DEVELOPMENT OF GALLIUM NITRIDE BASED DILUTE MAGNETIC SEMICONDUCTORS FOR MAGNETO-OPTICAL APPLICATIONS

By

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This dissertation is dedicated to my family and friends.
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The growth of gallium nitride doped dilute magnetic semiconducting films was studied for use in magneto-optical applications. The specific area of intended use was room temperature ferromagnetic layers for a spintronic device, (the spin polarized light emitting diode). The requirement for these layers is the ability to dope the host gallium nitride film with manganese, while still maintaining good crystallinity and semiconducting properties with the addition of room-temperature ferromagnetic properties. Codoping of the gallium manganese nitride films with oxygen was also investigated.

These materials were fabricated using the molecular beam epitaxy technique, whereby beams of the constituent elements are produced in an ultra high vacuum environment. Molecular beam epitaxy permits a wide range of growth parameters, to best allow for optimization of the prepared layers. The materials were deposited on sapphire and MOCVD gallium nitride substrates, with particular emphasis on the
correlation between the growth conditions and the final magnetic, chemical, and structural properties.

Results with GaMnN layers indicate that the growth conditions were very influential on the properties of the films. Magnetic measurements indicate that the best combination of properties were achieved for GaMnN films grown at a temperature of 700°C, containing three atomic percent manganese, and prepared on a commercially available MOCVD GaN substrate. A prototype spintronic device, (the spin polarized light emitting diode) was prepared. Unfortunately, no spin polarized emission was detected from the LED. The lack of polarization was traced to a high spin relaxation rate in the InGaN LED quantum wells.
CHAPTER 1
INTRODUCTION

Advances in the semiconductor and magnetic storage industries have jointly driven the information and technology age that we are currently enjoying. From ever more powerful laptop computers, to personal data assistants, to memory sticks capable of storing Gigabytes of data on something the size of a keychain, these industries have become billion-dollar enterprises. In an attempt to join these two areas, semiconductor spintronics as a research area is producing results that could only have been dreamed of 20 years ago. The next sections present some of the history and mechanisms behind the device applications that have driven these industries and present some of the motivation for our study.

Magnetic Devices

Data storage has become an area that has had a tremendous impact on the way information is manipulated and shared between users. One of the first examples of a device that would have a significant impact on the way people share information was introduced at the Paris International Exhibition of 1900 by the Danish inventor Valdemar Poulsen. The invention was the predecessor to our modern day telephone answering machine and was dubbed the Telegraphone by its inventor [1]. The device recorded electrical signals on a steel wire and was based on work done by an American mechanical engineer named Oberlin Smith who filed a patent caveat for the device in 1878 but did not pursue it to completion himself.
The following 100 years have seen tremendous advancements in the ability for people to store and handle information. Data storage has become a multibillion dollar industry with a significant impact on the world’s economy. These advancements have been achieved by reducing the size and power required for the storage of a particular size of data. Figure 1-2 shows the significant increases that have been made in aereal densities of magnetic memory in the past 40 years [2].

Since the 1980s, and the introduction of devices based on the giant magnetoresistance effect (GMR), the size of the individual storage units have shrunk even smaller, resulting in the high capacity disk drives now used in personal computers and laptops. The GMR effect has also been harnessed to create magnetic random access memory (MRAM), a non-volatile memory which is a forerunner to having instant on computers and memory that would retain its state even when the power to the unit is turned off. These devices usually consist of layers of ferromagnetic metals separated by insulating layers.

These magnetic devices operate by manipulating the spin of the electron. The electron spin exists in either one of two states: “spin up” or “spin down.” By manipulating the electron spins, these up and down states can be thought of as ones and zeroes, creating a binary code that can be used for data storage. There are two main requirements here: one is the ability to write data to a storage unit, and the second is the ability to read this data back at a later time. As device sizes continue to shrink, new materials and configurations will be needed to overcome the technological hurdles that these devices present.
Optoelectronic and Electronic Devices

The semiconductor industry has also become a multibillion dollar industry. There is some form of chip in almost every household device, from the refrigerator to the toys children use to entertain themselves. The electronic revolution began with the demonstration of the first solid-state transistor at Bell Laboratories, in New Jersey, in December, 1947 [3]. The invention of the solid-state transistor allowed the bulky vacuum tubes that were being used to be replaced with smaller, more energy-efficient devices. The integrated circuit took these advances to another level, allowing for millions of transistors to be produced on a chip the size of a quarter. The chips being produced by Intel for use in home computers currently have over 42 million transistors, allowing for the rapid processing of data by the user. While the transistor was being optimized and shrunk to even smaller dimensions, other scientists were working with semiconductors for a different purpose: generating light. In the early 1960s, several groups produced the first light emitting diode (LED) using Gallium Arsenide [4, 5]. The initial devices produced light that was invisible to the human eye, but soon became integrated into sensing and photoelectric applications using infra-red light that was produced by the diodes. Much like the development of the transistor, the LED advanced rapidly over the following years, with a visible LED being produced by the end of the 1960s. Today, LEDs are commercially available in the whole spectrum of visible colors, and have begun to be used in a wide range of applications. In the near future, the LED will become the lighting product of choice and lead to the phasing out of the traditional incandescent and fluorescent bulbs with which we are all so familiar. Reasons for this are two-fold but both are economically driven. First, the LED uses much less power than the traditional bulb to produce a similar amount of light; also, it generates much less heat
reducing cooling costs. Secondly the lifetime of the LED is much longer than that of traditional bulbs, further reducing costs by eliminating the need to be constantly replacing bulbs.

Both the electronic and optoelectronic devices that are used throughout the world today are based on the manipulation and movement of electrons. Whereas in the magnetic arena the spin of the electron was the property that was manipulated, here the charge of the electron is utilized to operate the various devices. In the transistor, charges are moved and manipulated to produce gain, and to turn logic circuits “on” and “off.” The LED produces light through the recombination of holes and electrons, with the emitted light being characteristic of the material’s energy band gap.

**Dilute Magnetic Semiconductors**

In an effort to combine the benefits of the magnetic, electronic, and optoelectronic areas, a new class of material has recently been demonstrated. Dilute magnetic semiconductors (DMSs) are projected to be the basis for devices that rely on the manipulation of both the charge and spin of electrons moving in a semiconductor host. DMSs are semiconductors that have been doped with magnetic ions. The magnetic dopants provide spin magnetic moments associated with their electron spins. Several novel device structures have been proposed that could take advantage of the magnetic properties of these materials. Some of these devices include the Spin-LED, spin transistor, magnetic sensors, biodetectors, and optical isolators. Additionally, DMS materials could lead to the integration of communications, memory, and calculation capabilities on a single chip. Other benefits of DMS-based devices include reduced power requirements compared to traditional semiconductor devices. This energy gain is due to the reduced power needed to flip an electron spin, as opposed to moving a charge
in an electric field. However, before these devices can be realized, it will be necessary to determine if the injection, transport, and detection of the carrier spins can be successfully carried out at meaningful temperatures [6-15].

One major incentive for finding a DMS material that can operate at meaningful temperatures (i.e., above room temperature), is that one could then integrate the new technology with the existing semiconductor industry. Recent theoretical work by T. Dietl et al. [16] generated interest in the possibility of achieving room-temperature ferromagnetism in a DMS that is based on GaN, using Mn as the transition metal dopant. Dietl’s model, (discussed in more detail later) has been shown to accurately model the Curie temperature of GaMnAs and InMnAs. Unfortunately, both of these materials have Tc’s well below room temperature. Results of both the theory and the experimental work on these III-Mn-As materials, however, holds promise for the III-Mn-N materials, as potential materials for having Tc’s above room temperature.

**Research Motivation**

The motivation for our study was to build on these theoretical predictions, and investigate the effect of doping GaN with transition metals, to achieve a material that can then be incorporated into the existing Nitride technology base. A DMS based on GaN would have potential to capitalize on many of the advantages that currently make GaN technology one of the leaders in the semiconductor industry. Some of these advantages include a high breakdown field, good thermal conductivity and stability, good chemical and physical stability, and the ability to combine with InN and AlN to allow for bandgap engineering.

In our study, the doping of GaN with transition metals was investigated to determine the optimal concentrations of these metals for magneto-electronic and
magneto-optical applications. Special emphasis was placed on maximizing the magnetic moments associated with the films that were produced. By understanding the role of various parameters associated with the growth process, a deeper understanding of these novel materials was attained, and a prototype spintronic device (the Spin-LED) was designed.
CHAPTER 2
REVIEW OF DILUTE MAGNETIC SEMICONDUCTORS

There has been much interest in the area of dilute magnetic semiconductors, dating back to the 1960s. Much of the early research focused on the Europium chalcogenides and semiconductor spinels. Found to have both magnetic and semiconducting properties, these materials have not advanced beyond the research stage for several reasons. It was found that Europium chalcogenides and semiconductor spinels were very difficult to synthesize, requiring near-perfect conditions which were difficult to reproduce. A second factor limiting further development was the lack of a suitable conventional lattice-matched semiconductor (such as Silicon or Gallium Arsenide) to be used as a substrate. This prevented the development of heterostructures based on these materials. The ability to integrate a magnetic semiconductor with existing semiconductor technology is highly desirable from a practical applications viewpoint. A final liability of the Europium chalcogenides and semiconductor spinels is that the Curie temperature ($T_C$) is only just above 0 K, again very impractical from an applications standpoint [17]. From these frustrating beginnings, research into DMS materials has progressed and increasingly the technological hurdles posed by these early DMSs are being overcome. This chapter reviews the leading theoretical and experimental achievements in the DMS area with an emphasis on their application to the III-V based materials.

Theories of Dilute Magnetic Semiconductor Ferromagnetism

The current state of the theories regarding DMS materials can be broken into two main groups. The first group is based on a mean field theory approach. The DMS lattice
is assumed to be made up of a random alloy where the dopant atom substitutes regularly for one of the lattice constituents. Further variations on the mean field theory have also been investigated, taking into account the effects of positional disorder, indirect exchange interactions, spatial inhomogeneities and free-carrier spin polarization. The second group of theories attributes the magnetic behavior to the magnetic atoms forming small clusters in the lattice. It is still unclear as to which of these groups most accurately depicts the origins of the ferromagnetism, but as more experimental data become available we can hope for a clearer understanding of the mechanisms affecting the ferromagnetism.

