Magnetic and Interfacial Properties of the Metal-Rich Phases and Reconstructions of Mn$_x$N$_y$ and GaN Thin Films

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This dissertation titled
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Abstract

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Magnetic and Interfacial Properties of the Metal-Rich Phases and Reconstructions of Mn$_x$N$_y$ and GaN Thin Films (201 pp.)

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The interfacial and magnetic properties of the metal-rich phases and reconstructions of Mn$_x$N$_y$ and GaN are investigated. Thin films of the two most metal-rich phases of Mn$_x$N$_y$ ($\varepsilon$ and $\zeta$) are grown on MgO(001) using a custom-built ultra high vacuum molecular beam epitaxy growth system. By the same means, thin films of GaN with the two most metal-rich reconstructions [c(6×12) and psuedo-1×1+1$\frac{1}{12}$] are grown on GaN(0001) and Al$_2$O$_3$(0001). The interfacial properties of these materials such as surface structure and local density of states are investigated in situ with low temperature scanning tunneling microscopy and reflection high energy electron diffraction. The bulk structure of these thin films are investigated using x-ray diffraction. Measurements of the morphology and magnetism of these thin films are made ex situ using atomic/magnetic force microscopy, spin-polarized scanning tunneling microscopy, scanning electron microscopy, vibrating sample magnetometry, and superconducting quantum interference device magnetometry techniques. Measurements of the chemical composition of the samples are made using back-scattered electron scanning electron microscopy, energy dispersive x-ray spectroscopy, and Rutherford backscattering spectrometry.

These techniques reveal that growth temperature heavily influences the quality of the $\varepsilon$-Mn$_4$N grown. A nucleation temperature below 480 °C is observed to result in the growth of substantial antiferromagnetic $\eta$-Mn$_3$N$_2$ grains alongside ferrimagnetic $\varepsilon$-Mn$_4$N grains. The most significant component of perpendicular magnetic anisotropy in $\varepsilon$-Mn$_4$N thin films (9 to 300 nm thick) grown on MgO(001) is attributed to the shape induced partial overlap of
Ising domains out-of-plane. Spin-polarized scanning tunneling microscopy and magnetic force microscopy measurements are consistent with the interpretation that these $\varepsilon$-Mn$_4$N thin films form single material out-of-plane spin valves due to this out-of-plane overlapping of Ising domains.

The $\zeta$-Mn$_{10}$N thin films, which are found to possess a regular surface corrugation along the [100]-direction, grown on MgO(001) are shown to be $\gamma$-type $\zeta$-phase. Conflicting evidence for both zero and non-zero net-magnetization is suggestive of the presence of both antiferromagnetic and ferromagnetic properties in $\zeta$-phase Mn$_x$N$_y$ thin films.

The interfacial structure of the Ga-rich reconstructions of GaN are investigated. The ground state of the pseudo-$1\times1+\frac{1}{12}$ surface reconstruction on GaN(0001) is found to consist of a $9\times12$ structure. The distribution of Ga at the surface of GaN thin films deposited under Ga saturation on Al$_2$O$_3$(0001) is found to consist of an equilibrium between Ga gas on the $c(6\times12)$ reconstruction of GaN(000$\overline{1}$) and on the pseudo-$1\times1+\frac{1}{12}$ reconstruction of GaN(0001) as well as liquid Ga droplets. A side by side comparison of $c(6\times12)$ and pseudo-$1\times1+\frac{1}{12}$ reconstructions shows contrast between the local density of states of the two reconstructions at multiple voltages between 0 and 3 V.
This dissertation is dedicated to my family.
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List of Symbols

$[100]_{\text{MgO}}$ [100]-Direction Relative to an MgO Substrate
$C_{11}$ Elastic Modulus Perpendicular to the (001) Surface
$C_{12}$ Elastic Modulus Parallel to the (001) Surface
$E_A$ Anisotropy Energy
$\frac{dI}{dV}$ Differential Conductivity
$H_C$ Coercive Magnetic Field
$H_K$ Anisotropic Magnetic Field
$K^I$ Interfacial Anisotropy
$K^V$ Strain Anisotropy
$K^S$ Shape Anisotropy
$K^{S_1}$ Single-Dipole Shape Anisotropy
$K^{S_2}$ Dipole-Dipole Shape Anisotropy
$M_r$ Remnant Magnetization
$M_S$ Saturation Magnetization
$m_{s\text{ or } t}$ Magnetic Local Density of States (Sample or Tip)
$n_{s\text{ or } t}$ Local Density of States (Sample or Tip)
$P$ Spin Polarization
$P_S$ Surface Localized Spin Polarization
$T_C$ Curie Temperature
$t$ Thickness
$t_C$ Critical Thickness
$V_{ID}$ Ising Domain Volume
$\lambda_{100}$ Magneto-Restriction Constant Along [100]
$\Theta$ Angle Between Sample Normal and the Easy-Axis
# List of Acronyms

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<th>Acronym</th>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AMR</td>
<td>Anisotropic Magnetoresistance</td>
</tr>
<tr>
<td>AHE</td>
<td>Anomalous Hall-Effect</td>
</tr>
<tr>
<td>AQHE</td>
<td>Anomalous Quantum Hall-Effect</td>
</tr>
<tr>
<td>BSE</td>
<td>Back Scattered Electron</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
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<tr>
<td>LT</td>
<td>Low Temperature</td>
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<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<tr>
<td>MFM</td>
<td>Magnetic Force Microscopy</td>
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<tr>
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<td>Molecular Beam Epitaxy</td>
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<tr>
<td>PMA</td>
<td>Perpendicular Magnetic Anisotropy</td>
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<td>RT</td>
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<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectrometry</td>
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<td>RHEED</td>
<td>Reflection High-Energy Electron Diffraction</td>
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<td>SEM</td>
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<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
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<tr>
<td>SP</td>
<td>Spin-Polarized</td>
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<tr>
<td>SQUID</td>
<td>Superconducting Quantum Interference Device</td>
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<td>TM</td>
<td>Transition Metal</td>
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1 INTRODUCTION

1.1 Background

Significant interest has been placed on the (Ga,Mn)$_x$N$_y$ system for its potential use in dilute magnetic semiconductor and spin-injection devices [5, 6, 7]. Functional spin-lifetimes have been observed in the semiconductor GaN [8, 9]. This behavior suggests that if magnetic polarization can be incorporated into GaN devices through the internal doping of or external interfacial growth of spin-polarizable Mn$_x$N$_y$, then a significantly greater density of information can be stored and/or transported than in traditional GaN devices.

Examples of internal magnetic incorporation into GaN include the argument for the formation of Mn$_x$N$_y$ phases within GaN being responsible for the dilute magnetic semiconductor behavior observed in Mn-doped GaN [10, 11]. As well, external magnetic incorporation has been observed in the heteroepitaxial growth of spin-polarizable Mn$_x$N$_y$ directly on GaN [12].

Understanding the magnetic properties of a material are absolutely necessary for determining its performance as a spin injector. In addition, the quality of an interface between the source and drain of a spin-current is critical to the quality of the spin signal [13]. For these reasons, an improved understanding of the magnetic and interfacial properties of spin-polarizable Mn$_x$N$_y$ as well as the interfacial properties of GaN would aid in the development of (Ga,Mn)$_x$N$_y$ based dilute magnetic semiconductor and spin-injection devices.

1.2 Significance of Study

Among the Mn$_x$N$_y$ system, three phases ($\eta$, $\varepsilon$ and $\zeta$) have shown evidence of net magnetization and hence spin-polarization [14, 15, 16]. All three of these phases ($\eta$, $\varepsilon$ and $\zeta$) have been observed to be in the upper range of Mn:N stoichiometry (Mn:N $\geq$ 3:2) within the Mn$_x$N$_y$ system [14]. Additionally, Ga-rich growths of GaN have been found
to produce the highest quality surfaces in the GaN system [17]. Due to the properties possessed by these metal-rich phases and reconstructions, a study into the interfacial and magnetic properties of specifically the metal-rich Mn$_x$N$_y$ phases and GaN reconstructions is of particular interest in the development of dilute magnetic semiconductor and spin-injection devices from (Ga,Mn)$_x$N$_y$ materials.

Certain questions concerning the interfacial and magnetic properties of the metal-rich Mn$_x$N$_y$ phases as well as the interfaces of GaN remain open. For example, certain studies indicate the significant contribution of shape anisotropy to the perpendicular magnetic anisotropy (PMA) observed in $\varepsilon$-Mn$_4$N while others do not find a significant shape contribution [18, 19, 20, 21]. Additionally, the ordering of the ferromagnetic behavior found in thin films of $\zeta$-Mn$_2$N$_{0.86}$ is still unknown [16]. In another case, theory has been proposed for the ground state structure of the pseudo-1×1 ("1×1") reconstruction on GaN(0001), while this ground state structure is still unconfirmed by experiment [22]. Finally, an equilibrium between gas- and liquid-phases of Ga has been determined during GaN growth, but an investigation into this equilibrium under Ga saturation ($>>$2 monolayers) remains [23, 24].

1.3 **Outline of Study**

Chapter 2 outlines the techniques and describes the growth facility used in this study. This outline includes a description of a magnetic force microscopy (MFM) technique developed in order to quantify the distribution of magnetization states in thin films, which possess strong easy-axis alignment, when the magnitude of $\vec{H}$-fields available is not sufficient to fully magnetize a sample. This MFM technique is a variation of a technique developed by Park et al., which requires $\vec{H}$-fields capable of fully magnetizing a sample [25]. At the end of Chapter 2, the first results of the growth facility used in this study are presented. These results demonstrate the growth facility used in this study is capable of
controlling sample growth to the atomic layer and then imaging the sample with atomic resolution.

Chapters 3, 4, and 5 discuss interfacial and magnetic properties of $\varepsilon$-Mn$_4$N ultrathin/thin films grown on MgO(001). First, Chapter 3 discusses an investigation into the growth of high phase-purity $\varepsilon$-Mn$_4$N thin films on MgO(001). Second, Chapter 4 presents an investigation into the source of PMA found in $\varepsilon$-Mn$_4$N ultrathin/thin films, which accounts for each significant contribution (greater than a few percent of the total) to PMA. These contributions are attributed to tetragonal strain as well as single-dipole and dipole-dipole shape anisotropy. The dipole-dipole anisotropy is connected to the out-of-plane partial overlap of Ising domains. Finally, Chapter 5 concludes the discussion of $\varepsilon$-Mn$_4$N with a presentation of magnetic microscopy measurements [magnetic force microscopy (MFM) and spin-polarized scanning tunneling microscopy (SP-STM)], which are found to be consistent with the regions with domain overlap within $\varepsilon$-Mn$_4$N ultrathin and thin films (9 to 310 nm) behaving as spin valves.

Chapter 6 begins with an investigation into the growth of high phase-purity $\zeta$-Mn$_{10}$N on MgO(001). Following the growth study in Chapter 6, an investigation finds evidence of ferromagnetic ordering within grains, which share the morphology observed for $\zeta$-Mn$_{10}$N in the previous growth study, embedded in $\varepsilon$-Mn$_4$N. This observed ordering serves as a potential exemplification of ferromagnetic ordering in phase-pure $\zeta$-phase films.

An investigation in Chapter 7 determines the ground (low temperature) state structure of the "1×1"+$\frac{1}{12}\text{ GaN reconstruction using reflection high-energy electron diffraction (RHEED) and STM measurements. Next in Chapter 7, the equilibrium between gas- and liquid-phases of Ga on GaN grown on Al$_2$O$_3$(0001) during Ga saturation is investigated post-growth. This investigation of the GaN surface under Ga-saturation is a continuation of a study, in which a Ga-gas phase was directly observed for the first time on the GaN surface, that this author assisted on [23]. The investigation of the GaN surface under Ga-saturation
indicates the presence of a Ga-gas phase, the c(6×12) reconstruction, the ”1×1”+$$\frac{1}{12}$$ reconstruction, and Ga droplets all in equilibrium on the surface. Finally, Chapter 7 discusses a $\frac{dl}{dV}$ contrast found between the c(6×12) and ”1×1”+$$\frac{1}{12}$$ reconstructions.

In Chapter 8, the discussion of the various investigations in this study is concluded and a discussion of potential future investigations is presented. The appendices contain information relevant to the discussions in the preceding chapters and descriptions of investigations ancillary to the main topic of this study. Appendix A shows examples of RHEED patterns of $\varepsilon$-Mn$_4$N and $\eta$-Mn$_3$N$_2$ samples and serves as a reference to RHEED patterns presented in the preceding chapters. Appendix B presents evidence that furthers a conclusion of Chapter 4; namely, Mn$_x$N$_y$ material is removed from samples and the remaining Mn$_x$N$_y$ material anneals predominately into $\varepsilon$-Mn$_4$N when annealing tetragonal Mn$_x$N$_y$ ultrathin films on MgO(001) under vacuum at 772 °C. Appendix C demonstrates that the growth direction ([111] or [001]) of GdN on Mn$_x$N$_y$ can be controlled. This change in growth direction may be related to growth temperature and/or Mn$_x$N$_y$ phase purity. Appendix D presents evidence that the introduction of Gd-doping strongly impacts the quality of GaN grown with MBE by reducing the incorporation of Ga.
2 Instrumentation

A custom-designed molecular beam epitaxy (MBE)/scanning tunneling microscopy (STM) facility is used to prepare the samples in this study as well as perform surface characterizations of samples using in situ reflection high-energy electron diffraction (RHEED), STM, and scanning tunneling spectroscopy (STS) measurements [4]. The individual fluxes of metallic elements (e.g., Ga, Mn, and Gd) are individually produced by different custom-built effusion cells. The N-plasma is produced by an RF N Plasma Source (SVTA Associates) using N\textsubscript{2} as a source gas. Substrate temperature is controlled during growth using either a custom growth stage with a lower temperature range (−80 °C to ∼ 800 °C) or another custom growth stage, which can be interchanged, with a higher temperature range [room temperature (RT) to ∼1000 °C].

RHEED measurements are performed in situ during and after growth to identify the surface structure of the samples in real time. From these RHEED measurements the in-plane spacings can be determined using the known spacings of the substrates [i.e. MgO (\(a = 4.21 \text{ Å}\))] to calibrate the measurements [1]. X-ray diffraction (XRD) measurements are used ex situ to determine sample structure outside the surface plane by detecting the common out-of-plane spacings between parallel atomic planes.

Following growth the samples can be transferred to the custom-built low temperature (LT) spin-polarized (SP) scanning tunneling microscope without breaking ultra-high vacuum (UHV) conditions (pressure below ∼ 5 \times 10^{-10} Torr), which allows the study of still pristine surfaces with LT-SP-STM. Surface measurements using SP-STM can provide insight into the structural, electronic and magnetic properties of the samples. A Stanford Research System lock-in amplifier is used to extract a \(\frac{dI}{dV}\) signal related to a 5 mV amplitude oscillation, which is provided by the lock-in amplifier, of the bias voltage of the STM at a frequency of 4.5 kHz during scanning.
In addition, a Park Scientific CP AFM/MFM head retrofitted with a controller system by Anfatec Inc., which is operated using the lift height method in non-contact dynamic mode, is used for \textit{ex situ} surface characterization of the morphology and magnetic domain structure of the samples. As well, in some cases the surface morphology is mapped out with \textit{ex situ} scanning electron microscopy (SEM) measurements, which use a 25 keV thermal emitter. The chemical composition is compared between different areas of individual samples using back-scattered electron (BSE) SEM and energy-dispersive x-ray spectroscopy (EDX) measurements, which both employ a Be window between the sample and the detector.

