefield(i)) - cfun(0));
end
if variabletemp==0  %regular mag vs. B data
%plot figures
aa=figure;
if(ploterror==1)
aa=errorbar(bgfield,bgmagdata,bgmagstdev,'x','MarkerSize',5);
end
hold on

end

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plot(cfun)
title({strcat('Diamagnetic Background at T=',num2str(mean(bgtemperature),'%3.0f'), 'K for Sample ',lotnumber);strcat(sampledesc,');
R^2 = ',num2str(gof.rsquare))},'fontsize',13)
xlabel('Field (Oe)')
if normalizedata == 1
ylabel('$\mathbf{M}\left(\frac{\mu_{\mathrm{B}}}{\mathrm{Gd}^{3+}}\right)$','interpreter','latex','fontsize',14)
else
ylabel('Long Moment (emu)')
end
grid on
if saveplots == 1
saveas(a,strcat(plotoutputfolder,'\',datafilename,'_diagbgplot.bmp'))
end
b=figure;
hold on
if(ploterror==1)
bb = errorbar(samplefield,bgcorrectedmag,samplemagstdev,'xr','MarkerSize',5);
end
plot(samplefield,bgcorrectedmag,'-b')
plot(samplefield,bgcorrectedlongmoment)
title({strcat('Background Subtracted Field Data for Sample ',lotnumber);
strcat(sampledesc,'); T=',num2str(mean(sampletemperature),'%3.0f'), 'K\'],$_3^+\}'},'fontsize',14)
xlabel('Field (Oe)','fontsize',14)
if normalizedata==1
ylabel('$\mathbf{M}\left(\frac{\mu_{\mathrm{B}}}{\mathrm{Gd}^{3+}}\right)$','interpreter','latex','fontsize',14)
else
ylabel('Long Moment (emu)')
end
grid on
if(ploterror==1)
errorbar_tick(bb,25,'UNITS')
end
axis([min(samplefield) max(samplefield) min(bgmagdata) max(bgmagdata)])
hold off
if saveplots == 1
saveas(b,strcat(plotoutputfolder,'\',datafilename,'_bgsubfieldplot.bmp'))
end
c=figure;
hold on
if(ploterror==1)
cc=errorbar(samplefield,bgcorrectedmag,samplemagstdev,'xr','MarkerSize',5);
end
plot(samplefield,bgcorrectedmag,'-b')
plot(samplefield,bgcorrectedlongmoment)
title({strcat('Background Subtracted Field Data for Sample ',lotnumber);
strcat(sampledesc,'); T=',num2str(mean(sampletemperature),'%3.0f'), 'K Low Field Region\}','fontsize',13)
xlabel('Field (Oe)','fontsize',14)
if normalizedata==1
ylabel('$\mathbf{M}\left(\frac{\mu_{\mathrm{B}}}{\mathrm{Gd}^{3+}}\right)$','interpreter','latex','fontsize',14)
else
    ylabel('Long Moment (emu)')
end
grid on
if(ploterror==1)
    errorbar_tick(cc,25,'UNITS')
end
axis([-2000 2000 min(bgcorrectedmag) max(bgcorrectedmag)])
hold off
if saveplots == 1
    saveas(c,strcat(plotoutputfolder,'\',datafilename,'_bgsubfieldplot ROI.bmp'))
end
elseif variabletemp == 1
d = figure;
hold on
if(ploterror==1)
    %dd = errorbar
end
plot(sampletemperature,bgcorrectedmag,'-b')
title(strcat('Variable Temperature Scan Sample ',lotnumber); strcat(sampledesc),'fontsize',13)
xlabel('Temperature (K)','fontsize',14)
if(ploterror==1)
    errorbar_tick(dd,5,'UNITS')
end
if normalizedata == 1
    ylabel('\(\mathbf{M} (\frac{\mu_B}{Gd^{3+}})\)')
    elseif\
    else
        ylabel('Long Moment (emu)')
end
grid on
if(saveplots==1)
    saveas(d,strcat(plotoutputfolder,'\',datafilename,'_vartempplot.bmp'))
end
end

%write ASCII output file to plots folder (if requested)
if (writeoutputfile)
    outfile = fopen(strcat(plotoutputfolder,'\',datafilename,' _ASCII_DATA.dat'),'w+');
    fprintf(outfile,'%s\n',strcat('# Sample ','lotnumber','_','sampledesc'));
    if (variabletemp)
        if (normalizedata)
            fprintf(outfile,'%s\n','#Temperature (K) Magnetization (\mu_B / Gd^{3+}) Std. Dev. in Magnetization (\mu_B / Gd^{3+})');
        else
            fprintf(outfile,'%s\n','#Temperature (K) Magnetization (emu) Std. Dev. in Magnetization (emu)');
        end
    for i = 1:length(samplemagdata)
fprintf(outfile,'   %3.2f        %1.8e
',sampletemperature(i),bgcorrectedmag(i),samplemagstdev(i));
end
else
    if (normalizedata)
        fprintf(outfile,'%s
',
            '#Field (Oe)   Magnetization (\mu_B / Gd^{3+})   Std. Dev. in Magnetization (\mu_B / Gd^{3+})');
    else
        fprintf(outfile,'%s
',
            '#Field (Oe)   Magnetization (emu)   Std. Dev. in Magnetization (emu)');
    end
    for i = 1:length(bgcorrectedmag)
        fprintf(outfile,'   %5.0f        %1.8e
',samplefield(i),bgcorrectedmag(i),samplemagstdev(i));
    end
end
end
fclose('all');