Perhaps the most well known of the mean field theory models is that presented by T. Dietl and coworkers [18-23]. Dietl premised his theory on Zener’s model, which proposed that ferromagnetism was driven by the interaction between charge carriers and localized spins. While the Zener model was found to be inappropriate for transition metals, Dietl found that it could be used to explain ferromagnetism and Curie temperatures \( T_C \) in the dilute magnetic semiconductors, GaMnAs, InMnAs, and ZnMnTe. In the case of the III-Mn-As, the Mn atoms introduce both spins and holes to mediate the spin coupling leading to the ferromagnetism. The correlation between the charge carriers and the spin moments introduced by the magnetic atom provides a way to tailor the ferromagnetism associated with these materials. These calculations were then extended to consider many of the other available semiconductor systems, including the III-Nitrides. For these calculations, a Mn concentration of 2.5 atomic percent, and a hole concentration of \( 3.5 \times 10^{20}/\text{cm}^3 \) were used. These results are plotted versus band gap in figure 2-1. Of particular interest are the predicted \( T_C \)s for GaN and ZnO which are both
above room temperature. These predictions for GaN have led to a serious experimental effort (discussed later).

Another theoretical effort to understand these materials has been undertaken by R. N. Bhatt and coworkers [24-26]. They also use a mean field treatment, however they consider the influence of positional disorder on the system. One difference between their approach and that of Dietl’s is the use of the bound magnetic polaron (BMP). Here the carrier concentration of the material is much lower than that of the magnetic ion density. The BMPs form around randomly positioned magnetic atoms with the charge carriers forming a localized tight binding band. Using the BMP model leads to predictions of ferromagnetism in materials having much lower carrier concentrations than can be predicted by using the Dietl carrier-mediated model. The ability to have ferromagnetism in semiconductors near the metal-insulator transition has implications for the III-Nitride based DMSs, as it is extremely difficult to dope p-type GaN to the $10^{20}$ hole concentrations required by the carrier mediated model. Both of these models agree that as the concentration of Mn atoms increases, there will be a decrease in the ferromagnetism due to an increase in the anti-ferromagnetic interactions that occur in Mn, (which in bulk form is an anti-ferromagnetic material). Bhatt and coworkers [24-26] are not the only groups to use this approach, similar results have been found for calculations using BMPs by Litvinov and Dugaev, Bhattacharjee and Guillaume, and Das Sarma and coworkers [27-30].

The second group of theories on the cause of the ferromagnetism observed in DMS materials attributes the magnetism to the presence of a strong short-range-attraction which leads to formation of small clusters of Mn atoms. These models predict that
clusters of Mn as small as 3-5 atoms have magnetic moments as large as 4-5 $\mu_B$ per atom and exhibit ferromagnetism [31-34]. Even in these clusters, there is a competition between the antiferromagnetic and ferromagnetic states, with the clusters showing evidence of both states in the same cluster. Also, as the cluster sizes are increased to include larger numbers (13-23 atoms) of Mn, it was found that the models predict that the magnetic moment will decrease with increasing numbers of Mn atoms. These clusters were predicted to increase in size with decreasing growth temperatures.

There have been other theoretical predictions made using other computational techniques to explore good candidates for DMS materials. One of these approaches uses a psuedopotential density functional calculation to analyze the expected electronic structure of several DMS materials, including GaMnAs and GaMnN. These calculations suggest that both GaMnAs and GaMnN should have band structures amenable to spin transport, a major criteria for a practical DMS. For GaMnN, the electronic structure calculations predict that a 1.5 eV wide impurity band is formed due to the hybridization of the Mn 3d and N 2p orbitals. The effect of the impurity band is to cause GaMnN to be half-metallic, this feature suggests GaMnN as an ideal candidate for spin injection [35-36].

The effect of codoping on the ferromagnetic properties has also been considered. The electronic structures of GaMnAs and GaMnN were calculated using a tight-binding-linear-muffin-tin-orbital method. This model considered the case of GaMnN codoped with either zinc or oxygen, and what effect these elements would have on the band structure and the magnetic properties. Zinc (substituting for Ga) was not predicted to
have an impact on the $T_C$ or magnetization of GaMnN. Codoping with oxygen, however, was predicted to significantly enhance both the moment and the $T_C$ of GaMnN [37].

While most of the theoretical efforts have focused on Mn as the transition metal dopant, some theoretical predictions were made considering other potential dopants. One study used ab initio calculations. The Local Spin Density Approximation was used to examine the ferromagnetic stability of GaN based DMS, which have been doped using a variety of transition metals (V, Cr, Mn, Fe, Co, and Ni). These results suggest that the ferromagnetic state will be stable over the spin glass state for V and Cr at all concentrations, and for Mn up to a concentration of 15%. It also predicts that in Fe, Co, and Ni the spin glass state dominates and is the stable state for all concentrations. Results of this work suggest that ferromagnetic ground states should be readily achievable without additional carrier doping in GaN based DMSs using Mn, V, or Cr. Figure 2-2 shows the predicted stabilities of these different 3d transition metal atoms [38].

**Review of Mn Doping in Semiconductor Host Materials**

The potential for a material to possess both ferromagnetic and semiconducting properties has been known and studied since the 1960s. In this section, a brief summary of this work is given here, along with a discussion of present day efforts to examine the role of transition metals (TMs) in semiconductors. Much of this focus has been on the III-As based DMS systems which have been studied continuously since their first synthesis in the 1980s.

The Europium chalcogenides and semiconductor spinels were investigated in the 1960s and 1970s. They were found to have both magnetic and semiconducting properties. These materials have not advanced beyond the research stage for several
reasons as mentioned earlier. They did however provide the starting impetus towards more practical materials.

Working toward a more practical DMS led researchers to begin examining II-VI semiconductors, and using Mn as a substitutional ion on the group II lattice site. This made preparation of samples much easier, as Mn has the same valence as the element it is replacing. The drawback for these materials is that despite the ease of doping with Mn to high levels, it is very difficult to dope the material n- or p-type. Additionally, the II-Mn-VI films tended to show antiferromagnetic, paramagnetic, or spin-glass behavior. The few films produced showing ferromagnetic ordering had a $T_C$ of just above 0 K.

A major breakthrough in this area was achieved with the successful preparation of InMnAs films that showed ferromagnetic ordering to ~35 K. The discovery of ferromagnetism in an III-As based material opened the possibility for integration of this material with established semiconductor applications, since devices and heterostructures based on the III-As are used in a variety of high-speed electronics and optoelectronics systems. The success of InMnAs however, has been tempered by the fact that despite efforts to raise it, the $T_C$ is still relatively low [39].

Successful preparation of ferromagnetic InMnAs films by low temperature molecular beam epitaxy (LT-MBE) ($T_{growth}<300°C$) led to efforts to explore the potential of GaAs based DMSs. As with InMnAs, LTMBE is used for the growth of GaMnAs. Low growth temperatures are needed to allow for the incorporation of the high levels of Mn (~5 atomic percent) that are necessary for obtaining ferromagnetic material. It was found that if the Mn flux and/or the substrate temperature were too high, an undesirable second phase of MnAs (having the NiAs crystal structure) forms. This
second phase is evidenced in both the in-situ RHEED patterns and in x-ray diffraction measurements. It was also found that for samples with Mn concentrations above 7 atomic percent, that segregation of Mn became a significant problem, even at low growth temperatures. Using optimized growth conditions, it was found that ferromagnetic GaMnAs films could be grown reproducibly. Unfortunately, like InMnAs, GaMnAs is limited by its Curie temperature (which is well below room temperature with the highest reported to be $\sim 180K$) [40-42].

The search for a DMS with a practical ferromagnetic ordering temperature has continued with the study of GaMnP. While the Dietl theory predicts a $T_C$ of only 100 K, GaMnP is an attractive system because it can be lattice-matched with silicon. Contrary to theoretical calculations, the $T_C$ is much higher than predicted, with a value of $\sim 300$ K. These films were produced epitaxially by MBE and by ion implantation into epi-GaP. For both the epitaxially produced and implanted films, the $T_c$ was much higher than predicted by the Dietl theory. As with the Arsenide based DMSs, the presence of second phases and segregation of Mn were major obstacles that needed to be overcome. Results with the GaMnP system are encouraging, because films were produced by two different methods showing comparable results, and because the ordering temperature is at (or just below) room temperature, making it more likely for a practical application to be developed [43].

Recent theoretical predictions by Dietl (above) that a p-type GaMnN sample with 2.5 atomic percent Mn and a carrier concentration of $3.5 \times 10^{20} /cm^3$ will have a $T_C > 400$ K has led to a strong interest in this area. Some of the first GaMnN crystals produced were microcrystals grown by an ammonothermal technique which is carried out at 500°C
and 5 kBar. These samples consisted of microcrystalline grains, with a color of varying shades of pink, depending on the amount of Mn incorporated into the lattice. This technique incorporated up to ~ 0.2% Mn into the crystals. X-ray diffraction studies showed a second phase of Mn3N2 in the crystals. The samples show a combination of paramagnetic and ferromagnetic behavior at low temperature. From electron spin resonance measurements, it was determined that Mn is an ionized acceptor in these crystals with a spin of 5/2 [44-46]. Additional research has been performed with bulk GaMnN crystals which are synthesized by reacting Ga/Mn alloys or GaN/Mn mixtures with ammonia at temperatures between 1200 and 1250°C under normal pressure. Results obtained with these samples were similar to results obtained with the previously discussed crystals. Samples were found to be paramagnetic with an antiferromagnetic component attributed to the interaction of Mn ions. Their study concluded that with proper doping, GaMnN could show the ferromagnetism predicted by theory.