Rutherford backscattering spectrometry (RBS) is used \textit{ex situ} to determine the stoichiometric composition of samples as well as the thickness of samples in some cases. In all other cases, sample thickness is calculated from the growth rate and the time of growth. In some of these cases, the growth rate is calculated from the time of growth and thickness (measured with RBS) of a test sample. The same growth rate is then used to grow other samples with a different time of growth.

In the remaining cases, the growth rate is determined from the \textit{in situ} measured flux of the material sources (e.g. N-plasma, evaporated/sublimated elements ...). The flux of the elemental sources are measured \textit{in situ} using an Inficon oscillating quartz crystal film thickness deposition monitor. The N-plasma flux is determined by identifying the transition between N- and Ga-rich growth of GaN when using a known Ga-flux [26].

Vibrating sample magnetometry (VSM) and superconducting quantum interference device (SQUID) measurements are used to plot magnetization versus $\vec{H}$-field ($\vec{M}$ vs $\vec{H}$). The contribution of the substrate to magnetization was measured using VSM performed on a bare substrate and then subtracted out in order to determine the $\vec{M}$ vs $\vec{H}$ of the sample by itself. The total magnetic moment, which is measured from VSM or SQUID, was scaled to sample volume, which is found from the measured thickness and sample area, in order to
determine the $\vec{\mathcal{M}}$ vs $\vec{\mathcal{H}}$ for each sample. WSxM and ImageJ software were used for image processing [27, 28].

2.1 Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy (MBE) is a technique that was originally developed in the 1960s and reached maturity by the mid-1970s [29]. Observed in the initial development of the technique, a high precision of material deposition (sub-monolayer) made the technique ideal for the growth of high-quality interfaces (atomically flat and abrupt) of heterogenous layers, which may differ in slight to large amounts of doping, stoichiometry, and/or even elemental composition [30]. This level of control makes MBE ideal for the investigation of systems, which possess properties sensitive to interfacial quality, stoichiometry and layer thickness (e.g. $\text{Mn}_x \text{N}_y$ on GaN).

MBE is a process in which epitaxial growth occurs following the deposition of material in the form of a molecular beam, which may be composed of either evaporated source material or an active gas species, onto a substrate. Evaporated and gas sources can be thought of as a molecular beam when the mean free path prior to a collision between the constituent atoms is greater than the distance to the substrate. The growth is considered epitaxial when the deposited sample forms into a crystalline structure, which is directed by the crystalline structure of the substrate functioning as an atomic scaffold. In this study, elemental sources (Mn, Ga, or Gd) are deposited along with N-plasma on MgO, $\text{Al}_2\text{O}_3$, or GaN to form various crystalline samples.

As with other thin film growth techniques, the three main growth mechanisms found in MBE are the Volmer-Weber (island), Frank-van der Merwe (layer-by-layer) and the Stranski-Krastanov (layer-plus-island) growth mechanisms [31, 32]. The mechanism of growth depends on whether the partial derivative of the chemical potential with respect to the number of atoms ($\frac{\partial \mu}{\partial n}$) is positive or negative [33]. When $\frac{\partial \mu}{\partial n} < 0$, the Volmer-
Weber (island) growth mechanism is present due to a decreasing chemical potential with increasing thickness, which is associated with the adatoms favoring occupation of the upper layers of the sample compared to base layers and results in 3-D island growth. When $\frac{\partial \mu}{\partial n} > 0$, the Frank-van der Merwe (layer-by-layer) growth mechanism dominates due to an increasing chemical potential with increasing thickness, which is associated with adatoms favoring filling an entire base layer before filling a layer at a higher thickness and results in layer-by-layer growth. When the sign of $\frac{\partial \mu}{\partial n}$ transitions at some critical sample thickness, the Stranski-Krastanov (layer-by-layer and island) growth mechanism is present due to a transition in whether the base or upper layers have the higher chemical potential during sample growth. The change in sign, which typically occurs at a critical thickness, is most often related to a strain relaxation between the substrate and sample with increasing thickness [33, 34]. This change in sign results in a transition between layer-by-layer growth and island growth at a critical thickness.

In this way, the diffusion of adatoms at the surface during growth can produce different morphologies. Therefore, studying the morphology at the sample surface with AFM and STM can further the study of surface diffusion. As well, surface morphology is directly related to the interfacial quality of a surface. Therefore, developing an understanding of the diffusion of adatoms at the sample surface is important for enhancing materials with applications for which high-quality interfaces are desired (such as Mn$_x$N$_y$ on GaN).

### 2.2 Atomic/Magnetic Force Microscopy (AFM/MFM)

Atomic/magnetic force microscopy (AFM/MFM) is a measurement technique, which maps out the topography as well as the magnetic domain structure of a sample area by taking individual topographic and magnetic measurements at a series of points across the sample surface. These topographic and magnetic measurements are found from the force on a tip attached to a cantilever. AFM was first introduced by Binnig et al. in 1986 with
the additional utility of magnetic force measurement introduced in the following year by Martin et al. [35, 36].

In non-contact dynamic mode, the tip/cantilever, which is driven to oscillate with a piezoelectric motor while the tip is not in contact with the surface, is treated as a damped harmonic oscillator. The force from the sample on this damped harmonic oscillator results in a resonant frequency specific to that force. The dominant forces on a tip near a surface (1 – 10 nm away) are capillary attraction and the van der Waals force, which both scale with the distance between the tip and the sample plane [37]. Therefore, when the distance between the tip/cantilever and the sample plane is 1 – 10 nm, the resonant frequency of the tip/cantilever indicates the magnitude of these forces on the tip/cantilever and in turn the distance between the tip and the sample. In non-contact mode, the topographic signal is found by actively measuring the relative displacement of the tip needed in order to maintain a constant resonant frequency while moving the tip across the surface.

In dynamic mode, the lift height method can be used to measure the spatial derivative of the magnetic force on a magnetic tip after pulling the tip a chosen distance (lift height) further away from the sample plane than the reference distance, which is reached immediately after each topographic measurement. When the tip is further away from the surface (typically around 40–500 nm), the dominant force on the tip becomes the magnetic force [37]. A technique for determining sample magnetization from measurements of this force was devised by Park et al. [25]. During MFM scanning, if the tip is magnetized out-of-plane and operated in dynamic mode, it senses approximately the out-of-plane spatial derivative of the magnetic force [38]. According to Porthun et al., this signal is also proportional to the out-of-plane magnetization of the sample as follows: [37].

\[ \Delta \theta \approx \frac{dF_{\perp \text{tip}}}{dz} \propto \langle M_{\perp \text{sample}} \rangle, \]  

(2.1)
where $\Delta \theta$ is the phase shift (MFM contrast), $dF_{\perp \text{tip}}$ is the *out-of-plane* component of the force on the tip, and $M_{\perp \text{sample}}$ is the *out-of-plane* component of the sample magnetization. It follows that the individual pixels, which compose any MFM image taken with the MFM in dynamic mode and with an *out-of-plane* magnetized tip, are each proportional to the *out-of-plane* magnetization of the sample near the pixel area. By mapping out the sample magnetization at a series of points across the sample surface, the magnetic domain structure as well as the magnetization of the sample can be found.

This technique of Park *et al.* for measuring sample magnetization requires MFM images taken when the sample is at positive and negative saturation magnetization ($M_S$) in order to bound the range of potential magnetization signals [25]. In this study, the technique of Park *et al.* is modified for use without this requirement. The nature of this modified technique is described below.

The distribution of magnetizations found for the individual pixels in an MFM image can be extrapolated to produce a distribution of the magnetization states of an entire sample surface. Certain aspects of an MFM measurement must be taken into account in order to accurately interpret how the distribution of magnetization states in a single image relates to the distribution across the entire sample surface. First, the total area of the MFM image must be large enough in order to be representative of the entire sample surface. Otherwise, smaller areas may be more homogenous (i.e. a single grain) than the full sample (possibly multiple grains). This requirement is met when an image contains examples of each type of grain in the proper abundance (within a few percent of the abundance of that type of grain in the total sample). This requirement is easily met for samples with high-phase purity because any image will have the proper abundances within a few percent.

Second, the full range of possible magnetization states must be represented in an image in order to normalize the distribution. Without a means to normalize the distributions, there is no way to determine the absolute value of the magnetization of an individual pixel.
This requirement is met when enough magnetic domains are seen in an MFM image of a sample, which is known to have a strong alignment with an easy-axis, in order to match the magnetizations seen in the MFM image with each of the possible easy-axis alignments of the sample.

Third, the area corresponding to each individual measurement (pixel) must be small enough that the distribution of magnetization states is homogenous across each area. An individual pixel could not be expected to be a measurement of an area with only one magnetization state without the third requirement being met. This requirement can be met by the pixel size being significantly smaller than the size of the magnetic domains in the sample because a significant majority of the pixels would be on the interior of the domains and measure only the homogenous magnetization found within a single domain.

In this study, several MFM images are taken across the full scan area of the AFM/MFM (>40 µm) in order to determine whether the sample is homogenous enough to be represented by a smaller image. As well, the material of interest (\(\varepsilon\)-Mn\(_4\)N) is known to have strong alignment with an easy-axis with two non-degenerate \textit{out-of-plane} values \cite{39,40}. Therefore, an MFM image of \(\varepsilon\)-Mn\(_4\)N showing multiple magnetic domains can be expected to show the full range of magnetizations. Finally, the width of pixels, 0.03 µm or less for all images used to determine magnetization distributions, is significantly smaller than the width of the magnetic domains found in the \(\varepsilon\)-Mn\(_4\)N samples (>0.5 µm). After considering all three of these aspects of the MFM measurements of the high-phase purity \(\varepsilon\)-Mn\(_4\)N samples in this study, the distribution of magnetizations of the individual pixels in the MFM images used in this study can be deemed representative of the distribution of magnetization states across the entire surface of these \(\varepsilon\)-Mn\(_4\)N samples.
2.3 Spin-Polarized Scanning Tunneling Microscopy (SP-STM)

Scanning tunneling microscopy (STM) was originally introduced by Binnig et al. in 1982 [41]. Six years later, Pierce proposed the means for magnetic measurement using STM techniques known as spin-polarized STM (SP-STM) [42]. Combined together, these techniques (STM/SP-STM) have shown the potential for atomic-scale resolution of structural, electronic and magnetic features [43, 44].

The contrast seen in SP-STM, which employs magnetized tips, is related to the current across the tunneling junction of the tip and sample being enhanced or diminished due to a magnetoresistive effect. This magnetoresistive effect is caused by the tunneling junction operating as a spin valve, in which electrons [magnetically polarized by the source (tip or sample)] tunnel more favorably into a drain with the same magnetic alignment as the source. The differential conductivity found in the tunnel junction between a tip and sample scales as:

$$\frac{dI}{dV}(z, V) \propto n_t(z, V)n_s(z, V) + |m_t(z, V) \cdot m_s(z, V)| \cos(\alpha),$$

(2.2)

where $z$ is the distance between the tip and the sample, $V$ is the bias voltage between the tip and the sample, $n_t$ and $n_s$ are the local density of states (LDOS) of the tip and sample respectively, $m_t$ and $m_s$ are the vectors of the local magnetic density of states of the tip and sample respectively, and $\alpha$ is the angle between $m_t$ and $m_s$ [45].

It can be seen from Eq. 2.2, that there is a total LDOS (first term) and a magnetic LDOS (second term) contribution to the differential conductivity ($\frac{dI}{dV}$) signal. Additionally, the contrast in $\frac{dI}{dV}$ signal found between two regions of a scan, in which the state of the tip remains unchanged, is due to either differences in the total LDOS and/or magnetic LDOS of the two regions of the sample surface.

Whether the $\frac{dI}{dV}$ contrast between separate regions of a sample surface is related to the total LDOS and/or magnetic LDOS can be investigated by scanning a surface with
magnetic and non-magnetic tips with varied $\vec{H}$-field. If a $\frac{dI}{dV}$ contrast is found between separate sample regions using a non-magnetic tip (e.g. W), that $\frac{dI}{dV}$ contrast is known to be related to differences in the total LDOS $[\Delta n_s(z, V)]$ of the separate sample regions because $n_t$ is unchanged and the zero magnetic LDOS of a non-magnetic tip makes the second term in Eq. 2.2 go to zero. For this reason, if zero $\frac{dI}{dV}$ contrast is found between separate sample regions using a non-magnetic tip (e.g. W), there is no difference in the $n_s(z, V)$ of the separate sample regions. Therefore, if the $\frac{dI}{dV}$ contrast is found with a magnetic tip (e.g. Fe-coated W) and not with a non-magnetic tip, the $\frac{dI}{dV}$ contrast is related solely to the second term of Eq. 2.2 and not the first term. Further investigation of the source of a $\frac{dI}{dV}$ contrast can be performed by varying the $\vec{H}$-field between scans. If the $\frac{dI}{dV}$ contrast can be altered (i.e. flipped, added or removed) by varying the external $\vec{H}$-field, then the contrast is related to some magnetic effect.

In this study, uncoated W tips are used to investigate the LDOS of samples. As well, W tips coated with $\sim$50 monolayers (ML) of Fe are used to observe the effect of an external out-of-plane $\vec{H}$-field on the magnetization of samples. The combination of MBE grown samples with in situ SP-STM allows the study of the LDOS and magnetization of sample surfaces down to the atomic layer.

2.4 Layout of Custom-Designed Molecular Beam Epitaxy/Scanning Tunneling Microscopy (MBE/STM) Facility

The facility consists of four custom-designed chambers: (1) a growth chamber (GC); (2) an analysis chamber (AC); (3) a central distribution chamber (CDC); and (4) a load lock chamber (LLC). A top view, which illustrates the layout of these four chambers, is seen in Fig. 2.1. The four chambers are all interconnected, which allows in situ transfer of samples and tips between the chambers using a commercially available Thermionics handling system [46]. The blue dotted lines seen in Fig. 2.1, which travel through the
various chambers, indicate the paths a tip and/or sample may be transferred through the chambers. The positions at which the samples are transferred between transfer arms are labeled A through F in Fig. 2.1.

The three main chambers (GC, AC, and CDC) are all ultrahigh vacuum (UHV) chambers. The GC, which houses up to eight sources including a N-plasma source, is used for sample preparation and Fe coating of tips. The CDC serves as storage for up to four samples as well as a site for annealing W tips. The AC houses a LT-SP-STM, which employs a L-He dewar for cooling the microscope and a split coil superconducting magnet for magnetizing samples/tips. The magnet in the AC can produce an out-of-plane $\vec{H}$-field up to $\pm 45$ kOe. The LLC is a high vacuum (HV) chamber, which serves as an intermediary for sample/tip transfer between atmosphere and the three main chambers.
Figure 2.1: A top view of the custom-designed MBE/STM system layout. All three main chambers (growth, analysis and central distribution) are depicted along with the load lock chamber. Each position of sample transfer is labeled A through F [4].

Figures 2.2(a) and (b) show the arrangement of the *in situ* RHEED system and the MBE system, respectively, within the GC. The RHEED gun produces an electron beam with an energy of 20 keV. The RHEED gun and RHEED screen are positioned on opposite sides of the GC so that the RHEED beam can strike the sample at a glancing angle of 1° and then continue to the RHEED screen. The diffraction pattern formed out of the RHEED
beam following the interaction of the beam with the sample is illuminated upon collision with the phosphor-coated RHEED screen. The growth stage allows 360° rotation of the sample around the out-of-plane axis of the sample. This allows the observation of the in-plane crystal structure of the sample surface along all in-plane directions using RHEED.

The sources of the MBE system are composed of up to seven elemental evaporators and one N-plasma source positioned around the bottom of the GC. The MBE sources all face the growth stage, which holds the substrate at the center of the GC. The Fe effusion cell is positioned opposite from position C in the GC as seen in Fig. 2.1. For the purpose of coating the tips with Fe, the tips may be placed at position C in order to put the tips in the path of the Fe flux.

Figure 2.2: N-plasma MBE growth system. (a) Illustration of the RHEED measurement geometries with respect to the growth stage. (b) Illustration of the MBE source geometries with respect to the growth stage [4].
2.5 First Results from this MBE/STM Facility

In order to calibrate this MBE-LT-STM facility and establish the limits in precision of sample growth and analysis of the facility, an experiment on GaN was carried out using this facility. In the experiment, a Ga-rich GaN(000$\bar{1}$) sample with a c(6×12) surface reconstruction is grown on an Al$_3$O$_2$(0001) substrate and analyzed with in situ RHEED and STM. This sample is selected as the calibration sample for several reasons: (1) the Ga-rich surface is metallic/highly conductive (a desirable trait for STM scanning); (2) the higher-order (Ga-rich) reconstructions are relatively easy to obtain by MBE growth; and (3) much is known about these N-polar GaN reconstructions. Ga-rich GaN(000$\bar{1}$) surfaces have been studied using RHEED and STM by Smith et al. previously [47, 48, 24]. Therefore, these samples are useful for x-y scanner calibration using the known structure of the surface reconstruction [c(6×12) where $a = 3.19$ Å] and for z calibration using the known step height ($c = 2.59$ Å).

The RHEED images, which are all taken along the [1$\bar{1}$0]-direction, in Fig. 2.3 are used to monitor the growth of a GaN(000$\bar{1}$) sample with a c(6×12) surface reconstruction on an Al$_3$O$_2$(0001) substrate. A discussion of RHEED image interpretation is found in Appendix A. The inset in the bottom left of Fig. 2.3(a) corresponds to the RHEED image of an Al$_3$O$_2$(0001) substrate before cleaning and annealing the substrate with N-plasma at $T = 700$ °C for ∼1 hour. As seen in the main image of Fig. 2.3(a), the streaky RHEED pattern taken after annealing indicates these cleaning parameters prepare a substrate, which is sufficiently flat and well-ordered for MBE growth. The RHEED pattern shown in Fig. 2.3(b) demonstrates the initial nucleation phase of the low temperature ($T = 620$ °C) GaN buffer layer. The absence of RHEED symmetry in Fig. 2.3(b) is typical in low temperature buffer layers used for GaN(000$\bar{1}$) growth and has been associated with these buffer layer being polycrystalline [49]. The streaky RHEED pattern in Fig. 2.3(c), taken at $T = 700$ °C, indicates the formation of a high-quality, low temperature GaN buffer layer. Subsequent
high temperature ($T = 700 \, ^{\circ}\text{C}$) growth of GaN results in a smooth Ga-rich GaN surface. After cooling the high-quality grown surface to temperatures below $\sim 300 \, ^{\circ}\text{C}$ and down to room temperature, the reconstruction streaks appear, and these streaks are clearly seen in the RHEED pattern taken at $T = 80 \, ^{\circ}\text{C}$ [shown in Fig. 2.3(d)]. In Fig. 2.3(d), the first Laue zone $3\times$ streaks as well as the slightly weaker first Laue zone $6\times$ streaks are clearly seen. The second Laue zone shows the short streak doublets having also $3\times$ spacing, centered at the $\frac{1}{6}$th, $\frac{3}{6}$th, and $\frac{5}{6}$th positions. This RHEED pattern is characteristic of the c(6×12) reconstruction [47].

Figure 2.3: Real-time RHEED patterns of wurtzite GaN(000¯1) growth on sapphire, taken along [1120]; (a) Sapphire substrate annealed with N-plasma at a high temperature. Inset is the sapphire substrate before annealing; (b) Initial stage of the low temperature GaN buffer layer; (c) At higher temperature after the growth of the low temperature GaN buffer layer; (d) Smooth GaN surface cooled toward room temperature.
The STM data shown in Figs. 2.4 and 2.5 are taken on the in situ grown GaN c(6×12) surface at L-He temperatures. Figure 2.4 shows an atomic resolution ~100 × 100 nm STM image of that surface. Epitaxially smooth terraces on GaN and atomically resolved c(6×12) reconstructions consisting of an arrangement of Ga adatoms are clearly visible in this image. The Ga adatoms are arranged into pairs, and these pairs repeat along parallel rows, with pairs at an angle of ~30° to the rows. Distinct domain boundaries are easily visible. The domains at two sides of the boundary have orientations that are 120° away from each other, as expected for hexagonal GaN, having threefold symmetry. It is also possible to observe brilliant step-edge structures all along the step edges. As well, it is possible to observe even finer scale features of the c(6×12) compared to what has previously been published for this surface, especially as voltage bias is varied [48]. Clearly, the image quality is very high.
Figure 2.4: STM image of c(6×12) reconstructions on wurtzite gallium nitride GaN(000\overline{1}), \(V_s = +1.00\ \text{V}, I_r = 0.1\ \text{nA}\), the system is cooled with LHe.
Figure 2.5: (a) Raw data of a zoomed-in region within Fig. 2.4; (b) Height profile of line 1 drawn on a); (c) Height profile of line 2 drawn on a). This line corresponds to the direction of the scan.
Figure 2.5(a) shows a further zoomed-in image of N-polar GaN c(6×12) surface, and height profiles along two lines are shown in Figs. 2.5(b) and (c). Along the high angle line (green), which is orthogonal to the c(6×12) rows and closest to the slow scan direction, the corrugation is measured to be \( \sim 1.0 \, \text{Å} \); the noise level is observed as variations from the ideal corrugation line of \( \sim 0.1 \) – \( 0.2 \, \text{Å} \). Along the fast scan direction (blue line), the overall corrugation amplitude is measured as \( \sim 1.1 \, \text{Å} \); the noise level is more difficult to measure here, but less than \( \sim 0.1 \, \text{Å} \). Certainly, the corrugations on this surface are large, but noise levels are very low, leading to the very high image quality. Further, the surface was scanned for intervals of 3–5 days without the observation of noticeable surface contaminants, which indicates an extremely clean UHV environment suitable for persistent high-quality surface measurements.

The first results from the molecular beam epitaxy low temperature scanning tunneling microscopy (MBE-LT-STM) system are presented in this section. The facility is demonstrated to be capable of growing samples with controlled accuracy down to the single atomic layer. The successful atomic-scale imaging of the GaN c(6×12) surface at L-He temperatures is achieved. The noise levels observed are low enough to allow for the acquisition of high-quality STM data. The x-y-z scanner calibration of the facility is achieved. An extremely clean UHV environment is maintained for studies, which extend for multiple days, of individual samples. These parameters are sufficient for the purpose of continued studies on the magnetic and interfacial properties of metal-rich Mn\textsubscript{x}N\textsubscript{y} phases and GaN reconstructions. These calibration results correspond to the results section of the construction paper, which describes the facility used in this study [4].
3 **HIGH PHASE-PURITY GROWTH OF $\varepsilon$-Mn$_4$N ON MgO(001)**

This chapter includes the work from an already published paper discussing the growth of $\varepsilon$-Mn$_4$N [50]. Single phase $\varepsilon$-Mn$_4$N thin films are grown on MgO(001) using molecular beam epitaxy. The films are identified and characterized using reflection high-energy electron diffraction, x-ray diffraction, back scattered electron scanning electron microscopy, atomic/magnetic force microscopy and Rutherford backscattering spectrometry. These films are found to be highly smooth with root-mean-squared roughnesses 4.1 nm and below. The quality of $\varepsilon$-Mn$_4$N grown is strongly dependent on substrate temperature during growth. Epitaxial growth of substantial grains composed of the antiferromagnetic $\eta$-phase Mn$_3$N$_2$ side by side with ferrimagnetic $\varepsilon$-phase grains is observed when temperature during initial nucleation is below 480 °C. Ising domains isolated within areas roughly 0.5 to 3.7 µm across are observed in the ferrimagnetic $\varepsilon$-phase grains of samples consisting of a mix of $\eta$- and $\varepsilon$-phase grains. Magnetic domains following semi-continuous paths, which are 0.7 to 7.2 µm across, are observed in single phase $\varepsilon$-Mn$_4$N.

3.1 **Introduction**

Transition metal (TM) nitrides such as (Mn,Fe,Co)$_x$N$_y$ have been demonstrated to possess a wide range of magnetic properties with tunability between different types of magnetism (e.g. ferromagnetic, antiferromagnetic, non-magnetic, or ferrimagnetic) via phase control of each material [1, 51, 52, 53]. As well, at least one phase ($\varepsilon$-Mn$_4$N, $\alpha$-Fe$_x$N$_y$, $\alpha''$-Fe$_{16}$N$_2$, and $\gamma$-Co$_3$N) of each of these three TM nitrides has shown perpendicular magnetic anisotropy (PMA) and consequently suitability for spin injection contacts [54, 55, 56, 57]. These two shared characteristics of tunable magnetic properties and suitability for spin injection contacts among these three TM nitrides suggest potential applications in giant magnetoresistance (GMR) devices.
Mn$_x$N$_y$ possesses three antiferromagnetic phases (θ-, η- and ζ-phase) and a single ferrimagnetic phase (ε-phase) [14]. The ε-phase exhibits PMA with a highly polarizable 
_{out-of-plane} easy-axis alignment [54]. In agreement, theoretical calculations on ε-Mn$_4$N suggest the material has a high spin injection efficiency [58, 59, 60].

In the past, reflection high-energy diffraction (RHEED) and X-ray diffraction (XRD) have served as the primary means for identifying the phase purity of ε-Mn$_4$N samples [1, 12, 20, 54, 61, 62]. However, phase impurities have been observed in epitaxially grown ε-Mn$_4$N when RHEED or XRD indicated otherwise [1, 63]. For this reason, an experiment determining the effect of growth temperature on phase purity of ε-Mn$_4$N grown on MgO(001) is of interest.

In a growth study of ε-Mn$_4$N, the growth is characterized using RHEED, XRD, and AFM/MFM; and then the growth temperature is used to control the phase purity. AFM/MFM measurements determine a dependence of magnetic domain shape on grain shape. Following initial nucleation at a lower growth temperature (450 °C) favoring mixed phase (η- and ε-phase) growth, η- and ε-phase grains are observed to continue to grow side by side at a higher growth temperature (480 °C), which favors high-phase purity ε-phase growth during initial nucleation. In this way, the initial nucleation step is found to be crucial to the phase purity of Mn$_x$N$_y$ samples.

3.2 Procedure

All samples were prepared in a custom designed ultra-high vacuum molecular beam epitaxy system [4]. The Mn$_x$N$_y$ samples were grown on MgO(001) substrates. Beforehand, the substrates were cleaned ex situ using solvent, first with acetone and then with isopropyl-alcohol. Additional in situ cleaning of the substrate was performed by annealing at a temperature of 1000 °C with nitrogen plasma incident for ~1 hr. Manganese flux was provided by a custom designed effusion cell operated at temperatures of ~1200 °C, whereas
N flux was supplied by an RF N Plasma Source (SVT Associates) with a forward power of 450 W and N₂ as the source gas. The Mn flux is measured using a quartz crystal thickness monitor giving readings in Å/s, while the effective N flux is determined by finding the crossover point between Ga- and N-rich GaN growth [23]. In total, ten MnₓNᵧ samples were grown using Mn fluxes in the range of \((0.4−3) \times 10^{14} \text{atoms cm}^{-2}\text{s}^{-1}\) and effective N fluxes in the range of \((0.5−1.4) \times 10^{14} \text{atoms cm}^{-2}\text{s}^{-1}\).

RHEED is actively used in situ during growth with a 20 keV incident electron beam energy in order to monitor the phase of growth based on the observation of phase specific surface structure/reconstruction; this is determined by measuring, for example, the characteristic RHEED streak spacings and from these determining the in-plane lattice constant(s) by means of the RHEED calibration. The calibration is performed for each growth using the MgO substrate post-annealing streak spacings as a reference. XRD is applied ex situ employing Cu Kα x-rays in order to determine the bulk crystal structure normal to the substrate surface including atomic spacings prevalent in the samples. Relative Mn concentration between different crystal grains is determined using back scattered electron scanning electron microscopy (BSE-SEM). Atomic/magnetic force microscopy is performed using a Park Scientific CP AFM/MFM head retrofitted with a controller system by Anfatec Inc., which is operated ex situ to obtain information about the topographical and magnetic properties of the samples. The MFM is performed in phase contrast mode, giving a picture of the stray field map of the samples at a certain height z above the sample plane. Analysis of the obtained stray field maps is used to infer sample domain structure.

### 3.3 Growth Summary

Variation of the sample growth parameters in this study enabled the synthesis of qualitatively three different types of MnₓNᵧ phase samples including approximately pure phase samples (ε) and two types of mixed-phase samples (η + ε with and without strain
on the $\varepsilon$-phase grains). Nucleation of $\eta$-phase is typically achieved at sample temperatures up to 450 °C; whereas, the nucleation of $\varepsilon$-phase can be achieved at sample temperatures above 450 °C. The types of phases grown following nucleation do not show this same dependence on growth temperature, but rather are primarily dependent on the composition of the originally nucleated phases.