GaMnN has also been synthesized by high dose ion implantation into p-GaN films which were grown by metal organic chemical vapor deposition on sapphire substrates. The implantation process incorporated 0.1-5 atomic percent Mn into the GaN lattice. The samples were annealed post implant and examined using x-ray diffraction (XRD), transmission electron microscopy (TEM), and SQUID magnetometry. No evidence of second phases was found using either XRD or TEM. The samples with 3 atomic percent Mn or higher show ferromagnetic ordering up to ~250 K, which is below the predicted ordering temperature. However, this lower T_c may be due to defects introduced by the implantation process [47].
The first report of MBE grown GaMnN showed a $T_C$ of ~25 K. The material had a Mn concentration of ~7% and an n-type carrier concentration of $2.4 \times 10^{19}$/cm$^3$. The samples were produced using solid source Ga and Mn, with reactive nitrogen provided using a RF plasma source. No second phases were detected in this material which was grown at a substrate temperature of 865°C. This substrate temperature is notable in that it is in the normal growth regime for GaN. In contrast, GaMnAs and InMnAs must be synthesized at temperatures less than those traditionally used for GaAs and InAs. As described earlier, the lower temperatures are needed to avoid formation of second phases and segregation of Mn. Also the measured $T_C$ of 25 K is much higher than the predicted $T_C$ for n-GaMnN which was only a few degrees Kelvin. This result is promising because it suggests that holes may not be necessary to mediate ferromagnetic ordering in GaMnN [48].

**Spin Polarized Light Emitting Diodes**

The ultimate test of a DMS material is whether or not it can be used to inject spin polarized carriers. One of the most unambiguous ways to investigate the injection and transport of spin is through the spin polarized light emitting diode (Spin-LED). The spin-LED operates the same as a conventional LED, however the light emitted from the spin-LED is circularly polarized. The degree of polarization is a measure of the efficiency of the spin injection process.

The spin-LED uses a ferromagnetic material to align spin polarized carriers which are then injected into a semiconductor heterostructure. After the spin polarized carriers are injected, they radiatively recombine with unpolarized carriers of the opposite type in the heterostructure and circularly polarized light is emitted. The first reported spin-LED used a semimagnetic ZnMnSe layer as a contact to an III-V based LED structure. The
III-V structure consisted of a GaAs quantum well (QW) sandwiched by 2 AlGaAs barriers. When an appropriate bias was applied, spin polarized electrons were injected from the ZnMnSe layer through the AlGaAs barrier into the GaAs QW where the holes radiatively recombined with unpolarized electrons and emitted light. ZnMnSe is a paramagnetic material and must be placed in a magnetic field to align the spins before the spin injection occurs. Despite not being a true magnetic semiconductor, it provides evidence that spin injection is possible and that the spin-LED can be used to measure spin injection efficiency [49-50].

Additional studies at NRL have looked at the effect of damage to the semiconductor interface on spin injection. Here the GaAs/AlGaAs QW structure was grown in an ultra high vacuum MBE machine, then exposed to air for 6 months. The sample then had the paramagnetic ZnMnSe epilayer grown with no cleaning of the surface before being introduced into the growth chamber. LED structures were then fabricated and tested to determine the spin injection efficiency. The results found the spin injection efficiencies were very comparable to the spin-LEDs that were fabricated without air exposure. This suggests that the manufacture of practical spintronic devices using commercial semiconductor substrates should be practical without much additional treatment needed before regrowth [51].

A second group used a similar approach to the NRL group with BeMnZnSe as the spin aligner. Here again, a magnetic field needed to be applied to align the spins, which were then injected into a GaAs/AlGaAs structure. This device also injected spin polarized electrons, which are desirable over holes because electrons have a reduced spin-orbit coupling which allows for less spin decoherence. Much like the NRL device,
the BeMnZnSe device emitted circularly polarized light when operated in a magnetic field. Again, while providing proof of principle, this device is impractical because of the need for an external applied field and the need to operate at only a few tens of degrees Kelvin [52].

A DMS based spin-LED device has been developed using p-GaMnAs as the source of spin polarized carriers. The use of a DMS layer allowed for the device to operate without an applied magnetic field. Circularly polarized light was measured emitting from the device using an InGaAs QW structure as the site of radiative recombination. By varying the distance of the QW from the GaMnAs layer, the depth of spin injection and its efficiency can be measured using the degree of polarization of the emitted light. The device operated at temperatures ranging from 6-52 K and demonstrated that spin polarized carriers can be transported from a DMS into a conventional semiconductor. This result is very encouraging for the development of spin transport based devices. The next step will be to develop a DMS layer which can inject spins at room temperature [53].

Another alternative to the DMS based injection layer is to use either a ferromagnetic metal or semi-metal layer as the source of polarized carriers. For both cases, using either a layer of MBE deposited Fe or MnAs for the ferromagnetic injection layer, spin polarized LEDs were produced that emitted circularly polarized light at room temperature using a GaAs based LED as the spin detector [54-55]. The spin injection efficiency of these spin polarized LEDs was found to be ~6% for the MnAs based devices and ~2% for the Fe injection layers. These injection efficiencies are much lower than that of the DMS based spin LEDs described earlier, but they do have the advantage
of operating at room temperature and using a ferromagnetic layer for the injector as opposed to the paramagnetic layers of the DMS devices. Potential sources of the lower injection efficiencies in the Fe and MnAs based spin LEDs include a loss of spin orientation at the metal-semiconductor interface and a lack of bandgap alignment between the layers. These detrimental properties could be potentially overcome with the development of a spin LED based on a DMS that is ferromagnetic at room temperature and is incorporated into a LED based on similar materials to allow for better interfacial quality and band alignment between the magnetic and non-magnetic layers.
Figure 2-1. Predicted Curie temperatures for the III-V semiconductors with 2.5 % Mn and a hole concentration of $3.5 \times 10^{20} / \text{cm}^3$. (T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science*, 287, p. 1019, February 2000.)
Figure 2-2. Predicted stability of the ferromagnetic states of different transition metals in GaN as a function of transition metal concentration. The vertical axis represents the energy difference between the ferromagnetic and spin glass states for each metal atom. (K. Sato and H. Katayama-Yoshida, *Jpn. J. Appl. Phys.*, 40, p. L485, (2001).)
CHAPTER 3
EXPERIMENTAL PROCEDURES FOR GROWTH AND CHARACTERIZATION OF GALLIUM NITRIDE BASED DILUTE MAGNETIC SEMICONDUCTORS

Currently two main techniques are used for the production of epitaxial films of Gallium Nitride (GaN). These are molecular beam epitaxy (MBE) and metal organic chemical vapor deposition. Both are well established techniques and have been shown to produce material that can be processed into working semiconductor devices. MBE has several advantages including thickness control and uniformity. One disadvantage results from the need to have down time to replenish source material due to the need for MBE to be performed under ultra-high vacuum (UHV) conditions. External sources are one of the advantages of MOCVD resulting in reduced down time for the reactor. Other advantages of MOCVD include high throughput and a higher growth rate than can be achieved using MBE. A major problem with this technique is a lack of precise control of the thickness of layers and difficulties producing sharp interfaces between layers. For GaN, additional complications arise from the lack of a lattice matched substrate and from the difficulties associated with the use of ammonia or nitrogen plasma sources. In particular, low temperature growth is difficult in MOCVD due to the poor decomposition efficiency of ammonia at low temperatures. Thus in this particular project, MBE offers a better initial choice for introducing transition metal dopants into GaN due to the desire to have a wide range of growth temperatures available for investigation. Additionally, MBE utilizes solid sources, which allows for more flexibility when trying to identify appropriate transition metals for doping purposes.
Molecular Beam Epitaxy as a Tool for Epitaxial Growth

The MBE growth described in this dissertation was performed in a Varian Modular Gen II system. A schematic of the main growth chamber is shown in Figure 3-1 [56]. The entire system consists of three chambers, isolated by gate valves to reduce cross contamination. These chambers are: a loadlock used for sample introduction, an intermediary buffer chamber, and finally the growth chamber itself where the epitaxy is performed. A tracked trolley is used to shuttle samples between the loadlock and buffer which allows for multiple samples to be grown in a single growth session. The use of the buffer chamber allows for the growth chamber to remain isolated from the outer atmosphere and the introduction of oxygen or water vapor into the growth arena. Samples are introduced into the growth chamber using a three-pinned transfer arm.

The Varian system is equipped with a variety of different style pumps to attain and maintain the UHV needed for the MBE technique. These include 2 CTI-8 cryo pumps on the main growth chamber, an ion pump for the buffer chamber, a CTI-100 for the loadlock and an Alcatel turbo pump backed by a Leybold roughing pump which is used for the initial roughing process after a vent of any portion of the system. In addition to the pumps, the growth chamber has two cryoshrouds which are used during growth to further enhance the vacuum level and increase the purity of the grown layers. These shrouds are filled with liquid nitrogen (LN2) during growth runs. One surrounds the source materials and prevents cross talk between sources and any potential contamination by trapping any excess ions on the LN2 cooled panel. The second surrounds the substrate holder and heater assembly, both protecting the outer chamber from the high temperature of the substrate heater (in excess of 1000°C at times) and to absorb any source material that is
not consumed during the growth process. In the rear of the machine is the source flange which has the potential to have up to eight sources installed. These sources are angled to allow for uniform coverage of the beams produced from either the effusion oven sources or the plasma source. A mass spectrometer is also attached to the system which can be used during leak checking or to identify any other gaseous species present during the growth process. The system is also equipped with a reflection high energy electron diffraction (RHEED) system which consists of an electron gun and a phosphor coated window. RHEED is a valuable in-situ technique that allows for instant feedback during the growth process. In order to achieve the UHV levels after venting, bake panels are used to encapsulate the system and heat it to approximately 150°C for several days to remove any oxygen or water that may have been trapped on the walls of the system during the time that the system was exposed to atmosphere.

**Group III Sources**

The Varian system is equipped with a number of effusion (Knudsen) ovens or K-cells which are used to heat the solid Group III sources and produce the flux of atoms needed for growth. Figure 3-2 shows a diagram of one of these K-cells [57]. The cells are individually charged with suitable Group III elements and shutters are used to expose the substrate to the source at the appropriate time. For this work, one K-cell was charged with 99.99999% (7N) pure Gallium and another with 7N Aluminum. Through resistive heating, the individual K-cell is heated causing the group III element to evaporate and be directed towards the substrate when the appropriate shutter is opened. The cells can only be replenished during a vent, which is one disadvantage of this technique. Ideally, this occurs only once every year.
**Group V Source**

Reactive nitrogen for the growth of III-N materials was supplied using 6N nitrogen gas which was ionized by an RF plasma unit operating at 13.56 MHz. The plasma head was coupled to a mass flow controlled nitrogen source which maintains a constant flow of gas into the plasma head which then produces atomic and molecular species that flow into the main chamber and react at the substrate with the group III sources. Because the nitrogen is introduced from standard gas bottles, replenishing or changing the group V source simply requires changing a bottle and then purging the appropriate gas lines before the next growth. Nitrogen is also a much safer gas to use for the growth of the III-N as compared to ammonia which has also been used for MBE growth of GaN.

**Dopant Sources**

Concurrent with the growth of the nitride material, dopants are added to optimize the magnetic and electrical properties of the grown layers. The transition metals used for this study, 6N manganese (Mn) and 5N chromium (Cr), were solid sources and heated in standard K-cells. Solid source magnesium and silicon were introduced to alter electrical properties. A gas mixture of UHP 97.0% nitrogen and 3.0% oxygen were used to introduce oxygen as a codopant with the reactive nitrogen produced by the RF plasma head. All of these sources were able to be controlled and adjusted in a similar manner as the group III and V sources discussed earlier.

**Sample Loading and Preparation**

Before beginning the growth process, the substrates need to be prepared and mounted for introduction into the growth chamber. Both (0001) sapphire and commercially grown MOCVD GaN substrates were used in this study. Very little preparation was required with the sapphire substrates. For the GaN substrates, an ex-situ
cleaning process was performed before mounting the samples for growth. The cleaning process is necessitated due to the contamination of the GaN surface with carbon, metals, and a native oxide. The cleaning process consisted of a 3 minute etch in a 1:1 HCl:H\textsubscript{2}O solution, followed by a 25 minute exposure to UV/O\textsubscript{3}, and finally a 5 minute etch in a buffered oxide etch (BOE) solution.

Both the sapphire substrates and the MOCVD GaN substrates are received as 2 inch diameter wafers. To maximize the material usage, the wafers are sectioned into smaller sizes depending on the experiment that is being performed. After sectioning, the samples are indium (In) mounted to solid molybdenum (Mo) blocks, which are heated on a hotplate. Tantalum tabs are then used to mechanically secure the corners of the samples to the block. These tabs are essential when growing at temperatures exceeding 700°C as the In used in the mounting process loses its cohesive force during the growth and allows the sample to fall off if not also secured. The tabs also produce a step edge on the substrate allowing for a thickness measurement of the film post-growth.

Once the mounting process has been completed, the Mo blocks are ready to be introduced into the system. The loadlock is vented and the samples are placed on the trolley. The loadlock is then evacuated using a series of pumps until the vacuum level reaches the 10\textsuperscript{-7} Torr range. The trolley can now be transferred through the gate valve and into the buffer chamber where the samples can remain at UHV until the growth process is ready to begin.

The growth process is ready when the cryo-shrouds are full with LN\textsubscript{2}, the appropriate K-cells are holding at the set temperature and the flux of the K-cell has been measured using the flux monitor. The gate valve between the buffer and growth
chambers is then opened and the sample introduced onto the substrate holder using the transfer arm. Once the sample is locked onto the substrate holder, the arm is retracted and the gate valve closed. The sample in this position is not exposed to the source flange and sources. Before being rotated to the growth position, the RF plasma is ignited and allowed to stabilize. The sample can then be rotated into the growth position. The RF plasma provides for a source of reactive nitrogen to maintain the cleanliness of the substrate surface before growth by keeping an overpressure of reactive nitrogen on the surface during the ramp up in temperature of the substrate heater to the growth temperature. During the growth process, the substrate holder is rotated at a speed of 5 r.p.m. to provide for uniformity in temperature across the substrate and to allow for a uniform coverage of the source materials. The details of the growth procedure and recipes will be expanded on in the chapters that follow. Once the growth is completed, the overpressure of reactive nitrogen is maintained until the sample has cooled to 300 °C, at which point the sample is flipped out of the growth position and the plasma is then subsequently extinguished and the nitrogen flow to the system halted allowing recovery to the UHV state before transferring the sample back to the buffer chamber.

**Sample Characterization**

After growth, the samples were removed from the system, demounted, then evaluated using a number of techniques. The characterization techniques were used to determine the effect that varying growth parameters had on the magnetic, electrical, structural, and chemical properties of the films. In the sections that follow, a brief review of the more important characterization techniques employed in the completion of the present work will be given.
X-ray Diffraction

Structural information was determined with powder x-ray diffraction (XRD), specifically to determine what phases are present within the epitaxial material. The XRD measurements were performed in a Philips APD 3720 system that uses a copper (Cu) x-ray source. The source predominantly emits Cu K\(\alpha_1\) x-rays with a 1.54056 Å wavelength for diffraction, although K\(\alpha_2\) and K\(\beta\) x-rays are emitted as well. In XRD, the incident x-rays are subjected to constructive and destructive interference due to their interaction with the repeating planes of the crystalline sample, in accordance with Bragg’s Law:

\[
n\lambda = 2d \sin \theta
\]

where \(d\) is the atomic plane spacing and \(\theta\) is the angle between the incident x-ray beam and an atomic plane (Figure 3-3) [57]. In the Philips diffractometer, the intensity of the diffracted x-rays is measured by a photomultiplier tube as a function of 2\(\theta\), the angle between the incident and diffracted x-ray beams. A plot of intensity versus 2\(\theta\) yields the sample diffraction pattern. The high intensity of the x-ray source allows polycrystalline samples to be measured. In this study, it can therefore be determined if the semiconductor possesses extra dopant-induced phases in addition to the main matrix semiconductor phase. These extra phases are highly undesirable for the films in this study and the information obtained from the powder XRD provides an excellent starting point in the characterization process.

Additional characterization was performed using a Philips X’pert High Resolution X-ray Diffraction system. From rocking curve measurement performed using this system, information about a thin films lattice constant and full width half maximum can
be determined. These measurements are especially useful when attempting to dope a material at high levels which may be at or near the solid solubility limit of a material.

**Auger Electron Spectroscopy**

Chemical composition information was determined using Auger Electron Spectroscopy (AES). AES involves the detection of electrons emitted from the sample surface due to the interaction of an incident electron beam. Auger electrons are of low energy and are released from the first few atomic layers of the sample. As a result, AES is a very surface-sensitive technique. However, the energy of an Auger electron is characteristic of the atom that released it. An Auger electron is the result of a three electron process. The incident electron beam, through interaction, first knocks an inner shell electron off of the atom in question. To lower the overall atom energy, an outer shell electron will then jump down, filling the inner shell void. The excess energy difference that results from this transition is given off as a photon, which is then reabsorbed by the same atom, ejecting another outer shell electron. It is this second outer shell electron that is detected as the Auger electron. The resulting detected energy spectrum then allows a qualitative compositional analysis to be obtained of the surface, and through peak height analysis using published elemental sensitivity factors, an approximate quantitative analysis can also be calculated. AES can be used for compositional information down to roughly 1 atomic %. The Auger system is also fitted with an Ar sputter gun allowing compositional depth profiling. The Auger system used in this dissertation was a Perkin Elmer 6600.

**Hall Effect**

The Hall effect is a very powerful method of obtaining electrical data about a sample. The number density, type, and mobility of charge carriers can be determined
through a proper Hall measurement. To prepare the hall samples, a 0.8 cm² section is cut from the main sample and four Indium dots are placed at the four corners of the square using a soldering iron. The Hall measurements in this work were performed at room temperature using a home built system using a 0.8 Tesla electromagnet and a computer controlled switching system that allowed for the Van der Pauw and Hall measurements to occur.

Superconducting Quantum Interference Device Magnetometry

Magnetic measurements were performed in a Quantum Design Magnetic Properties Measurement System, also known as a SQUID. The SQUID has the highest sensitivity for detecting magnetic fields. Two types of measurements were performed in this work. Magnetization versus field measurements (BH loops) produce the hysteresis loops that are easily identifiable and indicative of ferromagnetism. The second test for ferromagnetism is made by utilizing a Field Cooled/Zero Field Cooled (FC/ZFC) measurement. Here the sample is cooled to 10K under a set applied field while measuring the samples magnetization (FC) and then measured under zero field as the sample warms back to room temperature (ZFC).

Extended X Ray Absorption Fine Structure

Several of the films grown in this study were evaluated using Extended X-ray Absorption Fine Structure (EXAFS). EXAFS measurements require use of a cyclotron beamline. These EXAFS experiments were performed at the Advanced Photon Source beamline at Argonne National Laboratory. The measurement involves the detection of the x-ray photoabsorption of a selected element as a function of energy above its core shell binding energy after it has been exposed to the cyclotron beam. The beamline provides a source of monochromatic x-rays to irradiate the sample. The x-ray
fluorescence spectra obtained is a probe of the interatomic spacing and degree of disorder of atoms within a short distance (~5 Å) of the x-ray absorbing atom.

EXAFS requires much data analysis to obtain the results of the measurement. In our case, a commercially available software package was used to assist in the analysis of the data. Feff8, the package used, is a widely respected analysis tool for handling the large files generated by the EXAFS technique. Through the file manipulation capability of Feff8, the data generated at the beamline was able to be synthesized and allowed for sample to sample comparisons [58].