Figure 3.1(a) shows the RHEED pattern characteristic of all of the post-annealing MgO substrates on which each of the three types of samples were grown. The bright uniform streaks together with the sharp Kikuchi lines within the characteristic RHEED pattern of these substrates shows that the substrate surface was highly-smooth, well-ordered MgO suitable for RHEED calibration. Figures 3.1(b) to (d) and 3.2 present the RHEED and XRD patterns, respectively, for the three types of samples to be focused on in this study with all associated values tabulated in Table 3.1. A discussion of the RHEED patterns associated with single phase $\varepsilon$-Mn$_4$N(001) and $\eta$-Mn$_3$N$_2$(010) surfaces can be found in Appendix A. The presentation begins with a discussion of the diffraction (RHEED, XRD) data for the lower nucleation/growth temperature ($\eta + \varepsilon$) mixed phase (sample 3.A), the higher nucleation/growth temperature ($\varepsilon$) sample (sample 3.B) and then the higher growth temperature following a lower nucleation temperature ($\eta + \varepsilon$) mixed phase sample (sample 3.C).
Figure 3.1: RHEED taken in situ along the [100]-direction relative to the MgO substrate. (a) Taken on an annealed MgO substrate. (b) to (d) RHEED corresponding to Mn$_x$N$_y$ samples; (b) nucleated/grown at 450 °C, (c) nucleated/grown at 480 °C, and (d) nucleated at 450 °C then grown at 480 °C.
Figure 3.2: XRD taken *out-of-plane* for Mn$_x$N$_y$ samples. (a) Nucleated/grown at 450 °C. (b) Nucleated/grown at 480 °C. (c) Nucleated at 450 °C then grown at 480 °C.
Table 3.1: Comparisons of out-of-plane XRD and in-plane RHEED data with the values expected from literature for \( \eta \)- and \( \varepsilon \)-phase samples [1]. All RHEED measurements were taken along the MgO [100]-direction.

<table>
<thead>
<tr>
<th>Growth plane (h k l)</th>
<th>Observed (Å)</th>
<th>Expected (Å)</th>
<th>Observed (Å)</th>
<th>Expected (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRD out-of-plane</td>
<td>RHEED in-plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \varepsilon )-phase</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(0 0 2)</td>
<td>3.86±0.01</td>
<td>3.86</td>
<td>3.88±0.01</td>
<td>3.86</td>
</tr>
<tr>
<td><strong>Mixed phase (( \eta )-phase &amp; ( \varepsilon )-phase) ( T_{growth} = 450 , ^\circ C )</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>( \eta )-(0 2 0)</td>
<td>obscured by 4.213 MgO peak</td>
<td>4.21</td>
<td>4.04/4.21 or 4.13 avg.</td>
<td>3.97±0.02</td>
</tr>
<tr>
<td>( \varepsilon )-(0 0 2)</td>
<td>3.87±0.01</td>
<td>3.86</td>
<td>3.86</td>
<td>3.86</td>
</tr>
<tr>
<td>**Average of ( \eta )-(0 2 0) &amp; ( \varepsilon )-(0 0 2) **</td>
<td></td>
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<tr>
<td>( \eta )-(0 2 0) &amp; ( \varepsilon )-(0 0 2)</td>
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<tr>
<td><strong>Mixed phase (( \eta )-phase &amp; ( \varepsilon )-phase) ( T_{growth} = 480 , ^\circ C )</strong></td>
<td></td>
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<tr>
<td>( \eta )-(0 2 0)</td>
<td>obscured by 4.213 MgO peak</td>
<td>4.21</td>
<td>4.04/4.21 or 4.13 avg.</td>
<td>3.86±0.02</td>
</tr>
<tr>
<td>( \varepsilon )-(0 0 2)</td>
<td>3.83±0.01</td>
<td>3.86</td>
<td>3.86±0.02</td>
<td>3.86</td>
</tr>
</tbody>
</table>

The presentation finishes with a discussion of the microscopy data (AFM, MFM, BSE-SEM) of samples 3.A, 3.B and then 3.C. The requirement of a substrate temperature over 450 \(^\circ C\) for growth of sample 3.B (\( \varepsilon \)-phase) is consistent with Yang et al., in which at 450 \(^\circ C\) the growth of high purity \( \varepsilon \)-phase was unobserved [1]. Samples in this project were not intentionally annealed for any significant times, although it has been shown that \( \theta \), \( \eta \), \( \zeta \),
and ε (up to as high as 4:1 Mn:N) can be achieved by successively increasing annealing temperatures which results in increasing levels of N loss [64].

3.4 Crystallography

The RHEED and XRD taken from the 450 °C sample with strained ε-Mn₄N grains (sample 3.A) are shown in Fig. 3.1(b) and Fig. 3.2(a) respectively. Figure 3.1(b) shows 1st order streaks and faintly visible half-order streaks, with the 1st order streak spacing corresponding to an a-spacing of 3.97±0.02 Å in the lattice. This value agrees well with an average (3.99 Å) between values for ε-phase (3.86 Å) and η-phase (4.04/4.21 Å), thus indicating a mixture of η- and ε-phases [14]. As well, the faint half-order streaks indicate a partial occupation of ε-phase at the surface of sample 3.A. It should be noted that the same a-spacing was reported by Yang et al. for a sample reported as ε-phase with some η-phase impurity [1]. As shown in Fig. 3.2(a), XRD finds 5 significant peaks within the 2θ range of 35−50 degrees, including a substantial ε-phase 002 peak occurring at 2θ = 47.00°, a very small ζ-phase 101 peak, a barely visible ζ-phase 002 peak, a large MgO 002 peak (split peak due to saturation of the detector), and a small intensity MgO 111 peak (coming from the back-side of the substrate). The ε-phase 002 peak is slightly shifted compared to the expected, giving a 3.87±0.01 Å c-spacing, while the η-phase Mn₃N₂ 020 peak is indistinguishable from the MgO 002 peak. A perspective view of the η-Mn₃N₂ and ε-Mn₄N structures can be seen, in which (010) and (001) Mn planes are indicated, in Fig. 3.3(a-b) respectively.
Figure 3.3: (a)-(b) Models corresponding to values found in literature of each of the two phases grown shown in perspective view [1]. The images correspond to the phases as follows (a) $\eta$-phase with a (010) Mn-plane (b) $\varepsilon$-phase with a (001) Mn-plane.

A substrate temperature of 480°C was used to grow the $\varepsilon$-Mn$_4$N sample (sample 3.B); with the [100] surface reconstruction demonstrated by RHEED and the bulk composition determined from XRD. First order [100] RHEED streak spacings are measured in Fig. 3.1(c), resulting in a deduced (after calibration) $3.88\pm0.01$ Å $a$-spacing. Clearly visible half-order streaks agree with the accepted structure (4 Mn in fcc structure with a single N at the body center) by showing a 2× periodicity perpendicular to the [100]-direction [65]. This 2× periodicity is due to the non-degeneracy between face-centered and corner Mn atoms doubling the distance between degenerate Mn atoms along this direction. The appearance of faint Kikuchi lines suggests a high quality, flat, and well-ordered $\varepsilon$-phase surface. The XRD pattern for sample 3.B shown in Fig. 3.2(b) contains the same set of XRD peaks as for sample 3.A, but with strongly increased $\varepsilon$-phase 002 peak intensity and a significant reduction in the $\zeta$-phase peaks. From the $\varepsilon$-phase peak position, a $c$-spacing of
3.86±0.01 Å is determined. The 3.88 Å $a$-spacing and 3.86 Å $c$-spacing, as determined by RHEED and XRD respectively, both agree well with the expected value for $\varepsilon$-phase (3.86 Å) [14].

A substrate temperature of 450°C was used during the initial nucleation (15±2 nm) of a mixed phase sample with unstrained $\varepsilon$-Mn$_4$N grains (sample 3.C). Then, a growth temperature of 480°C was used to grow the rest of this sample; with the $[100]$ surface reconstruction demonstrated by RHEED and the bulk composition determined from XRD. First order $[100]$ RHEED streak spacings are measured in Fig. 3.1(d), resulting in a deduced (after calibration) 3.86±0.02 Å $a$-spacing. In addition with clearly visible half-order streaks, this matches the RHEED from sample 3.B seen in Fig. 3.1(c). The appearance of faint Kikuchi lines suggests a high quality, flat, and well-ordered $\varepsilon$-phase surface. However, the XRD pattern for this sample shown in Fig. 3.2(c) contains the same set of XRD peaks as samples 3.A and 3.B, but with a much weaker $\varepsilon$-phase 002 peak intensity than samples 3.A and 3.B. From the $\varepsilon$-phase peak position, a $c$-spacing of 3.83±0.01 Å is determined. The 3.86 Å $a$-spacing and 3.83 Å $c$-spacing, as determined by RHEED and XRD respectively, both agree well with the expected value for $\varepsilon$-phase (3.86 Å) [14].

### 3.5 Morphology and Magnetism

AFM, MFM and BSE-SEM images from a mixed phase sample nucleated/grown at 450 °C (sample 3.A) are shown in Figs. 3.4 and 3.5. These results reveal the growth of a smooth surface consisting of a mix of mostly $\varepsilon$- and $\eta$-phase domains. Two distinct morphologies, a smaller and larger cross-hatching, are seen in the AFM image in Fig. 3.4(a). These cross-hatchings consists of islands overlapping and elongated along the two degenerate $[110]$-directions, which is consistent with the cubic structure of the material. A Fast Fourier Transform (FFT) is taken for each of these cross-hatched morphologies. These FFT both exhibit a ring-shape. A cross-section through the center of a ring-shaped
FFT consists of a double peak, and the average of the two widths at 1/e of the maxima provides the range of distances typically found along a particular direction within an image [66]. This analysis is performed on the small and large cross-hatching to determine a range of the width and length of the islands in each. The range of the width and length of the islands found in the small cross-hatching are 0.6 to 1.0 µm and 0.4 to 7.5 µm respectively. The range of the width and length of the islands found in the large cross-hatching are 0.3 to 1.8 µm and 1.8 to 13.3 µm respectively. Unlike the cross-hatching, the edges of the grains follow irregular paths without any particular alignment(s).
Figure 3.4: Microscopy data of the mixed phase sample nucleated/grown at 450 °C. (a) AFM image showing the domain boundary between an ε-phase domain left and an η||-phase domain right. (b) MFM image of the same area shown in a). (c) Topographic line profile (orange dotted) and magnetic line profile (green solid) seen in a) and b) respectively.
Figure 3.5: Microscopy data of the mixed phase sample nucleated/grown at 450 °C. (a) Larger scale AFM image showing adjacent domains of the two phases. (b) A 3D SEM topographic image overlaid with a heat map of Mn concentration.

The MFM image in Fig. 3.4(b) shows the magnetic contrast corresponding to the area shown in Fig. 3.4(a). The dotted and solid line profiles, showing topographic and magnetic signals respectively, in Fig. 3.4(c) indicate that the two different types of cross-hatched morphologies correspond to regions having different magnetic properties. From the magnetic line profile (solid) the magnetic domains are roughly half a micrometer across. In agreement, an FFT analysis of sample 3.A following the procedure of Bai et al. gives
a range of magnetic domain widths of 0.25 to 1.62 µm [66]. The up-to-1.62 µm wide domains are therefore having a flat 2D-like shape given the film thickness of 0.2 µm.

The magnetic domains in the larger cross-hatched morphology of sample 3.A are identified as "pancakelike" Ising domains by the associated magnetic domain structure (isolated and flattened) [67]. The magnetic domains appear to be partially aligned with the same two degenerate [110]-directions as the two cross-hatching morphologies. Conversely, the areas having smaller cross-hatched morphology do not reveal any observable magnetic contrast.

The presence of magnetic domains identifies the larger cross-hatching as either ferrimagnetic or ferromagnetic. Meanwhile, the indiscernible magnetic contrast identifies the smaller cross-hatching as either antiferromagnetic or non-magnetic. Ferrimagnetism and antiferromagnetism are the only two types of magnetism found in the Mn$_x$N$_y$ system [14]. Therefore, the larger and smaller cross-hatched regions are identified as being ferrimagnetic and antiferromagnetic respectively. The ferrimagnetic domains are readily identified as ε-Mn$_4$N because this is the only ferrimagnetic phase of Mn$_x$N$_y$ and there is a sufficiently large ε-phase 002 XRD peak to explain the fraction of the surface containing ferrimagnetic domains (roughly half).

Larger AFM images such as Fig. 3.5(a) find that the antiferromagnetic grains are consistently raised above the ferrimagnetic domains. An example of this height difference is shown in the line profile (dotted) in Fig. 3.4(c), in which there is a rise of roughly 5 nm during the transition from ferrimagnetic to antiferromagnetic areas. These raised antiferromagnetic areas are identified to be Mn-poor compared to the lower lying grains using BSE-SEM as seen in Fig. 3.5(b), in which a heat mapping of Mn concentration is laid over the 3-D topography of a 190 µm area.

Due to the raised grains being observed with AFM/MFM in an abundance covering roughly half the surface, a corresponding XRD peak would be expected to occur with a
number of counts of the same order of magnitude as the ε-phase 002 peak. However, the only peaks in Fig. 3.2(a) aside from the ε-phase peak are two ζ-phase peaks, which even together are too small to explain the raised grains with lower Mn concentrations occupying roughly half the surface. Therefore, we can identify the raised grains as having \( \eta\text{-Mn}_3\text{N}_2\text{(010)} \) structure because this is the only known Mn\(_x\)N\(_y\) structure with a peak that would be completely obscured by another, specifically the MgO 002 peak. Additionally, the observations that the raised grains are antiferromagnetic and have a lower Mn concentration agree with an \( \eta\)-phase identification of the antiferromagnetic grains. Furthermore, this is consistent with the RHEED data from Fig. 3.1(b), including a diminished half-order streak intensity and a 1st order spacing the average of eta- and epsilon-phase spacings, supporting a mix of \( \eta\)- and \( \varepsilon\)-phase grains for this sample (3.A).

Roughness analysis of the 30 \( \mu\text{m} \) image in Fig. 3.5(a) indicates an RMS roughness of 3.4 nm with a height range of 19.8 nm across the surface. The origin of the roughness comes mainly from the height difference between \( \eta\)- and \( \varepsilon\)-phase regions. The relatively low RMS roughness and height range are favorable values for potentially patterning a mix of antiferromagnetic and ferrimagnetic domains on a surface. It should be noted, there are two morphologies, cross-hatched and disordered (circled), observed within the \( \eta\)-phase regions in Fig. 3.5(a) compared to the single morphology seen within the \( \varepsilon\)-phase regions. This lack of morphological uniformity is likely explained by the Mn-rich growth conditions, which are not ideal for \( \eta\)-phase growth (Mn:N ratio significantly greater than the 0.87 identified by Yang et al.) [1].

AFM/MFM results for an \( \varepsilon\)-phase sample (sample 3.B) are shown in Fig. 3.6, which presents the growth of a highly smooth surface. The 20 \( \mu\text{m} \) AFM image shown in Fig. 3.6(a) demonstrates an RMS roughness of 0.33 nm with a height range of 1.52 nm. The morphology of the \( \varepsilon\)-phase sample (sample 3.B) can be seen more clearly in Fig. 3.6(c). This morphology consists of exceptionally flat square-shaped terraces (generally between
0.1 to 0.5 \( \mu m \) in width). The line profile (dotted) in Fig. 3.6(d) further illustrates a highly smooth surface with a small height variation, less than 1.5 nm.

Figure 3.6: (a) Larger scale AFM image of epsilon surface (b) MFM image over the same area shown in a) (c) Smaller scale AFM image of the epsilon surface (d) Topographic (orange dotted) and magnetic (green solid) line profiles shown in a) and b)

The MFM image corresponding to Fig. 3.6(a) is shown in Fig. 3.6(b), which demonstrates the magnetic domains characteristic of sample 3.B. The sample 3.B magnetic domains do not show any crystalline alignment. It is evident from the magnetic line profile (green solid) in Fig. 3.6(d) that the sample 3.B magnetic domains are from roughly 0.5 to 5 \( \mu m \) across. In agreement, an FFT analysis of sample 3.B following the procedure of Bai et
*al.* gives a range of magnetic domain widths of 0.7 to 7.2 µm [66]. The up-to-7.2 µm wide magnetic domains are relatively 2-dimensional given the only 0.3 µm thick film. Many of the magnetic domains are laid out in paths, which are continuous across the entire image shown in Fig. 3.6(b).

The sample 3.B magnetic domain shape (0.7 to 7.2 µm across and laid out in semi-continuous paths) is in contrast to the sample 3.A magnetic domain shape (roughly half a micrometer across and isolated). There are multiple potential causes for the ε-phase in sample 3.A having smaller magnetic domains than sample 3.B, including the following: the smaller ε-phase grain size and/or strain induced by the adjacent η-phase grains affecting the domain size [18, 20]. Additionally, the RMS roughness and height range of sample 3.B (0.33 and 1.52 nm respectively) are both an order of magnitude below those of sample 3.A (3.4 and 19.8 nm respectively). Clearly, an ε-phase sample with greatly enhanced crystal phase purity can be grown when the nucleation and growth temperature is raised to 480 °C.
AFM/MFM images from a mixed phase sample nucleated at lower temperature and grown at higher temperature (sample 3.C) are shown in Fig. 3.7. Two distinct morphologies, flat square terrace and crater-like, are seen in the AFM image in Figs. 3.7(a).
The flat square terrace morphology matches the morphology of a high phase purity $\varepsilon$-Mn$_4$N sample (3.B). The grains with a crater-like morphology are found to be on the order of 10 $\mu$m across and to bow roughly 10 nm below the surface of the flat square terrace morphology. The edges of the grains show alignment with the [100]- and [110]-directions, which is consistent with the tetragonal structure of the material. The 20 $\mu$m $\times$ 30 $\mu$m AFM image shown in Fig. 3.7(a) demonstrates an RMS roughness of 4.1 nm with a height range of 50 nm. The origin of the roughness is due mainly to the height difference from the crater-like morphology bowing down below the surface of the flat square terrace morphology. The relatively low RMS roughness is a favorable value for potentially patterning a mix of antiferromagnetic and ferrimagnetic domains on a surface.

The MFM image in Fig. 3.7(b) shows the magnetic contrast corresponding to the area shown in Fig. 3.7(a). The dotted and solid line profiles, showing topographic and magnetic signals respectively, in Fig. 3.7(c) indicate that the two different types of morphologies (square terrace and crater-like) correspond to regions having different magnetic properties. From the magnetic line profile (solid) the magnetic domains are roughly 1 micrometer across. In agreement, an FFT analysis of sample 3.A following the procedure of Bai et al. gives a range of magnetic domain widths of 0.7 to 3.7 $\mu$m [66]. The up-to-3.7 $\mu$m wide domains are therefore having a flat 2D-like shape given the film thickness of 0.3 $\mu$m.

The magnetic domains in the flat square terrace morphology of sample 3.A are identified as "pancakelike" Ising domains by the associated magnetic domain structure (isolated and flattened) [67]. Conversely, the areas having crater-like morphology do not reveal any observable magnetic contrast. Near some of the edges of the crater-like morphology, additional regions in small abundance show a small amount of magnetic contrast.

The phase composition of the flat square terrace and crater-like morphologies can be concluded when comparing the diffraction and microscopy findings for the mixed phase
sample grown at lower temperature (3.A) with that of the mixed phase sample grown at higher temperature (3.C). The presence of magnetic domains with a corresponding ε-002 XRD peak identifies the flat square terrace morphology in sample 3.C as ε-Mn$_4$N. These ε-Mn$_4$N grains have far less strain than the ε-Mn$_4$N grains of the sample grown at lower temperature (450 °C) based on RHEED (3.86±0.02 Å) and XRD (3.83±0.01 Å) measurements. The morphology of these unstrained grains is the same morphology observed for the high phase purity ε-Mn$_4$N sample (3.B), which is also unstrained and grown at T > 450°C. Therefore, this flat square terrace morphology is consistent with unstrained ε-Mn$_4$N grown at T > 450°C.

The indiscernible magnetic contrast and lack of identifying XRD peak (only MgO and ε-Mn$_4$N peaks in XRD) indicates the crater-like morphology is composed of η-Mn$_3$N$_2$(010). The bowing observed in the crater-like morphology may be due to in-plane strain. In agreement with this possibility, the unstrained in-plane lattice of η-Mn$_3$N$_2$(010) is significantly larger than that of ε-Mn$_4$N (4.21 Å and 4.03 Å spacings compared to 3.86 Å) [1]. Therefore, the η-Mn$_3$N$_2$(010) grains are expected to be under in-plane compressive strain because the RHEED measurement shows a 3.86 Å in-plane spacing. The small magnetic contrast in some of the edges of the crater-like domains may be due to ε-Mn$_4$N growing over parts of the η-Mn$_3$N$_2$(010) in a few instances. Despite changing growth conditions after nucleation to conditions, which produced high purity ε-phase samples, the growth of η-phase grains was found to persist for hundreds of nanometers. Clearly, controlling the growth conditions during nucleation is critical for controlling the phase purity of samples because a mix of grains will propagate through the entire film, even if growth conditions are non-ideal for some or all of the grains.

The square terrace morphology being consistent with unstrained ε-Mn$_4$N and the crater-like morphology being shaped by in-plane strain suggests the differences in surface morphology between the three types of samples (3.A, 3.B and 3.C) are strain induced.
Additionally, an abundance of isolated magnetic domains is found in the $\varepsilon$-Mn$_4$N grains of both samples 3.A and 3.C, which are strained and unstrained respectively. In contrast, semi-continuous domains are present in the unstrained $\varepsilon$-Mn$_4$N 3.B sample. Clearly, the change in magnetic domain shape is influenced much more significantly by grain shape compared to strain. In turn, this suggests that the most significant factor for determining magnetic domain shape in $\varepsilon$-Mn$_4$N is grain shape.

3.6 Conclusions

In conclusion, beyond the Mn:N flux ratio, a high dependence on substrate growth temperature is reported. Increasing the nucleation and growth temperatures from 450 to 480 °C results in single phase $\varepsilon$-Mn$_4$N growth without the significant incorporation of $\eta$-phase grains as found in 450 °C growths. Growth of $\varepsilon$- and $\eta$-phase grains side by side under growth conditions favoring $\varepsilon$-phase growth demonstrates that the control of growth parameters during initial nucleation is especially important. Side by side growth of $\varepsilon$- and $\eta$-phases is of interest as a method for the organization of magnetic properties within a sample. However, a method for controlling the nucleation sites of $\varepsilon$- and $\eta$-phases would still need to be determined in order to controllably pattern the magnetism. The vertical direction of this side by side growth indicates the Mn$_x$N$_y$ has greater suitability for lateral organization compared to vertical layering.
4 PERPENDICULAR MAGNETIC ANISOTROPY OF $\varepsilon$-Mn$_4$N ON MgO(001)

This chapter includes the work from a paper under review/revision discussing the perpendicular magnetic anisotropy (PMA) observed in $\varepsilon$-Mn$_4$N ultrathin/thin films. Single phase $\varepsilon$-Mn$_4$N thin and ultrathin films are grown on MgO(001) using molecular beam epitaxy. Reflection high-energy electron diffraction and out-of-plane x-ray diffraction measurements are taken for each sample in order to determine the in- and out-of-plane strain for each sample. Vibrating sample magnetometry (VSM) and superconducting quantum interference device (SQUID) measurements, which are performed on the thin and ultrathin films respectively, are used to plot the magnetization of each sample versus both in- and out-of-plane $\vec{H}$-fields.

After accounting for the shape anisotropy energy due to a single dipole and the strain anisotropy energy, these $\mathbf{M}$-$\vec{H}$ measurements show the presence of a large component of out-of-plane perpendicular magnetic anisotropy energy ($K_{Sz} = 0.8$ to $4.9\: \text{Merg cm}^{-3}$), which maintains a negative linear relationship with sample thickness (310 to 9 nm). MFM measurements reveal that the sample surfaces each have a surface-localized magnetic polarization ($P_S = \frac{N_1-N_2}{N_1+N_2} = 21.6\%$ to $81.8\%$) when the net sample has zero magnetic polarization.

The simultaneous presence of surface-localized magnetic polarization and absence of net magnetic polarization are explained by Ising domains with opposing magnetic polarization partially overlapping out-of-plane. These overlapping Ising domains result in the magnetic polarization local to the surface being cancelled out by an equal, but opposite, magnetic polarization local to the base. This overlap of magnetic dipoles demands the consideration of a model in which the molecular field interaction between adjacent dipoles is taken into account. This leads to a proposed model for shape anisotropy, which takes into
account a second order (dipole-dipole) term in addition to the initial term (single dipole), in order to explain the observed thickness dependent anisotropy energy. The relationship between surface polarization and shape anisotropy predicted by this model shows a good fit with measurement.

4.1 Introduction

Manganese anti-perovskites [\( \text{Mn}_3AX \) (A: transition metal or semiconducting element, X: N or C)] have shown a wide range of magnetic properties including spin-glass behavior, piezomagnetic effect, giant magnetoresistance, and magnetocaloric effect [68, 69, 70, 71]. In particular, the \( \text{Mn}_3AX \) material \( \varepsilon\text{-Mn}_4N \) exhibits potential applications in dilute magnetic semiconductors, spin-injection contacts, magnetoresistive devices, microwave shielding, electrochemical capacitors, the synthesis of water-purifying catalysts and as a Cu diffusion barrier in silicon chip manufacturing [10, 50, 62, 72, 73, 74, 75]. This wide range of applications is supported by the many practical aspects of the material. These aspects of \( \varepsilon\text{-Mn}_4N \) include a high Néel temperature (\( T_N = 738 \) K) and temperature/chemical stability as well as suitability for growth on a myriad of substrates, such as technologically relevant semiconductors (Si and GaN) and metals (Cu and Al) [1, 12, 18, 20, 54, 59, 65, 76, 77, 78]. One property of \( \varepsilon\text{-Mn}_4N \) [perpendicular magnetic anisotropy (PMA)] can be linked with three of the applications of \( \varepsilon\text{-Mn}_4N \) (spin-injection contacts, magnetoresistive devices, and microwave shielding) [19, 56, 63, 72].

Initial studies into \( \varepsilon\text{-Mn}_4N \) PMA by Ching et al. indicate that grain size and strain both affect PMA [18, 54, 77]. Since then, multiple studies arguing that the strain term is the primary component of PMA in \( \varepsilon\text{-Mn}_4N \) have been put forward [20, 21, 63, 72, 79]. This is supported by the theoretical predictions and experimental evidence that lattice distortions and temperature changes mediate transitions among many different types of magnetism (non-magnetic, multiple antiferromagnetic/ferrimagnetic orderings, and even mixtures of
these types) in $\varepsilon$-Mn$_4$N [21, 40, 58, 59, 60, 62, 80, 81]. These theoretical predictions and experimental evidence indicate that strain has a significant role in the magnetic properties of $\varepsilon$-Mn$_4$N.

On the other hand, an association between columnar grain structure and PMA in $\varepsilon$-Mn$_4$N is found by Ching et al. [18]. In addition, measurements from Yuping et al. demonstrate a strong dependence of magnetic permeability and microwave absorption on $\varepsilon$-Mn$_4$N grain size [19]. Finally, it is shown in the previous chapter (Chapter 3) that magnetic domain shape appears to be dependent on $\varepsilon$-Mn$_4$N grain size. Together these three studies suggest that grain size, and therefore shape, in addition to strain play an important role in the magnetic properties of $\varepsilon$-Mn$_4$N. Therefore, additional study of the effect of shape anisotropy on PMA in $\varepsilon$-Mn$_4$N while taking care to consider the effect of strain is of particular interest.

In this study, $\varepsilon$-Mn$_4$N thin films of varying thickness ($t = 9$ to $310$ nm) and tetragonal strain (difference between out-of- and in-plane Cauchy strain from $2.3 \times 10^{-3}$ to $-15.5 \times 10^{-3}$) are grown on MgO(001). The influence of strain and shape anisotropy on PMA are investigated for each sample and it is found that the shape is the most significant factor of PMA in each case. In addition, the strain component is found to have a significant contribution, which is 11% to 63% the size of the shape contribution, in each case. The focus on shape anisotropy leads to the consideration of two terms of shape anisotropy. Among these samples, the first term of the shape anisotropy, which is due to the energy of a single magnetic dipole, is responsible for an effect ranging only 5% to 6% the size of the total PMA. On the other hand, in these ultrathin/thin films a second order (dipole-dipole) term of shape anisotropy is attributed to the most significant component of PMA. It is predicted that this second shape term is a significant component of PMA in films with $t$ up to $\sim 360$ nm. This second shape term is attributed to the energy inherent in a shape
induced dipole-dipole interaction, which is mediated by the internal (molecular) magnetic fields produced by opposing Ising domains.

4.2 Procedure

All sample growths were performed in a custom designed ultra-high vacuum molecular beam epitaxy system [4]. Thin samples (4.A and 4.B), which were $310 \pm 33 \text{ nm}$ and $106 \pm 12 \text{ nm}$ thick respectively, were grown with the method outlined for high-purity $\varepsilon$-Mn$_4$N on MgO(001) growth in our previous work [50]. One or more annealing step(s) using a substrate temperature of 772 °C were used in addition to the previous method on the ultrathin samples (4.C and 4.D), which were each $9 \pm 1 \text{ nm}$ thick.

Reflection high-energy diffraction (RHEED) is actively used in situ with a 20 keV incident electron beam energy in order to monitor surface structure as well as the lattice values parallel to the sample plane during growth. In-plane lattice measurements based on the RHEED streak spacings are calibrated using the post-annealing MgO substrate streak spacings as a reference for each growth. Out-of-plane x-ray diffraction (XRD) measurements are taken ex situ using Cu K$_\alpha$ x-rays in order to determine the bulk crystal structure and the lattice values normal to the sample plane. A growth rate calibration is performed using Rutherford backscattering spectrometry (RBS) to determine Mn flux from the Mn deposition over time for one test sample. The thicknesses of samples 4.A and 4.B are known by using the same growth rate as the test sample for different known times. On the other hand, the thicknesses of 4.C and 4.D are determined individually using separate RBS measurements so that any Mn lost during annealing step(s) is accounted for.

Vibrating sample magnetometry (VSM) and superconducting quantum interference device (SQUID) measurements are performed on the thin and ultrathin films, respectively, in order to determine magnetic hysteresis, as well as the anisotropic magnetic field ($H_K$), saturation magnetization ($M_s$) and remnant magnetization ($M_r$). The diamagnetic signal
from the MgO substrate is subtracted from the VSM and SQUID measurements for each sample using the VSM measurement of a blank MgO substrate as a reference.