**Reflection High Energy Electron Diffraction**

One of the most common in-situ analysis techniques available during MBE growth is Reflection High Energy Electron Diffraction (RHEED), which provides structural information about the surface of the film. The RHEED system consists of an electron gun aimed to produce a beam that strikes the sample surface at a grazing angle (~1-2°). The beam interacts with only the top few monolayers of the sample surface, diffracting and then impinging on a phosphor coated screen. The pattern that is generated on the screen is indicative of the surface reconstruction of the film. The pattern contains information on the surface crystal structure, crystal orientation, and the degree of surface roughness. In epitaxy, RHEED is used to determine the surface reconstruction and growth mode. A surface growing layer by layer (2D) produces streaky lines, a spotty pattern is indicative of islanding (3D) growth, while rings are indicative of a polycrystalline surface. Amorphous films have no long range order, therefore they produce no RHEED pattern.
Figure 3-1. Varian Intevac Gen II growth chamber
Figure 3-2. A Knudsen Effusion Oven (K-cell) used on the Varian MBE system.
Through resistive heating of the filament the charge material is evaporated.
Figure 3-3. Bragg’s Law of Diffraction in a crystalline sample.
CHAPTER 4
GROWTH OF SINGLE PHASE GALLIUM MANGANESE NITRIDE

In this chapter the doping of GaN with Mn will be investigated with the goal of achieving single phase ferromagnetic material. There have been conflicting reports in the literature as to the origins of the ferromagnetism observed in DMS materials. For GaMnN to be integrated with the existing GaN technology base it will be necessary to obtain material that is of the highest crystalline quality possible with both semiconducting and magnetic properties. One set of theories is based on a mean field approach which originates from the original model of Zener magnetism. The theories that fall into this theory assume that the DMS is more or less a random alloy with the Mn substituting for Ga in the crystal lattice. The second set of theories suggests that the magnetic atoms form small (a few atoms) clusters that produce the observed ferromagnetism. It is conceivable that one could produce material that encompasses all of the above theories by changing the growth conditions employed for growing the GaMnN films. It is likely that one could readily produce samples that span the entire spectrum of possibilities from single-phase random alloys to nanoclusters of the magnetic atoms to precipitates and multi-phase material. To examine this, a series of GaMnN films will be grown and characterized in an attempt to produce GaMnN with the widest range of material properties.

Additionally, the effect of composition on GaN based DMS semiconductor films will be investigated. To explore the effect of Mn concentration on GaMnN layers, a series of samples have been produced with varying amounts of Mn. These samples will
be used to help determine the optimal concentration of Mn to achieve the most effective combination of properties. There have also been theoretical predictions that by codoping GaMnN with oxygen, the magnetization of the sample may be enhanced.[38] Samples of GaMnN codoped with oxygen have been prepared to examine what effect if any oxygen has on GaMnN. Finally, the effects of rapid thermal annealing on GaMnN layers will be investigated. Annealing of electrical contacts is an important factor for development of spintronic devices and thus the thermal stability of the DMS layers must be determined.

**Growth of GaMnN**

A series of films were produced using the growth procedures outlined in Chapter 3. For this study, layers were grown at 700°C on sapphire substrates using RF-plasma assisted MBE. A 20 nm low temperature GaN buffer was deposited before the growth of the GaMnN layer. Three different samples, each ~400 nm thick, were examined. The first sample was grown at a growth rate of 100 nm/hr with ~5 at. % Mn as determined by Auger Electron Spectroscopy (AES). The growth conditions for this sample were optimized to produce single phase material. The process of phase determination will be discussed later in this chapter. The growth conditions of substrate temperature, V/III ratio and growth rate were optimized to produce this single phase material. Figure 4-1 is a reflection high energy electron diffraction (RHEED) pattern observed during the growth of the sample. The RHEED pattern is indicative of a mixture of layer by layer and islanding growth or a 2D/3D pattern. The second sample also had a Mn concentration of ~5 at. %, but was grown with a different V/III ratio than the single phase sample. The change in these parameters produced material in which second phases were observed. The third sample had a Mn concentration of ~50 at. % and was designed to
have a large concentration of second phases. The presence of these second phases is observable in the RHEED image shown in figure 4-2.

**Characterization of GaMnN with and without Second Phases**

Post growth, the samples were analyzed using a variety of techniques, including Powder X-ray diffraction (XRD), AES, SQUID magnetometry, and EXAFS. Figure 4-3 shows the XRD scan for the film grown under the optimized growth conditions with 5 at. % Mn. Here only peaks due to hexagonal c-axis aligned GaN and GaMnN were observed in addition to that of the sapphire substrate. As the growth conditions are changed from the optimum condition, peaks begin to appear that are associated with the family of compounds associated with Ga$_x$Mn$_y$. Figure 4-4 is the XRD plot associated with a GaMnN layer grown with ~5 at. %, but with clear evidence of second phases present. As the growth conditions are pushed even farther from optimum, even more second phases become evident. These are shown in Figure 4-5 which is of the sample grown with ~50 at. % Mn.

Further examination of the optimal sample was performed using high-resolution transmission electron microscopy. Figure 4-6 is a cross section of this sample and Figure 4-7 is the associated selected area diffraction pattern (SADP) for the GaMn(5%)N found to be single phase using the Powder XRD. No extra spots are observed in the SADP which would be indicative of second phases. There is also no evidence of clusters in the cross sectional image. It is expected that magnetically relevant clusters would be on the order of tens of nm which should be observable in the TEM image. The structural difference between the single-phase and multi-phase samples is also seen when the samples containing ~5 at. % Mn were examined using EXAFS. Figure 4-8 presents the Fourier transform of the Mn K-edge $\chi$ function versus lattice position for these two films.
The $\chi$ function predicted theoretically for substitutional Mn in a wurtzite GaN matrix is presented as well. There is a clear difference in the experimentally generated curves. The peaks obtained from the film known to possess Ga$_x$Mn$_y$ clusters is shifted significantly from the film shown to be single phase by the other techniques utilized. There is also seen to be a good similarity between the single phase film and the theoretically predicted curve. The observable difference in EXAFS spectra provides another tool for detecting the presence of multiple phases in the GaMnN layers.

The three samples were then examined using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. All of the samples exhibited hysteresis in 300 K magnetization versus field loops. These loops are presented in Figures 4-9, 4-10, and 4-11 for the single-phase sample with ~5% Mn, the multi-phase sample with ~5% Mn, and the multi-phase sample containing ~50% Mn respectively. The coercivities of these films were in the range of 125-200 G. The more instructive measurement is that of the temperature dependence of the field-cooled (FC) and zero field-cooled (ZFC) magnetization. Here there are clear differences in the magnetic signatures associated with the films. Figure 4-12(a) is the FC-ZFC plot for the single phase film. There is clear evidence of ferromagnetism in the film to the temperature limit of the SQUID as seen by the separation of the FC and ZFC curves. In sharp contrast, figure 4-12(b), which shows the FC-ZFC plot for the film with 50% Mn, shows behavior typical of a spin glass at temperatures below 100K. The data presented in figure 4-12(c), which is the multi-phase sample with ~5% Mn, shows behavior which is consistent with the presence of at least two ferromagnetic phases. These results are all consistent with the XRD, TEM, and EXAFS results.
Effect of Mn Concentration on GaMnN

To investigate the effect of Mn concentration on GaMnN layers, a series of samples were prepared varying the Mn concentration from 0-12 at % by gas source molecular beam epitaxy (GSMBE) in a Varian Gen II machine. The details of the growth process are outlined in chapter 3. For this study, the samples were prepared at 700°C on sapphire substrates. Film thicknesses were between 300-500 nm thick. The Mn concentrations were determined using auger electron spectroscopy and the presence of second phases were investigated using Powder X-ray diffraction. It was found that films with Mn concentrations between 0 and 9 at. % were found to be single phase, while the sample with 12 at. % Mn contained second phases of Ga$_x$Mn$_y$. The films were then measured using SQUID magnetometry to determine the magnetic properties of the layers. Figure 4-13 is a hysteresis loop at 300 K for a film containing ~3 at. % Mn. The samples were then analyzed using High Resolution X-ray Diffraction (HRXRD). The c-plane lattice constants of the single phase films were determined from rocking curves. A rocking curve from the sample containing 5 at. % Mn is shown in Figure 4-14.

The lattice constants of the single phase films are plotted in Figure 4-15 and were found to vary with Mn concentration. The lattice constant for the film with 3 at. % Mn decreased when compared to an undoped GaN layer grown under similar conditions. It is likely that the decrease in lattice constant is due to incorporation of Mn substitutionally on the Ga sublattice. However, as the Mn concentration is increased beyond 3 at. %, the lattice constant began to increase. The increase in lattice constant was also accompanied by a decrease in the magnetic moment per Mn in the film. Since non-substitutional Mn is not expected to contribute to the magnetic ordering and in fact may produce antiferromagnetic coupling, the decrease in moment per Mn suggests that the increase in
lattice constant is due to incorporation of interstitial Mn, and that the maximum for complete Mn substitutionality is ~3 at.

Additional information about the structure of the GaMnN films is shown in Figure 4-16, where the c-plane lattice constant and full width half maximum (FWHM) are plotted versus the Mn concentration. The largest value of FWHM was obtained for the sample~ 3 at.

 percent Mn. The FWHM decreases with increasing Mn concentration until at 9 at.

 percent, the film has the same FWHM as the undoped GaN control sample. When one considers both Figure 4-15 and Figure 4-16 together, the maximum value of both magnetic moment and FWHM occur at the minimum in lattice constant, which is for the sample containing ~ 3 at.

 percent Mn. This suggests that at this value the films are at a maximum solubility for substitutional Mn. Then as additional Mn is added, it incorporates interstitially leading to an increase in the lattice constant and a decrease in both magnetic moment and FWHM.

Optical transmission measurements have also been performed to examine the effect of Mn on the bandgap of GaMnN, shown in Table 4-1. The bandgap of GaMnN was found to increase only 20-30 meV compared to an undoped GaN film grown under similar conditions. As the Mn concentration is further increased, the bandgap returns to a value of 3.33 eV which is the value of the undoped GaN film. In agreement with the structural data, the additional Mn does not appear to incorporate substitutionally. These results suggest that the maximum solubility for substitutional Mn in GaMnN is ~3 at.

 percent and that as more Mn is added it incorporates interstitially and does not contribute to the ferromagnetic ordering.
Effect of Oxygen Codoping on GaMnN Layers

It is highly desirable to produce a DMS material which has the ability to have its electrical characteristics controlled without impacting the magnetic properties of the layers. Oxygen is a potential candidate for use in GaMnN because it is believed to behave as a shallow donor, which should allow for the attainment of n-type material. In addition, a theoretical study by Kulatov and coworkers suggests that the presence of oxygen may possibly enhance the magnetization observed in GaMnN due to a change in the occupancy of the Mn bands. To evaluate the potential value of oxygen as a codopant in GaMnN, a series of samples were prepared at growth temperature of 700°C on MOCVD GaN substrates. The films were determined to contain between 3-5 at. % Mn as determined by auger electron spectroscopy (AES) and were found to be single phase. Film thicknesses were 200 nm.