Atomic (magnetic) force microscopy is performed using a Park Scientific CP AFM/MFM head retrofitted with a new controller system by Anfatec Inc., which is operated ex situ to obtain information about the topographical and magnetic properties of the sample. The magnetic polarization states in proximity to the surface of the samples are measured using MFM in a method similar to that of Park et al. [25]. Details of this method are described in Section 2.2. The magnetic polarization \( P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} \) is determined for each sample by using the distributions of the magnetic contrast in MFM images of each sample as an approximation of the distribution of magnetization states in the sample. These distributions of magnetic contrast are normalized to the range of the distribution. Then, the relative number of states in the distribution above compared to below zero magnetic polarization is found and used to calculate \( P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} \). A Fisher Scientific FS60 Ultrasonic Cleaner was used to vibrate the samples for \( \sim 10 \) min intervals in order to remove any net magnetic polarization in the samples.

4.3 Results and Discussion

4.3.1 Ultrathin \( \varepsilon \)-Mn\(_4\)N Growth and Strain Control

The steps of growth, which involve annealing and regrowth, for samples (4.A and 4.D) can be followed in Fig. 4.1. The first two steps follow the method of our previous work by cleaning and annealing an MgO(001) substrate [RHEED image shown in Fig. 4.1(a)] and then depositing a Mn\(_x\)N\(_y\) thin film [RHEED image shown in Fig. 4.1(b)] [50]. Thirdly, the sample is annealed at 772 °C, which is found to remove Mn\(_x\)N\(_y\) material from the sample while at the same time the Mn\(_x\)N\(_y\) is annealed towards a higher phase purity of \( \varepsilon \)-Mn\(_4\)N.
Figure 4.1: RHEED images taken along the MgO [100]-direction of (a) an MgO substrate before any deposition, (b) an initially grown \( \text{Mn}_x \text{N}_y \) material, (c) an ultrathin \( \varepsilon \)-\( \text{Mn}_4 \text{N} \) sample after annealing, and (d) an ultrathin sample after regrowth. (e) Profiles across RHEED patterns in a) to c) (f) \textit{ex situ} XRD of an ultrathin sample. (g) Zoom-in of the \( \varepsilon \)-\( \text{Mn}_4 \text{N}(002) \) peak in f).

In the initial growth (first step) of samples 4.C and 4.D, some undetermined \( \text{Mn}_x \text{N}_y \) phase and/or mix of \( \text{Mn}_x \text{N}_y \) phases, which cannot be identified from RHEED (the only \textit{in situ} measurement available), are grown. Removal of some of the \( \text{Mn}_x \text{N}_y \) material is confirmed in RBS measurements, which find the finished samples to be thinner than expected based on the known Mn flux and total time of growth. The material is most likely...
removed during the annealing process through evaporation. Further analysis performed on a Mn$_x$N$_y$ sample, which was annealed until the surface was mostly MgO, is found in Appendix B.

Among the phases of the Mn$_x$N$_y$ system, 2× streaks are the unique signature for ε-Mn$_4$N [1]. Therefore, an increase in ε-Mn$_4$N phase purity is observed in the appearance of 2× streaks in Fig. 4.1(c) after an annealing step (second step) when there were previously no 2× streaks as in Fig. 4.1(b). Annealing from Mn$_x$N$_y$ to ε-Mn$_4$N is in agreement with the observation of Suzuki et al., in which the tetragonal phases of the Mn$_x$N$_y$ system could all be annealed into ε-Mn$_4$N [64].

The second step (annealing) is concluded just as inner first order streaks (4.21 Å) begin to reappear alongside the outer first order Mn$_x$N$_y$ streaks (3.93 Å) along the MgO [100]-direction as seen in Fig. 4.1(c). The spacing of the inner first order streaks matches the streak spacing of the MgO [100]-direction [1]. The outer first order streaks (3.93 Å) in Fig. 4.1(c) are identified as ε-Mn$_4$N streaks because of the signature 2× streaks corresponding to them.

In the third step (regrowth), high phase purity ε-Mn$_4$N is deposited to the desired $t$ on what is expected to be a mostly ε-Mn$_4$N template at 641°C for samples 4.C and 4.D. The high ε-Mn$_4$N phase purity of each finished sample (4.A through 4.D) is confirmed through the three methods established in our previous work; namely, a single set of 1st order streaks with corresponding bright 2× streaks along the MgO [100]-direction in RHEED as seen in Fig. 4.1(d), the presence of only the ε-Mn$_4$N peak among the known MgO substrate peaks in XRD as seen in Figs. 4.1(f)/(g), and the presence of a single uniform morphology with magnetic contrast throughout in AFM/MFM images [50].

In a previous study, if Mn$_x$N$_y$ grains other than ε-Mn$_4$N were grown in the nucleation step, these Mn$_x$N$_y$ grains would continue to grow alongside ε-Mn$_4$N grains when growth conditions favored ε-Mn$_4$N phase purity [50]. Therefore, it is expected that if the ultrathin
samples (4.C and 4.D) are grown on a template, which has Mn$_x$N$_y$ phase grains alongside $\varepsilon$-Mn$_4$N grains, then Mn$_x$N$_y$ grains would be present throughout the sample. However, the $\varepsilon$-Mn$_4$N phase purity of the samples has been confirmed by RHEED, XRD and AFM/MFM measurements, which show that Mn$_x$N$_y$ phase grains are not present throughout the sample. Hence, due to the high $\varepsilon$-Mn$_4$N phase purity of the final growths together with the clear 2× signature and dim 4.21 Å (spacing in agreement with MgO) streaks in Fig. 4.1(c), only $\varepsilon$-Mn$_4$N and to a lesser extent MgO are expected to be present following the annealing step (second).

Before the second step (annealing), the sample is composed of a mix of phases (such as $\eta$-Mn$_3$N$_2$ and $\varepsilon$-Mn$_4$N). These mixed phase samples are known to have lattice constants larger than pure $\varepsilon$-Mn$_4$N samples because of the larger lattices of the other phases, such as $\eta$-Mn$_3$N$_2$ ($a = 4.21$ Å and $c/3 = 4.03$ Å), compared to $\varepsilon$-Mn$_4$N (3.86 Å) leading to a net increase in lattice values [50]. As observed by Suzuki et al., annealing can be used to obtain $\varepsilon$-Mn$_4$N from Mn$_x$N$_y$ phases with lower Mn:N ratios [64].

In this study, it is found that repetition of the second and third steps (annealing and regrowth) sequentially reduces the lattice values of the sample towards the unstrained lattice value of $\varepsilon$-Mn$_4$N (3.86 Å) after starting with the larger lattice of a mixed phase sample. Therefore, if the lattice value(s) observed with RHEED following the third step (regrowth) are larger than those desired, the second and third steps (annealing and regrowth) can be repeated until the desired lattice value(s) are reached.

In this study, the range of lattice constants of high-purity $\varepsilon$-Mn$_4$N samples grown without annealing step(s) are from 3.85–3.88 Å. This range roughly agrees with the ranges found in other investigations [20, 21]. The method in this study, which uses annealing step(s) in the growth of ultrathin samples (4.C and 4.D), had the benefit of increasing the upper limit of the range of the in-plane and out-of-plane lattice constants to 3.93 and 3.87 Å respectively. The larger lattice constants are confirmed using in-plane RHEED
measurements as seen in the line profiles in Fig. 4.1(e) and out-of-plane XRD as seen in Fig. 4.1(g). In this way, the use of annealing step(s) allowed this study to investigate the influence of lattice values on the magnetic properties of $\varepsilon$-Mn$_4$N over a wider range than previously available.

### 4.3.2 Observation of an Additional Component of Out-of-Plane Anisotropy

The total uniaxial anisotropy energy ($E_A$) of each sample is calculated from the magnetization versus $\vec{H}$-field measurements (VSM/SQUID). $E_A$ corresponds to the energy difference between magnetizing a sample under two different field directions. For this study, this energy difference corresponds to the area between the curves (in- and out-of-plane $\vec{H}$-field) seen in Figs. 4.2(a) through (d) for each individual sample. The area is approximated using the well known triangle approximation ($E_A = M_S H_K/2$). The triangle approximation treats the area between the in- and out-of-plane $\vec{M}$-$\vec{H}$ curves as a right triangle with catheti equal to the $M_S$ and $H_K$. $M_S$ is the maximum magnetic polarization of the sample. $H_K$ is the minimum field magnitude at which both the in- and out-of-plane $\vec{M}$-$\vec{H}$ curves intersect at $M_S$. The $(M_S,H_K)$ points for the samples are extrapolated from the $\vec{M}$-$\vec{H}$ curves and are shown as squares on the ends of the extrapolated lines (dotted) in Fig. 4.2 for samples 4.A to 4.D.
Figure 4.2: Two RT-VSM and two RT-SQUID taken of the ε-Mn₄N samples [(a) 4.A, (b) 4.B, (c) 4.C and (d) 4.D] with the applied \( \vec{H} \)-field parallel (dotted) and perpendicular (solid) to [100]. Dotted lines and squares illustrate the extrapolated magnetic polarization curves and the point \((H_K, M_S)\), respectively, for each sample.

In all four samples, a smaller \( \vec{H} \)-field is needed to fully magnetize the samples \textit{out-of-plane} than to magnetize them \textit{in-plane} as seen in Fig. 4.2. This favorability to \textit{out-of-plane} magnetization over \textit{in-plane} means the samples all possess \textit{out-of-plane} PMA. In addition, a large area, which means a large anisotropy energy, is present between the \( \vec{M}-\vec{H} \) curves for all four samples as seen in Fig. 4.2. Therefore, each sample has a large \textit{out-of-plane} PMA.
A much larger $M_S$ is found for sample 4.D ($195 \pm 24 \text{ emu/cm}^3$) compared to the other three samples ($120 \pm 12, 122 \pm 13,$ and $127 \pm 13 \text{ emu/cm}^3$). In agreement within error, the theoretical saturation magnetization of e-Mn$_4$N is $185 \text{ emu/cm}^3$ [39, 63]. This higher $M_S$ ($195 \text{ emu/cm}^3$ compared to $\sim 120 \text{ emu/cm}^3$) may be due to a larger shape component for the ultrathin samples combined with sample 4.D having a much smaller magnitude of tetragonal strain $\left[ (-2.6 \pm 2.6) \times 10^{-3} = \frac{-a-c}{a_0} \right]$ compared to the other ultrathin sample $\left[ (-15.5 \pm 2.6) \times 10^{-3} = \frac{-a-c}{a_0} \right]$ as seen in Table 4.1. An elevated $M_S$ ($145 \text{ emu/cm}^3$) was seen by Yasutomi et al. in samples a little thicker (12 to 28 nm) and with a little more tetragonal strain $\left( -\frac{a-c}{a_0} = -5.2 \times 10^{-3} \text{ to } -10.4 \times 10^{-3} \right)$ than sample 4.D [20].

Table 4.1: This table shows the thickness, strain coefficient, anisotropy field, saturation magnetization and surface polarization for each sample. These values are found using RBS, RHEED/XRD, VSM (samples 4.A and 4.B)/SQUID (samples 4.C and 4.D), VSM (samples 4.A and 4.B)/SQUID (samples 4.C and 4.D), and MFM distributions respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness $t$ (nm)</th>
<th>Strain Coefficient $\frac{-a-c}{a_0}$ ($10^{-3}$)</th>
<th>Saturation Magnetization $M_S$ (emu/cm$^3$)</th>
<th>Anisotropy Field $H_K$ (kOe)</th>
<th>Surface Polarization $P_S$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.A</td>
<td>310 ± 33</td>
<td>$2.3 \pm 2.3$</td>
<td>$120 \pm 12$</td>
<td>$20.0 \pm 0.5$</td>
<td>$21.6 \pm 0.8$</td>
</tr>
<tr>
<td>4.B</td>
<td>106 ± 12</td>
<td>$-5.4 \pm 2.6$</td>
<td>$122 \pm 13$</td>
<td>$28.0 \pm 0.5$</td>
<td>$37.3 \pm 3.3$</td>
</tr>
<tr>
<td>4.C</td>
<td>9 ± 1.1</td>
<td>$-15.5 \pm 2.6$</td>
<td>$127 \pm 13$</td>
<td>$28.0 \pm 0.5$</td>
<td>$78.0 \pm 3.0$</td>
</tr>
<tr>
<td>4.D</td>
<td>9 ± 0.9</td>
<td>$-2.6 \pm 2.6$</td>
<td>$195 \pm 24$</td>
<td>$42.5 \pm 0.5$</td>
<td>$81.8 \pm 2.5$</td>
</tr>
</tbody>
</table>

Strangled hystereses such as that seen in the out-of-plane SQUID measurements of the ultrathin samples in Figs. 4.2(c) and (d) are associated with samples composed of separate regions, which possess different ferromagnetic (or in this case ferrimagnetic) structures (for example regions with different $M_S$ and coercivity) [82]. Experimental and theoretical
evidence has shown that lattice parameters influence the magnetic properties ($M_S$ and coercivity) of $\varepsilon$-Mn$_4$N [21, 58, 60, 59, 77, 81]. Therefore, it is reasonable to conclude that regions with different ferrimagnetism ($M_S$ and coercivity) exist in the ultrathin samples because of the wide variation of lattice parameters found in the ultrathin samples (4.C and 4.D) as seen in the full width half maximum (FWHM) from the RHEED (0.29 Å) in Fig. 4.1(e) and of the XRD (0.07 Å) in Fig. 4.1(g).

The angle of the easy-axis with respect to the sample surface normal ($\Theta$) can be calculated from the remnant magnetization ($M_r$) when a field is applied perpendicular and parallel to the sample surface: $\Theta = \tan^{-1}(\frac{M_r\parallel}{M_r\perp})$ [2]. This calculation gives easy-axis angles of $8^\circ = \tan^{-1}(\frac{15}{109} \text{ emu/cc})$, $5^\circ = \tan^{-1}(\frac{10}{116} \text{ emu/cc})$, $13^\circ = \tan^{-1}(\frac{10}{44} \text{ emu/cc})$, and $7^\circ = \tan^{-1}(\frac{8}{63} \text{ emu/cc})$ for samples 4.A, 4.B, 4.C, and 4.D respectively. The values associated with the easy-axis calculation are shown in Table 4.2. In all cases, the easy-axis has a large out-of-plane component (more than 4 times larger than the in-plane component), which is a useful property for a spin-injection contact [56]. Both ultrathin samples (4.C and 4.D) have smaller $M_{r\perp}$ than the thin samples (4.A and 4.B) due to the lower slope ($\mathbf{M}$ vs $\mathbf{H}_\perp$) related to the strangled shape of the hysteresis loops of samples 4.C and 4.D.
Table 4.2: This table shows the in-plane remnant magnetization, the out-of-plane remnant magnetization and the angle the easy-axis makes with the surface normal for each sample. The remnant magnetizations were measured using VSM (samples 4.A and 4.B)/SQUID (samples 4.C and 4.D). The angle the easy-axis makes with the surface normal was calculated from the equation \( \Theta = \tan^{-1}\left(\frac{M_{r\parallel}}{M_{r\perp}}\right) \) [2].

<table>
<thead>
<tr>
<th>Sample</th>
<th>In-Plane Remnant Magnetization ( M_{r\parallel} ) (emu/cm(^3))</th>
<th>Out-of-Plane Remnant Magnetization ( M_{r\perp} ) (emu/cm(^3))</th>
<th>Angle Between Easy-Axis and Surface Normal ( \Theta ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.A</td>
<td>15 ± 2</td>
<td>109 ± 11</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>4.B</td>
<td>10 ± 1</td>
<td>116 ± 12</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>4.C</td>
<td>10 ± 1</td>
<td>44 ± 5</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>4.D</td>
<td>8 ± 1</td>
<td>63 ± 8</td>
<td>7 ± 1</td>
</tr>
</tbody>
</table>

The energy difference between the curves \((E_A)\) is expected to be the sum of various individual components with each individual component caused by separate phenomena. It is proposed by Yasutomi et al. that \(E_A\) in \(\varepsilon\)-Mn\(_4\)N(001) films with \(t\) significantly greater than a few nanometers \((3 - 5 \text{ nm})\) can be calculated from the sum of the strain and shape components \((K^V\) and \(K^{S1} = -2\pi M_S^2\) respectively):

\[
K^V = -\frac{3}{2} \lambda_{100}(C_{11} - C_{12})(\frac{a - c}{a_0}),
\]

where \(\lambda_{100}\) is the magnetostriction constant along [100], \(C_{11}\) is the elastic modulus perpendicular to the surface, \(C_{12}\) is the elastic modulus parallel to the surface and \(\lambda_{100}\) is known to be negative [18, 20, 54].

The in-plane lattice values are calculated from in situ measurements of the RHEED streak spacings of the samples using the post-annealing RHEED patterns of the MgO
substrates as a reference. The \textit{out-of-plane} lattice values are calculated from the XRD measurements of the samples using the MgO 002 peak as a reference. The value for \(a_0\) is taken from the accepted literature value of 3.86 Å [65].

The main difference, which is relevant to the \(E_A\) of the samples, between samples #3 to #4 is that sample #3 has a substantially larger tetragonal strain compared to sample #4 because these samples have the same thickness and similar shape. Due to this, the difference between the \(E_A\) of samples 4.C to 4.D should be almost completely due to strain after accounting for \(K^{S1}\). Any differences due to thickness should be minimal because the samples have the same thickness (9 ± 1 nm). Therefore, \(\frac{3}{2} \lambda_{100}(C_{11} - C_{12})\) is calculated using the values shown in Table 4.3 as follows:

\[
K^{V}_{4,C} - K^{V}_{4,D} \approx E_{A_{4,C}} - E_{A_{4,D}} - \left(-2\pi(M_{S_{4,C}} - M_{S_{4,D}})\right) \quad (4.2)
\]

and after inserting Eq. 4.2 into Eq. 4.1

\[
\frac{3}{2} \lambda_{100}(C_{11} - C_{12}) \approx \frac{K^{V}_{4,C} - K^{V}_{4,D}}{(-\frac{a_{4,C} - c_{4,C}}{a_0}) - (-\frac{a_{4,D} - c_{4,D}}{a_0})}. \quad (4.3)
\]

This gives a positive value for \(\frac{3}{2} \lambda_{100}(C_{11} - C_{12}) = 193 \pm 60 \text{ Merg cm}^3\). A positive \(\frac{3}{2} \lambda_{100}(C_{11} - C_{12})\) and a negative \(\lambda_{100}\) means that \(C_{11} < C_{12}\) and \(K^{V}\) is negative when \(a > c\). A \(C_{11} < C_{12}\) is unusual in comparison to many other cubic materials and anti-perovskite nitrides [20, 83, 84].
Table 4.3: This table shows the anisotropy energy, each individual component of the anisotropy energy and the relative size of the dipole-dipole term. These values are calculated from the data in Table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anisotropy Energy</th>
<th>Strain Anisotropy</th>
<th>Single-Dipole Shape Anisotropy</th>
<th>Dipole-Dipole Shape Anisotropy</th>
<th>Relative Size of $K^S_2$ Term</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_A (\text{Merg/cm}^2)$</td>
<td>$K^V (\text{Merg/cm}^2)$</td>
<td>$K^S_1 (\text{Merg/cm}^2)$</td>
<td>$K^S_2 (\text{Merg/cm}^2)$</td>
<td>$\frac{</td>
</tr>
<tr>
<td>4.A</td>
<td>1.2 ± 0.1</td>
<td>0.4 ± 0.3</td>
<td>−0.09 ± 0.01</td>
<td>0.8 ± 0.3</td>
<td>62 ± 24</td>
</tr>
<tr>
<td>4.B</td>
<td>1.7 ± 0.2</td>
<td>−1.1 ± 0.4</td>
<td>−0.09 ± 0.01</td>
<td>2.9 ± 0.5</td>
<td>71 ± 11</td>
</tr>
<tr>
<td>4.C</td>
<td>1.8 ± 0.2</td>
<td>−3.0 ± 1.0</td>
<td>−0.10 ± 0.01</td>
<td>4.9 ± 1.0</td>
<td>61 ± 13</td>
</tr>
<tr>
<td>4.D</td>
<td>4.1 ± 0.5</td>
<td>−0.5 ± 0.3</td>
<td>−0.24 ± 0.03</td>
<td>4.9 ± 0.6</td>
<td>87 ± 6</td>
</tr>
</tbody>
</table>

The strain components are calculated using the value for $\frac{3}{2}A_{100}(C_{11} - C_{12})$ and are shown in Table 4.3. Samples 4.B to 4.D all have large positive $E_A (1 \text{ Merg/cm}^2)$ despite having negative contributions from both the strain ($K^V$) and shape due to single dipole ($K^S_1$) components. In addition, after accounting for the $K^V$ and $K^S_1$ components there remains an additional large and out-of-plane anisotropy (circles) seen in Fig. 4.3. This additional anisotropy energy shows a negative linear relationship with $t$. From this, the presence of an additional component of $E_A (K^S_2)$, which is large, positive (out-of-plane), and varies proportionally with $-t$ for $t = 9$ to 310 nm is found.
4.3.3 Observation of an Out-of-Plane Separation of Magnetically Opposing Regions

AFM images of the surface morphology of the thin samples (4.A and 4.B) are seen in Figs. 4.4(a) and (b). The morphology of samples 4.A and 4.B consists of flat square-shaped terraces. The MFM images of the thin samples when at zero net magnetic polarization, which correspond to the areas seen in Figs. 4.4(a) and (b), are seen in Figs. 4.4(c) and (d) respectively. The magnetic domains of samples 4.A and 4.B are arranged in semi-
continuous paths. The morphology and magnetic domain structure seen in Fig. 4.4 are consistent with the morphology and magnetic domain structure, which were observed in thin films composed of single-phase $\varepsilon$-Mn$_4$N as detailed in our previous work [50].

![AFM/MFM images of the thin samples 4.A (310 nm) and 4.B (106 nm).](image)

Figure 4.4: AFM/MFM images of the thin samples 4.A (310 nm) and 4.B (106 nm). (a) and (b) each show a 10 $\mu$m AFM topographic image of the samples 4.A and 4.B respectively. (c) and (d) each show a 10 $\mu$m MFM image, which are taken when each sample is demagnetized and correspond to the same area shown in a) and b) respectively.

AFM images of the surface morphology of the ultrathin samples (4.C and 4.D) are seen in Figs. 4.5(a) and (b). The morphology of samples 4.C and 4.D consists of box canyon-shaped valleys and mesa-like islands. The box canyon-shaped valleys are separated from one another and contain multiple isolated islands, which have widths generally 0.1 to 0.2 $\mu$m across and heights generally 1 to 6 nm tall. In contrast, the mesa-like islands are
interconnected, possess a larger range of widths (0.1 to 1 \( \mu m \) across) and taller heights (7 to 10 nm).

![AFM/MFM images of the ultrathin samples 4.C (9 nm) and 4.D (9 nm).](image)

Figure 4.5: AFM/MFM images of the ultrathin samples 4.C (9 nm) and 4.D (9 nm). (a) and (b) each show a 3 \( \mu m \) AFM topographic image of the samples 4.C and 4.D respectively. (c) and (d) each show a 3 \( \mu m \) MFM image, which are taken when each sample is demagnetized and correspond to the same area shown in a) and b) respectively.

The MFM images of the ultrathin samples when at zero net magnetic polarization, which correspond to the areas seen in Figs. 4.5(a) and (b), are shown in Figs. 4.5(c) and (d) respectively. The areas over the mesa-like islands are found to generally have an opposing magnetic polarization to the box canyon-shaped valleys. This difference in polarization indicates the magnetic polarization at the surface depends on surface height in the ultrathin samples.
The mesa-like island heights are in some cases taller than the $t$ of the corresponding sample because $t$ is the average thickness and does not account for surface morphology. The mesa-like island heights and positions are found with AFM to be very uniform in the ultrathin samples as seen in Fig. 4.6. Using these AFM measurements, samples 4.C and 4.D are found to typically have islands 7 nm and 10 nm tall, which cover 52 ± 5% and 54 ± 5% of the surface, respectively. The thickness of the base layer of each sample is calculated by subtracting out the contribution of the islands to the total thickness ($t$), which gives $5.5 \text{ nm} = 9 \text{ nm} - (52\% \times 7 \text{ nm})$ and $3.5 \text{ nm} = 9 \text{ nm} - (54\% \times 10 \text{ nm})$ thick base layers for samples 4.C and 4.D respectively.
Figure 4.6: (a) AFM image from a 15 µm area of an ultrathin sample. (b) Line profile seen in a).

STM images taken from ultrathin samples shown in Fig. 4.7 demonstrate that the complete area within the box canyon-shaped valleys are conductive. Therefore, due to the identification of the ultrathin samples as high-phase purity ε-Mn₄N, the box canyon-shaped valleys contain only ε-Mn₄N at the surface and no MgO or other MnₓNᵧ phases. The observed morphology in the box canyon-shaped valleys (islands on top of an ultrathin layer) matches that of a Stranski-Krastanov wetting layer and islands. In agreement, a large
lattice mismatch exists between the substrate \((a=4.21 \, \text{Å})\) and sample \((a=3.86 \, \text{Å})\), which is a known cause of Stranski-Krastanov transitions \([34]\). In addition to the Stranski-Krastanov morphology in the box canyon-shaped valleys, another transition is observed when the box canyon-shaped valleys are filled in as the samples grow beyond the ultrathin regime \((>15 \, \text{nm})\) as shown in Fig. 4.7(b), in which nearly all of the valleys are filled in for a \(~15 \, \text{nm}\) thick sample (thickness estimated based off of growth time after the final annealing step). As well, even thicker samples [4.A (310 nm thick) and 4.B (106 nm thick)] possess a square terrace morphology without box canyon-shaped valleys as seen in Figs. 4.4(a) and (b). This second transition (box canyon-shaped valleys filling in) is unexplained by the Stranski-Krastanov model, which only expects a single transition due to lattice mismatch \([34]\).
Figure 4.7: Two 1 μm STM images of (a) a 9 nm thick sample with several box canyon-shaped valleys and (b) a ~15 μm thick sample with very few box canyon-shaped valleys.

Using our variation of the Park et al. technique, the magnetization measurements, which correspond to the individual pixels within the MFM image of each sample, are assembled into a distribution for each sample as seen in Fig. 4.8. The distributions in Figs. 4.8(a) and (b) are the distributions of magnetic states in samples 4.A and 4.B, respectively, over the whole morphology in the image areas. The distributions in Figs. 4.8(c) and (d)
are the distribution of magnetic states in samples 4.C and 4.D, respectively, over the whole morphology in the image areas (black squares) and over only the mesa-like islands (red circles).

![Diagram](image-url)

Figure 4.8: The distribution of the surface magnetization of each sample when the sample is demagnetized: (a) 4.A (310 nm thick), (b) 4.B (106 nm thick), (c) 4.C (9 nm thick), and (d) 4.D (9 nm thick). The distributions in c) and d) show the unit area magnetic polarizations (black squares) of the complete area and the unit area magnetic polarizations (red circles) of only the island areas.

A non-zero local magnetic polarization ($P_S$) is found in each of the samples when the samples have net zero magnetization as seen in the higher spin-up populations ($N_\uparrow > N_\downarrow$) in Fig. 4.8. The MFM data in Figs. 4.4(c) and (d) shows no correlation to the topography of the thin samples (4.A and 4.B); namely, the flat square terrace morphology seen in Figs. 4.4(a) and (b). On the other hand, a clear correlation between polarization and topography
is observed as film thickness drops below \(\sim 15 \text{ nm}\) (samples 4.C and 4.D). Due to the correlation between surface height and magnetic polarization, the state distributions [Fig. 4.8(c) and (d)] taken using the area above the mesa-like islands (red circles) are used to determine the magnetic polarization near to the surface for these samples.

The non-zero local magnetic polarization measured from above the surface of the samples, which overall have zero magnetic polarization, is explained by the observed polarization near the surface being canceled out by an equal and opposite polarization further from the surface. This separation in polarization near and away from the sample surface can be explained by partially overlapping magnetic domains. A feature, which is predicted by partially overlapping magnetic domains, is that the magnitude of the magnetic signal in an MFM image would vary across single domains at the surface depending on whether an opposing domain lies beneath. Such a varied signal is observed for samples 4.A and 4.B in Figs. 4.4(c) and (d), in which different regions within individual magnetic domains appear brighter and darker. As well, a varied signal can be observed across the mesa-like islands in Figs. 4.5(c) and (d), in which the signal over the mesa-like islands goes from brighter to darker without transitioning to a fully dark signal, for samples 4.C and 4.D respectively.

In the case of the thin samples (4.A and 4.B), a decrease in the separation of the \(N_\uparrow\) and \(N_\downarrow\) peaks in the magnetic polarization distributions can be seen when comparing Fig. 4.8(a) to Fig. 4.8(b). The peak separation in Fig. 4.8(b) decreases for the thinner and more polarized sample (106 nm and 37\%) when compared to the peak separation in Fig. 4.8(a) of the thicker and less polarized sample (310 nm and 22\%). This decrease in peak separation can be explained by the opposing domains below the surface masking some of the signal coming from the domains near the surface. This masking would be expected to be greater in the thinner and more polarized sample (4.B) because the anticipated opposing domains, which lie beneath much of the surface domains, would be closer to the point
of measurement (above the surface) and occupy a larger fraction of the area under the surface domains. In the case of the ultrathin samples (4.C and 4.D), a significant portion of opposing polarization must be below the surface because the polarizations observed across the entire morphology of the samples, 26±1% and 40±1%, are both positive as seen in Figs. 4.8(c) and (d) for samples 4.C and 4.D respectively.

Previously, the domain structure in this system was identified to consist of ”pancake-like” Ising domains with magnetic force microscopy [50]. Ising domains partially overlapping out-of-plane serves as an explanation of the previous identification of an Ising domain structure as well as the MFM evidence, which is presented in this study, of magnetic polarization near the surface in these demagnetized samples. Not dissimilar to ε-Mn$_4$N, Ising domains with a ”pancake-like” shape, a large uniaxial anisotropy, and out-of-plane packing have been observed in single crystal LuFe$_2$O$_4$ (also a ferrimagnet) by Wu et al [67].