Using optimized nitrogen flow rates and plasma settings as described in chapter 3, single phase GaMnN and GaMnN:O films were grown. Codoping with oxygen was accomplished by using a commercially available UHP mixture of 97.0% nitrogen and 3.0% oxygen gas. The gas flow rates and plasma settings were the same as for the optimized nitrogen condition. The oxygen concentration in the films was found to be ~10 at. % as measured by AES.

As reported earlier in this work, GaMnN films grown under similar conditions to those used in this study were single phase, showed evidence of ferromagnetism, and were highly resistive. When oxygen is added to the system during growth under optimal conditions, the resultant room temperature hysteresis trace of the oxygen codoped film is similar to that grown without oxygen as shown in figure 4-17 as is the magnetization versus temperature curves as shown in Figure 4-18(a) (without oxygen) and Figure
4-18(b) (with oxygen). By contrast, when nonoptimal conditions were used and a higher Mn concentration incorporated into the film, the oxygen does produce a significant improvement in the room temperature magnetization as shown in Figure 4-19. This suggests that oxygen does enhance the substitutionality of Mn in situations where substantial amounts of interstitial Mn may be incorporated. This is similar to the case of Er doping in semiconductors.

Though the addition of oxygen does not appear to substantially alter the magnetic properties, it does have a rather dramatic effect on the electrical properties and the thermal stability of GaMnN. While the non-oxygen doped GaMnN is highly resistive, the oxygen doped layers are quite conductive with resistivities of \( \approx 2.5 \times 10^{-2} \, \Omega \cdot \text{cm} \). This conduction is presumably due the formation of shallow donors upon the addition of oxygen. This is an encouraging result in that it appears possible to independently control the magnetic and electrical properties of these films, making incorporation into useful device structures more likely. Perhaps even more importantly, the addition of oxygen dramatically improves the thermal stability of the magnetic behavior. As shown in Figure 4-20, annealing of the non-oxygen doped GaMnN at even the relatively low temperature of 500°C virtually eliminates all evidence of ferromagnetism at room temperature. By sharp contrast, oxygen doped material shows only a modest drop in saturation magnetization, even after annealing at 700°C. Figure 4-21 is a comparison of annealed and unannealed GaMnN:O showing the slight decrease in magnetization at room temperature for the sample annealed at 600°C. It is possible that the Oxygen co-doping enhances the soluble fraction of Mn and reduces the concentration of Mn\(_t\) that couple anti-ferromagnetically, as suggested for GaMnAs. These annealing results are
significant from a device standpoint in that some processing sequences for GaN based
devices, such as the p-contact Ohmic anneal, can now be carried out on devices which
contain a DMS layer, possibly leading to enhanced device performance and extended
lifetime.
Figure 4-1. RHEED image during growth of single phase GaMn(5%)N. Pattern is of the \(<11-20>\) direction.
Figure 4-2. RHEED image during growth of multi-phase GaMn(50%)N. Pattern is of the <11-20> direction.
Figure 4-3. Powder XRD scan of single-phase GaMn(5%)N.
Figure 4-4. Powder XRD scan of multi-phase GaMn(5%)N
Figure 4-5. Powder XRD scan of multi-phase GaMn(50%)N.
Figure 4-6. XTEM of GaMn(5%)N shown to be single phase by XRD.
Figure 4-7. SADP of GaMn(5%)N found to be single phase by XRD.
Figure 4-8. Mn K-edge EXAFS $\chi$ functions for GaMnN films with 5% Mn concentration. The single phase film was grown using optimized nitrogen plasma settings while the multi-phase film was not, resulting in the formation of Ga$_x$Mn$_y$ in addition to the GaMnN. The theoretical spectrum for GaN containing 5 at.% substitutional Mn is also shown.
Figure 4-9. BH loop for single-phase GaMn(5%)N at 300K.
Figure 4-10. BH loop for multi-phase GaMn(5%)N at 300K.
Figure 4-11. BH loop for multi-phase GaMn(50%)N at 300K.
Figure 4-12. Magnetization vs. Temperature for single and multi phase GaMnN films. 
A) Single phase GaMn(5%)N.  B) Multiphase GaMn(50%)N.  C) Multiphase GaMn(5%)N.
Figure 4-13. Hysteresis loop at 300K for GaMn(3%)N grown on sapphire at 700 °C.
Figure 4-14. Rocking curve of GaMn(5%)N grown on sapphire at 700 °C.
Figure 4-15. C-plane lattice constant and moment per Mn for GaMnN layers grown on sapphire at 700 °C plotted at various Mn concentrations.
Figure 4-16. FWHM values of rocking curves taken from GaMnN layers grown on sapphire at 700 °C with various Mn concentrations.
Table 4-1. Dependence of bandgap on Mn concentration.

<table>
<thead>
<tr>
<th>Mn content (atomic%)</th>
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<th>3</th>
<th>5</th>
<th>9</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
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<td>3.35</td>
<td>3.36</td>
<td>3.33</td>
<td>3.33</td>
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<tr>
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<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>GaxMny</td>
</tr>
</tbody>
</table>
Figure 4-17. Room temperature hysteresis curve for GaMn(3%)N and GaMn(3%)N:O.
Figure 4-18. Magnetization versus temperature measurement for GaMn(3%)N (top) and for GaMn(3%)N:O (bottom).
Figure 4-19. Room temperature hysteresis curves for GaMn(5%)N and GaMn(5%)N:O.
Figure 4-20. Effect of RTA annealing (1 minute anneals) on magnetization for GaMn(3%)N grown with and without oxygen codoping.
Figure 4-21. Room temperature hysteresis curves for GaMn(3%)N films codoped with oxygen before and after annealing at 600 °C.
CHAPTER 5
EFFECT OF GROWTH CONDITIONS ON EPITAXIAL GAMNN FILMS

In this chapter, the effects of nucleation layer and growth temperature on the properties of GaMnN films grown epitaxially by gas source molecular beam epitaxy (GSMBE) will be investigated. There have been studies that indicate that spin injection across interfaces is considerably affected by the presence of defects at the interface. It has also been found that there was an inverse correlation between the number of defects and the efficiency of the spin injection. This indicates that improving the crystal quality is an important consideration in developing spintronic devices. A number of studies have also reported on the effect of nucleation sequence on the defect density and crystal quality in subsequently grown GaN layers. It has also been demonstrated that the defect density and crystal quality in metalorganic chemical vapor deposition (MOCVD) GaN layers is superior to that of GSMBE grown GaN. To examine the effect of structural quality on GaMnN layers, a series of samples have been prepared with all samples containing ~3 at. % Mn as measured using Auger Electron Spectroscopy and were single phase as determined by Powder XRD studies.

GaMnN films were prepared using the methods described in Chapter 3. They were grown in a Varian Gen II by GSMBE on (0001) sapphire and MOCVD GaN substrates. Three growth temperatures were employed for the GaMnN layers: 600, 700, and 925°C. Film thicknesses were 200-500 nm. Two types of nucleation layers were employed: (1) a ~ 200 Å GaN buffer layer grown by GSMBE at 575°C or (2) a 2000 nm MOCVD GaN
buffer purchased commercially. Films deposited directly on sapphire with no nucleation layers were also grown for comparison.

**Effect of Substrate on GaMnN Layers**

To study the effect of nucleation layer on GaMnN layers, films were deposited on either low temperature MBE grown buffers on sapphire, MOCVD GaN grown buffers, or directly on sapphire with no nucleation layer. There have been numerous studies performed that show that the nucleation layer has a significant effect on defect density and crystal quality of GaN layers. By using the different nucleation layers here, the effect of defect density and crystal quality on GaMnN will be studied. The layers will be deposited under identical conditions other than the change in the nucleation layer utilized. The films were prepared at a growth temperature of 700°C, which has been found to be the optimal growth temperature for GaMnN and with a Mn concentration of 3 at. %.

During growth, in-situ reflection high energy electron diffraction (RHEED) was used to monitor the growth mode of the layers. Figure 5-1 shows the RHEED reconstruction obtained during growth of GaMnN using the LTMBE GaN nucleation buffer. The reconstruction shows a streaky pattern with some additional spots indicative of a film which is growing in the 2D/3D mode. Figure 5-2 is the RHEED reconstruction pattern during growth of GaMnN using a MOCVD grown GaN buffer layer. Here the pattern is indicative of 2D or layer by layer growth. The initial indication from these patterns is that the crystal quality of the layer grown on the MOCVD GaN buffer is superior to that deposited on the LTMBE GaN buffer. Additional structural information on these layers is obtained by utilizing High Resolution X-ray Diffraction (HRXRD) and measuring the rocking curve of the GaN peak. Figure 5-3 shows the rocking curve for
the sample prepared on the LTMBE GaN buffer. The FWHM of this curve was found to be 367.2 arc-sec.

The three samples were also examined using SQUID Magnetometry. As can be seen from the $M$ vs. $T$ data, shown in Figure 5-4, the GaMnN layer prepared with no nucleation buffer exhibits only weak magnetization even at very low temperatures (Figure 5-4a). This is in sharp contrast to the GaMnN film grown on the MOCVD GaN buffer which shows strong magnetization (Figure 5-4b). The same trace for the GaMnN film grown on the LTMBE GaN buffer (Figure 5-4c) shows a magnetization at room temperature which places it in an intermediate level of magnetization when compared to the other 2 films.

The contrast in magnetization between the 3 layers is also evidenced in the hysteresis loops measured at room temperature for the prepared films. Figure 5-5a shows both the loops for the films prepared with the LTMBE GaN buffer and that of the layer prepared with no buffer on sapphire. The film prepared with no nucleation layer shows weak magnetization at room temperature. In sharp contrast, the GaMnN layer grown on MOCVD GaN shows strong magnetization as shown in the hysteresis loop in Figure 5-5b. Given the superior crystal quality of the material grown on the MOCVD buffer, the data suggest that defect density does play an important role in determining the magnetization. This is further confirmed by the magnetic data of the GaMnN layer grown on the LTMBE GaN buffer as shown in figure 5-5a. The magnetization is found to be lower than that for the film on the MOCVD GaN buffer, yet better than that prepared with no buffer. The material grown on the LTMBE GaN layer is expected to have a higher defect density than that grown on the MOCVD GaN layer yet lower than
that grown with no nucleation layer. Thus, the magnetization appears to follow the trend in defect density.

The apparent dependence of magnetic behavior on defect density may be due to interactions between the defects and the substitutional Mn atoms or to defect-induced differences in the position of the Mn in the lattice. To address this issue, EXAFS measurements have been performed. Figure 5-6 is a plot of the Mn K-edge EXAFS $\chi$ functions for films prepared on MOCVD GaN buffer vs. those deposited on GSMBE GaN buffer. The $\chi$ functions are very nearly identical within experimental resolution, indicating that the position of the Mn in the lattice is not affected by the starting buffer conditions. These results suggest that the degradation of the magnetic behavior is due to defect interactions and not to variations in the amount of substitutional Mn. This is consistent with the improved magnetization observed in ion-implanted GaMnN samples after passivation of defects by annealing in hydrogen [60].

**Effect of Substrate Temperature on GaMnN**

The effect of substrate temperature on GaMnN layers was investigated by preparing a series of samples that contained 3 at. % Mn and were single phase. The samples were prepared on MOCVD GaN substrates at 600, 700, and 925°C. The grown layers were 200 nm thick. All three films were found to be ferromagnetic to 350 K, which is the detection limit of the SQUID magnetometer utilized in this study.

Figure 5-7 shows the magnetization as measured by the zero field cooled-field cooled (ZFC-FC) M vs. T for the variously prepared films. The magnetization for the film prepared at 700°C is clearly much greater that that of the film prepared at 600°C or 925°C. In most cases it has been found that the crystal quality of GaN films increases
with increasing growth temperature, therefore the observed effects are not believed to be due to differences in defect densities. It is more likely that by changing the growth temperature the incorporation of Mn into the lattice changes, with the higher growth temperature of 925°C leading to more interstitial Mn. For the lower growth temperature of 600°C it is likely that the Mn does not have sufficient mobility on the growth surface and instead incorporates as an interstitial and that the defect densities in the GaN matrix are increasing as well.

Electrical resistivity measurements were also performed on these samples. The hall measurements were performed on samples grown on sapphire substrates to eliminate confusion when measuring samples grown on the MOCVD buffers. It was found that the films prepared at 600 and 700°C were insulating in nature. By contrast, the film grown at 925°C was found to be conductive with a resistivity of 0.53 ohm-cm. Hall measurements were performed and the carrier concentration was found to be $3.7 \times 10^{18}$ /cm$^3$ and the material was found to be n-type. The decreased resistivity and increased carrier concentration in the layer grown at 925°C is most likely attributable to the presence of nitrogen vacancies that are more prevalent in the material grown at higher growth temperatures.

It is evident from these measurements that the effect of growth temperature has a significant impact on the magnetic properties of prepared layers, with the optimal growth temperature found to be 700°C. While the film prepared at 925°C was conductive as compared to the insulating films prepared at 600 and 700°C, the improvement in magnetic properties of the sample prepared at 700°C makes it a superior choice when choosing a layer based on its magnetic properties for spintronic applications.
Figure 5-1. RHEED pattern showing the 2D/3D growth mode for GaMnN layer prepared on a LTMBE GaN buffer. Pattern is of the <11-20> direction.
Figure 5-2. RHEED pattern showing the 2D growth mode for GaMnN layer prepared on a MOCVD GaN buffer. Pattern is of the <11-20> direction.
Figure 5-3. Rocking curve of GaMnN layer prepared on a LTMBE GaN buffer with a FWHM of 367.2 arc-sec.
Figure 5-4  Magnetization versus temperature measurement for GaMn(3%)N layers prepared at 700 °C with different nucleation layers.  A) Sapphire.  B) MOCVD GaN buffer.  C) LTMBE GaN Buffer
Figure 5-5. Hysteresis loop for GaMn(3%)N layers. A) prepared with a LTMBE GaN buffer and no nucleation layer on sapphire. B) MOCVD GaN.
Figure 5-6. Mn K-edge EXAFS chi functions for films prepared on MOCVD GaN buffer vs. those deposited on LTMBE GaN buffer.
Figure 5-7. Magnetization versus temperature measurement for GaMn(3%)N layer prepared on MOCVD GaN. A) Tg: 600°C. B) Tg: 925°C. C) Tg: 700°C.
CHAPTER 6
SPINLED DEVELOPMENT AND TESTING

In this chapter, the development and testing of a GaN based Spin-Light Emitting Diode (Spin-LED) will be investigated. To date, there has not yet been a pure semiconductor based spintronic device that can operate at room temperature. If a device based on GaMnN, which has been shown to be ferromagnetic at room temperature, could be developed showing polarized emission at room temperature, it would be the first such demonstration at room temperature. The current chapter will follow the growth, processing and subsequent testing of a prototype GaMnN based spin-LED.

**SpinLED Growth and Processing**

The spin-LED structures that will be investigated in this work have an inverted geometry with n-type layers on the top and were grown on sapphire substrates starting with a 2μm thick buffer layer of undoped semi-insulating GaN, followed by (1) a 2-μm thick layer of Mg doped p-type GaN for electrical injection of holes into the spin detector; (2) a non-magnetic spin detector of five periods of In$_{0.4}$Ga$_{0.6}$N (3 nm)/GaN:Si (10 nm) multiple quantum wells (MQW); (3) a 20 nm GaN:Si spacer; (4) a spin injector of 100 nm thick GaMn(3%)N; and finally (5) a 100 nm top layer of n-type GaN:Si to facilitate making ohmic contact to the device. Additionally a companion LED structure was prepared without the spin injector layer for comparison. All of the layers but the final two were grown by metal organic chemical vapor deposition. The final 2 layers of GaMnN and GaN:Si were deposited by molecular beam epitaxy at 700°C using the methods described previously in this work. Figure 6-1 is a RHEED image captured during the growth of the
GaMnN layer and shows a 2D reconstruction indicative of good crystal quality and a smooth surface.

For electroluminescence (EL) studies, mesa diodes were then defined by dry etching in Cl₂/Ar. Ti/Al/Pt/Au was used as an ohmic contact to the n-type GaN, whereas Ni/Au was used as an ohmic contact to the p-type GaN. The diodes were narrow rings of 100 μm in diameter with a 100 μm x 100 μm contact pad. Figure 6-2 shows a schematic of the processed LED structure. Figure 6-3 is a photo image looking down on the finished diode. When the finished LED is operated under an applied bias with no magnetic field, the spectral output is shown in Figure 6-4, demonstrating the successful integration of a DMS layer into a working GaN based device. The next step will be to determine if the degree of polarization of the light emitted by the spin-LED.

### Device Testing and Results

Magneto-optical experiments were performed in the Faraday configuration in magnetic fields up to 5 T. Even though no remnant polarization is expected in this geometry, spin injection efficiency of the diodes can be evaluated by comparing the field dependencies of the magnetization and light polarization. Photoluminescence (PL) was excited with a frequency-doubled Argon laser line (244 nm) or a tunable dye laser (420-435 nm) for above and below barrier excitation, respectively. The circular polarization of luminescence was analyzed by using a photoelastic modulator and a linear polarizer. The polarization degree was defined in percentage by: $100(\sigma^+ - \sigma^-)/(\sigma^+ + \sigma^-)$ where $\sigma^+(\sigma^-)$ is the PL intensities measured at the right (left) circular polarization.

Spin-dependent properties of the diodes during electrical and spin injection were evaluated by analyzing polarization of light emission measured by EL and PL. Figure
6-5 is a room temperature EL and PL measurement of the GaMnN based spin-LED. The EL is operated under 15 V forward bias and the PL was excited using a linearly polarized light at 5.08 eV (244 nm). However, in spite of the ferromagnetic nature of the GaMnN layer, no polarization of light emission at room temperature is observed in applied magnetic fields ranging from 0-5 T. Unfortunately, no low temperature EL measurements were possible due to degradation of the contacts at temperatures below 230 K.

In order to evaluate whether the lack of spin polarization in the emitted light is related to the DMS layer or the LED structure, a series of PL measurements were made comparing the GaMnN spin-LED and the comparison structure grown with no magnetic layer. Figure 6-6 is the PL spectra obtained when the DMS layer is optically pumped, generating carriers that recombine in the MQW. Figure 6-7 is the PL spectra from direct pumping of the MQW with circularly polarized light. These 2 figures (6-6 and 6-7) can be compared to the optical excitation from the GaN in the reference diode (Figure 6-8). From these three plots, several things can be determined. First, the optical (spin) polarization is generally very weak (<10%) in the spin-LED and reference samples. Secondly, the intrinsic optical (spin) polarization of the InGaN QW shows polarization of 5-10 % when optically excited with circularly polarized light at 2 K with an applied magnetic field up to 5 T, due to population distribution between spin sublevels at a low temperature. This is similar to what is obtained in the reference LED samples. Finally, there is a high rate of spin relaxation in the InGaN QW leading to a loss of spin alignment before recombination. This is shown in Figure 6-9. Here the InGaN QWs were optically pumped with circularly polarized light at both 0 T and 3 T. There is no spin polarization
observed at 0 T indicating that the spins have relaxed before recombination. The lack of
polarization at 3 T indicates that the emitted polarization is independent of the
polarization of the optically pumped light used. From these results, it is clear that more
research is needed into determining an optimal spin detector for use with GaMnN spin
injection layers and that there is a need for a device having a longer spin relaxation
lifetime.
Figure 6-1. RHEED image obtained during growth of GaMnN layer on the LED structure at the growth temperature of 700°C. Pattern is of the <11-20> direction.
Figure 6-2. Spin-LED schematic showing the various layers in the device.
Figure 6-3. Photo of the processed diode without electrical bias applied.
Figure 6-4. EL emission of spin-LED measured at room temperature with no applied magnetic field.
Figure 6-5. EL and PL spectra measured at room temperature for the spin-LED structure as well as their polarization (upper part of each figure). A) EL. B) PL.
Figure 6-6. Two Kelvin PL from the Spin-LED using optical injection from the GaMnN layer (top) and PL polarization percentage as a function of magnetic field (bottom).
Figure 6-7. Two Kelvin PL from the spin-LED using direct optical injection into the MQW (top) and PL polarization percentage as a function of magnetic field (bottom).
Figure 6-8. Two Kelvin PL from the undoped reference LED using optical injection from the GaN layer (top) and PL polarization percentage as a function of magnetic field (bottom).
Figure 6-9. PL intensity and polarization at 2 K of spin-LED at either 0T (left) or 3T (right).
CHAPTER 7
SUMMARY AND FUTURE DIRECTIONS

In this dissertation, GaN has been doped with Mn to produce a semiconductor that is single phase and ferromagnetic at room temperature. It was found that the growth conditions had a significant impact on the properties of the layers produced. The layers were characterized and optimized to allow for incorporation into a LED structure to study the ability to control the spin polarization of the LED. This chapter summarizes these findings and also gives some promising results, which should lead to the future continuation of work in the area of GaN based spintronics and provides a promising starting point for these future explorations.

Both single phase and multi-phase films of GaMnN were grown and characterized. There were clear differences in the X-ray diffraction spectra, EXAFS spectra and most notably in the magnetic data for the single phase versus multi-phase films. Through careful control of the V/III ratio, growth rate, and substrate temperature, the properties of the layers were able to be controlled successfully and optimized to produce single phase material.

The amount of Mn in the GaMnN films also had an effect on the properties of the layers. At a growth temperature of 700°C, single phase films were produced with Mn content ranging from 0-9 atomic percent. The highest magnetic moments were found to be in the film with 3 atomic percent Mn. Further incorporation of Mn into the lattice was found to reduce the magnetization. The reduction in magnetic moment is attributed to the increase in non-substitutional Mn in the GaMnN lattice for the layers above 3 atomic
percent. When more than 9 atomic percent Mn is incorporated at the growth temperature of 700°C, second phases of Ga$_x$Mn$_y$ begin to form in the films. It is very important to control the amount of Mn in GaMnN to produce material of the highest quality.

Growth temperature and choice of substrate were also found to have a significant impact on the properties of the grown films. Films with 3 atomic percent Mn were prepared at 600, 700 and 925°C. The films prepared at 600 and 925°C showed little or no magnetization, while the films grown at 700°C showed significantly higher magnetization. Films were then grown at 700°C on different starting buffers. It was found that the films prepared on commercially grown MOCVD GaN templates had superior characteristics to those grown on a low temperature MBE GaN buffer, which were in turn superior to those grown without a buffer on sapphire. The improvements in magnetization could clearly be linked to the reduction in defect density and improvement in crystal quality that the MOCVD GaN buffer provided.

An annealing study was performed on the GaMnN films, and it was found that by rapid thermal annealing under nitrogen ambient at 500°C, the magnetization of the films dropped below the detection limit of the SQUID magnetometer. The loss of magnetization in the GaMnN films after annealing is significant when attempting to process devices utilizing GaMnN as the ohmic contacts used in GaN technology have to be annealed at ~700°C in order to properly activate the contacts. The lack of thermal stability in the GaMnN films, led to a study on the effects of codoping with oxygen. Here it was found that oxygen incorporation had no effect on the magnetization of the layers, but did increase the thermal stability, with only a slight reduction in the magnetization after annealing at 700°C.
A prototype spin polarized light emitting diode was designed and developed. While the device was operable at room temperature and emitted blue light, the emission was not polarized. During further investigation of the LED structure, it was determined that the lack of polarized emission was unrelated to the magnetic semiconductor layer of GaMnN. The InGaN multiple quantum wells that served as the spin detector and point of recombination for the LED was found to have a highly efficient spin relaxation time and that even when pumped with circularly polarized light, no spin polarized emissions were detected. In order to develop the next generation spin LED, the dimensions of the LED and magnetic semiconductor layers must be reduced in order to promote an increase in the spin relaxation time. Preliminary work towards the goal of producing the next generation LED will now be discussed.

To study the effects of reduced dimensionality on the magnetic properties of GaMnN, a series of multiple quantum wells (MQWs) were prepared. The MQW samples were grown at 700 and 925°C on MOCVD GaN substrates and compared to bulk GaMnN samples created under identical conditions. Figure 7-1 is a schematic drawing of the MQW structure. Two GaMnN/AlN MQW structures were grown with GaMnN layer thicknesses of 100 and 50 Å. The samples were prepared under conditions to incorporate ~3 at. % Mn into the layers. It has been reported that AlN has an incorporation rate of Mn that is much less than that of GaN, leading to AlN being an excellent choice of a barrier layer between the GaMnN layers.

Post growth, the samples were evaluated using high resolution x-ray diffraction. Figure 7-2 shows the rocking curve for a 40x GaMnN/AlN (50 Å/100 Å) MQW grown at
700°C. The curve shows sharp satellite peaks that are indicative of good interfacial quality between the GaMnN layers and the AlN barrier layers.

The 40x MQW was then measured using SQUID magnetometry and was found to be magnetic at room temperature. The magnetization versus temperature plot is shown in Figure 7-3. The sample shows strong magnetization very similar to that of bulk GaMnN layers on MOCVD GaN. Surprisingly, when the room temperature hysteresis curves for the bulk GaMnN sample and the 40x MQW sample are compared, the MQW shows an increase in magnetization at room temperature. The cause of the improved magnetization is possibly related to GaMnN layers of higher structural quality in the MQW structure as the AlN layers may lead to a reduction in defect density in the GaMnN layers. The 20x MQW was grown at 925°C and also showed ferromagnetism at room temperature, but the magnetization was lower than the bulk sample that was prepared for comparison.

There have been several theoretical studies that suggest that Mn is not the only potential candidate for use in a GaN based DMS. One of these other materials is a DMS that uses Cr as a dopant. To examine the viability of GaCrN as a DMS material, a series of samples were prepared using both sapphire and MOCVD GaN substrates at a growth temperature of 700°C. The growth conditions were identical to that used to produce the optimal GaMnN layers, with only Cr being used as the transition metal as opposed to Mn.

The GaCrN layers were found to be single phase as determined by powder x-ray diffraction. Figure 7-5 shows the XRD scan for a GaCrN sample grown on a sapphire substrate with a LTMBE GaN buffer used to aid nucleation. The only peaks found in the XRD plot are those associated with GaN or the sapphire substrate. Electrically, the films
were found to be resistive, much like the GaMnN films grown under similar conditions.
Cr is expected to be an even deeper acceptor than Mn in GaN.

Magnetization measurements were performed in a SQUID magnetometer and the GaCrN films were found to be magnetic to at least 350K, the temperature limit of the magnetometer. Figure 7-6 is a magnetization versus temperature plot of the ZFC-FC trace. The sample shows good magnetization, with a magnetic signature similar to that of GaMnN. Shown also in Figure 7-7 is the hysteresis loop at 300K for this film which was found to contain ~ 2.5at. % Cr as measured by AES.

The area where GaCrN distinguishes itself from GaMnN films is in the area of thermal stability. GaCrN films were annealed in the RTA for 1 minute under nitrogen ambient at a series of temperatures and then measured in the SQUID to examine the effect of annealing on the magnetic properties of the layers. Figure 7-8 shows that unlike the GaMnN layers, the GaCrN is thermally stable during anneals to 700 °C. While it was found that GaMnN layers codoped with oxygen were also thermally stable under similar anneals, it is very attractive to have an uncodoped DMS layer for use in situations where it would be undesirable to introduce oxygen into the growth chamber.

These results are very encouraging for the GaN based spintronics efforts. The ability to produce thin ferromagnetic layers of GaMnN holds promise for the development of nanorod LEDs and for tunneling structures. The thermal stability of the GaCrN layers is promising for device related processing where annealing at elevated temperatures is required and unlike in GaMnN, oxygen is not required to retain thermal stability of the layers.
Figure 7-1. Schematic of the MQW structure used to investigate the effects of layer thickness on GaMnN.
Figure 7-2. Rocking curve of a 40x GaMnN/AlN MQW grown at 700°C.
Figure 7-3. Magnetization versus temperature measurement for a 40x GaMnN/AlN MQW grown on MOCVD GaN at 700°C.
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BIOGRAPHICAL SKETCH

Gerald Thaler, Jr. was born on June 24, 1971 in Allentown, Pennsylvania, and grew up on his family’s dairy farm in Williams Township, Pennsylvania. After graduating in 1989 from Notre Dame High School in Bethlehem, Pennsylvania, he spent the next 8 years exploring various career options ranging from farmer to mechanical engineer. In 1997, he graduated with a Bachelor of Science degree from Indiana University of Pennsylvania, in Indiana, Pennsylvania, with a major in physics. The next 3 years were spent working at HY-Tech Research corporation in Radford, Virginia doing research on pulse power systems and plasma physics as a research assistant. Desiring to advance his position in the scientific community, he accepted an Alumni Fellowship to the University of Florida in the Department of Materials Science and Engineering, beginning in the Fall of 2000. He joined Dr. Cammy Abernathy’s research group at that time, and began research on magnetic properties of doped III-V semiconductors. He was the recipient of the AVS’s Hoffman Scholarship in the fall of 2003, which is an international award of which only 2 are awarded per year, and was a finalist for the Varian award the same year. Post-graduation plans include constructing and managing an MOCVD lab under the guidance of Dr. Abernathy to study III-N semiconductors, and to continue research into spintronics materials.