### 4.3.4 Energy of the Dipole-Dipole Interaction

After considering the MFM evidence, samples 4.A through 4.D are each found to contain adjacent opposing dipoles, which have out-of-plane overlap, while demagnetized and under zero external field. Therefore, a model of the system energy of these samples should consider the energy associated with the local magnetic polarization due to this out-of-plane overlap when the sample is demagnetized and there is no external field. The component of the system energy related to the magnetization of a material when there is no externally applied field is given by:

$$E \propto MB = \lambda AM \propto M^2; \quad (4.4)$$

where $\lambda M$ is the molecular (internal) field and $\lambda$ is the Curie temperature divided by the Curie constant [83].
The Brillouin expression for magnetization, which includes the effect of a dipole-dipole interaction (multiplying by the hyperbolic tangent shown below) when no external magnetic field is applied, is as follows:

\[
M = N\mu \tanh\left(\frac{\mu^2 \lambda N}{k_B T}\right),
\]

(4.5)

where \(\mu\) is the magnetization of a single unit cell, \(N = N_\uparrow - N_\downarrow\) is the net number of unit cells magnetized, \(T\) is the temperature, and \(\mu^2 \lambda N / k_B = T_C\) is the Curie temperature.

When \(T_C \approx 738\, K > T \approx 298\, K\), the approximation:

\[
\tanh(N\xi) \approx 1 - 2e^{-2N\xi} ..., \tag{4.6}
\]

where \(\xi = \mu^2 \lambda / k_B T\), is valid [65, 83]. In addition, \(N \propto P\). Therefore,

\[
\Delta M = M(0) - M(P) \approx aP(-1 + 2e^{-bP} ...) \tag{4.7}
\]

and from inserting Eq. 4.7 into the change in \(E\) from Eq. 4.4,

\[
\Delta E \propto M\Delta M \approx -CP^2 + DP^2 e^{-bP} ..., \tag{4.8}
\]

where \(a, b, C,\) and \(D\) are constants.

The first term in Eq. 4.8 \((\propto -P^2)\) matches the energy of a single magnetized dipole (i.e. the hyperbolic tangent in Eq. 4.5 is equal to 1) and is proportional to the square of the net magnetization of the entire sample. In the considered case (a demagnetized sample under no externally applied field) the sample has zero net magnetization. Therefore, the first term in Eq. 4.8 \((\propto -P^2)\) is expected to go to zero. It should be noted, when the sample is at \(M_S\) the first term is non-zero and corresponds to the first term of shape anisotropy \((K^{S_1})\). On the other hand, in this case, in which out-of-plane Ising domains overlap, a second term,

\[
K^{S_2} = DP^2 S e^{-bP_S}, \tag{4.9}
\]

(where \(P_S\) is the MFM measured surface localized polarization) exists due to the consideration of the molecular field interaction between adjacent dipoles (i.e. the
hyperbolic tangent in Eq. 4.5 is not necessarily equal to 1). Therefore, $K^{S^2}$ relates to the stored energy of the molecular field interaction between opposing Ising domains, which overlap out-of-plane, in the case of samples 4.A through 4.D.

As seen in Fig. 4.9, there is a strong fit (R-squared 98.5%) between the second term in Eq. 4.8 due to the molecular field interaction ($\propto P^2_s e^{-bP_s}$) and the additional anisotropy energy term ($K^{S^2}$), which shows a proportionality to $-t$. Therefore, the second term of Eq. 4.8 (dipole-dipole) is an energy due to a magnetization, which is attributed to changes in sample shape ($\Delta K^{S^2} \propto -t$). In the same way, the first term of Eq. 4.8 (single-dipole shape anisotropy) is an energy due to a magnetization, which is attributed to sample shape. This leads to this large positive (out-of-plane) PMA term ($K^{S^2}$) being attributed to a dipole-dipole interaction associated with a second (dipole-dipole) term of shape anisotropy.

Any mechanism, which increases the favorability of the formation of a single dipole, would naturally decrease the favorability of dipole-dipole formation. Therefore, the energy related to single dipole formation is expected to oppose the energy related dipole-dipole formation. In this way, the opposition of single dipole and dipole dipole formation serves as a physical explanation for the differing directions (in-plane versus out-of-plane) of the single dipole and dipole-dipole shape anisotropies in Eq. 4.8.
Figure 4.9: Plot of $P_S$ versus $K^{S_2}$. The red rounded dashed line marks the $K^{S_2} \approx DP_S^2 e^{-bP_S}$ model fit. See Table 4.3 for a full list of these values and corresponding errors.

A peak value is observed in the fit of the second term of Eq. 4.8 with the $K^{S_2}$ data ($K^{S_2} = 42.1P_S^2 e^{-2.13P_S}$) at $(P_S, K^{S_2}) = (94\%, 5 \text{ Merg/cc})$ as shown in Fig. 4.9. The presence of this peak value predicts a decrease in energy for $P_S > 94\%$. This decrease may be associated with the film approaching the transition to the superparamagnetic limit found in ultrathin ferro/ferrimagnetic films at which point the film would transition towards a single dipole.

The linear behavior of $t$ vs. $K^{S_2}$ can be described by the following model:

$$K^{S_2} = K_{max}^{S_2} - k^{S_2}t, \text{ for } t_0 \leq t \leq t_C$$  (4.10)
where \( t_0 \) is the superparamagnetic limit and \( t_C \) is the critical thickness at which the domains begin to overlap out-of-plane. In this model, \( K^{\perp} \) descends away from a maximum value associated with the ideal dipole-dipole polarization as thickness increases.

An increasing area of the domains at the surface as thickness decreases is seen in Figs. 4.4(c) and (d). Fast Fourier Transforms (FFT) are taken of the magnetic domain maps of samples 4.A and 4.B. These FFT both exhibit a ring-shape. A cross-section through the center of these FFT results in two peaks, and the average of the two widths at \( 1/e \) of the maxima provides the range of distances typically found within an image [66]. This analysis of the FFT taken of the domain maps shows typical domain widths of \( 1.3 \mu m > l_d > 8 \mu m \) and \( 1.2 \mu m > l_d > 21 \mu m \) for samples 4.A and 4.B respectively. The maximum of each range is taken to be representative of the domain width of the more common polarization because they are larger at the surface than the domain widths of the less common polarization. Under this convention, a simple calculation of domain volume \( (V_{ID}) \) based on the domain area being equal to \( \frac{V_{ID}}{t} \) due to Ising domains being bounded by the shape of the sample gives \( (V_{ID} = \text{Avg. of } [(8 \mu m)^2 \times 310 \text{ nm}, (21 \mu m)^2 \times 106 \text{ nm}]) = \sim 30 \mu m^3 \). This \( A = \frac{V_{ID}}{t} \) model predicts domain widths of \( (\sqrt{\frac{30 \mu m^3}{9 \mu m}} = ) 58 \mu m \) for samples 4.C and 4.D. In agreement, the domains for the ultrathin samples (4.C and 4.D) continue across the mesa-like islands beyond the range of the scan area of the MFM (>40 \mu m) as seen in Fig. 4.10, in which the islands maintain the same polarization across the overlapping AFM/MFM images. A map showing the relative positions of the AFM/MFM images in Fig. 4.10 is shown in Fig. 4.11.
Figure 4.10: Consecutive AFM/MFM of $\varepsilon$-Mn$_{4}$N sample 4.C with relative positions shown in Fig. 4.11. Horizontal lines indicate position at which images overlap. The number to the left of each AFM/MFM pair of images identifies each area. The vertical dotted lines between AFM/MFM image pairs point out the same feature on either side of the dotted line.
Figure 4.11: Map of the positions of the AFM/MFM images shown in Fig. 4.10. Each square represents an AFM/MFM area scanned. The number in each square matches each area scanned with one of the numbered AFM/MFM pairs of images in Fig. 4.10.
From the observation of increasing domain width with decreasing domain height, it is proposed that when a critical thickness is reached then the Ising domains begin to overlap out-of-plane in order to maintain a constant volume. Speculatively, this limit is associated with $t$ reaching the height at which the domain must begin to partially overlap with an adjacent Ising domain in order to reduce the magnetic field external to the sample. Otherwise, the external field would continue to increase as the in-plane area of the domains increases with decreasing $t$ in order to maintain a constant domain volume.

Additionally, the need to reduce the external field may explain the second transition in morphology, which is unexplained by the Stranski-Krastanov model. This second transition is demonstrated by the highly polarized surface of the ultrathin samples (4.C and 4.D) forming into mesa-like islands (7 to 10 nm in height) as opposed to the less polarized samples (4.A and 4.B), which form into a flat square terrace morphology. The formation of a highly polarized surface into mesa-like islands allows a direct path for the field lines to reach the oppositely polarized box canyon-shaped valleys. The availability of a direct path for the field reduces the external field of the sample. When the linear model in Eq. 4.10 is fit to the $K_{S2}$ values as seen in Fig. 4.3, a $t$ of $\sim 360$ nm is predicted as the limit at which $K_{S2}$ goes to zero and the critical $t$ ($t_C$) at which the domains begin to overlap out-of-plane.

The type of domain structure in this study (Ising domains) was determined to result from the pinning of domain boundaries [25, 67]. From the observation of increasing domain width with decreasing domain height, it can be seen that in $\varepsilon$-Mn$_4$N the domain boundaries are pinned by sample shape. A decrease in microwave absorption with decreasing $\varepsilon$-Mn$_4$N grain size, which is expected to result from a corresponding decrease in the number of magnetic dipoles, is observed by Yuping et al. [19]. A likely explanation for this decrease in microwave absorption of $\varepsilon$-Mn$_4$N is as follows: the decrease in microwave absorption is caused by the number of dipoles, which are not pinned by sample shape, being
limited within a particle at grain sizes approaching the volume of a few Ising domains (a few \(\sim 30 \mu m^3\)).

4.4 Conclusions

In conclusion, the significant components of PMA in \(\varepsilon\)-Mn\(_4\)N ultrathin/thin films have been accounted for. The scale between the strain component of PMA (\(K^V\)) and tetragonal strain (\(-\frac{a-c}{a_0}\)) in \(\varepsilon\)-Mn\(_4\)N has been quantified \([\frac{3}{2}a_{100}(C_{11} - C_{12}) = 193 \pm 60 \frac{Merg}{cm^3}]\). The existence of a large positive component of PMA (\(K^{S2}\)), which shows a negative linear relationship with \(t\), is determined. A good agreement between a model for the energy inherent in dipole-dipole overlap *out-of-plane* (due to a second shape term) and the large positive PMA component of ultrathin/thin films of \(\varepsilon\)-Mn\(_4\)N (Eq. 4.9) is found. As well, the inversely proportional relationship deduced between the area of the domains (\(A_{ID}\)) and the sample thickness (\(t\)) suggests the previously observed Ising domains in the system roughly maintain a volume of \(\sim 30 \mu m^3\) across films of varying \(t\). Further, the negative linear relationship between \(K^{S2}\) and \(t\) (Eq. 4.10) predicts that the previously observed Ising domains in this system begin to overlap *out-of-plane* when the sample thickness drops below a critical thickness \((t_C = \sim 360 \text{ nm})\) in order to reduce the external field produced by the sample.

In the future, direct measurements of the PMA associated properties (i.e. anomalous Hall effect, spin injection efficiency, and microwave absorption) in \(\varepsilon\)-Mn\(_4\)N samples with a range of values for the individual components of PMA would be of interest for determining if/how specific PMA components relate to these associated properties. In addition, whether or not the term \(K^{S2}\) has a significant influence on PMA and the associated properties thereof in ultrathin/thin films of other materials, which contain Ising domains, such as LuFe\(_2\)O\(_4\) remains to be investigated.
5 Magnetic States in $\varepsilon$-Mn$_4$N under $\vec{H}$-Field Loops

This chapter includes the work from a paper in development discussing the $\vec{H}$-field dependence of magnetic domain motion in $\varepsilon$-Mn$_4$N ultrathin/thin films and how this motion may relate to magnetoresistance in the films. SP-STM measurements are taken on an $\varepsilon$-Mn$_4$N ultrathin film (9 nm thick) during a major hysteresis loop ($\pm 20$ kOe) at L-He temperature and compared with SQUID measurements of the magnetization of the film during a major hysteresis loop ($\pm 30$ kOe) at room temperature. Conversely, MFM measurements are taken on an $\varepsilon$-Mn$_4$N thin film (310 nm thick) during a minor hysteresis loop ($\pm \sim 0.17$ kOe) at room temperature and compared with VSM measurements of the magnetization of the film during the same minor hysteresis loop. The major hysteresis measurements of the ultrathin sample at L-He temperature indicate the presence of a spin-valve, which is formed from overlapping Ising domains within a single crystal, within the sample. The minor hysteresis measurements of the thin samples at room temperature indicate the Ising domains, which are present in the sample, reverse the direction they overlap out-of-plane without significantly affecting the total magnetization of the sample.

5.1 Introduction

In Chapter 4, a shape anisotropy (type of PMA) in $\varepsilon$-Mn$_4$N thin films is attributed to the dipole-dipole interaction of Ising domains, which partially overlap out-of-plane. Further, shape anisotropy can be connected to the observation of microwave absorption diminishing in $\varepsilon$-Mn$_4$N with decreasing grain size [19]. In addition, an anomalous Hall effect, of which the underlying mechanism is still being investigated, has been observed in $\varepsilon$-Mn$_4$N thin films [63, 79, 85]. More recently, Kabara et al. presented an argument that the source of an anisotropic magnetoresistance (AMR) in a pseudo-single crystal $\varepsilon$-Mn$_4$N thin film is caused by $s$-orbital conduction electrons scattering into $d$-orbitals [85].
Due to the high conductivity of \(\varepsilon\)-Mn\(_4\)N, a PMA in this material can be expected to result in an anomalous Hall effect [63]. Therefore, the dipole-dipole shape anisotropy, which is related to Ising domains partially overlapping \textit{out-of-plane} in Chapter 4, is expected to have a corresponding anomalous Hall effect. As well, it is reasonable to expect scattering of electrons traveling between anti-aligned dipoles, which are shown to be related to this \textit{out-of-plane} shape anisotropy. In this way, the scattering process proposed by Kabara \textit{et al.} to be responsible for AMR in the material may be related to electrons scattering at the boundary between \textit{out-of-plane} separated dipoles. For these reasons, an investigation into the potential relationship between the dipole-dipole interaction in \(\varepsilon\)-Mn\(_4\)N thin films and the observed magnetoresistances is of interest.

A \(\varepsilon\)-Mn\(_4\)N ultrathin film (~9 nm) near L-He temperature (~4.2 K) is taken through a major hysteresis loop while spin-polarized scanning tunneling microscopy (SP-STM) images are recorded at various \(\vec{H}\)-field values of the loop. Magnetic \(\frac{dI}{dV}\) contrast, which indicates the local magnetization of this sample at different points of the hysteresis loop, is obtained with SP-STM for \(\varepsilon\)-Mn\(_4\)N. This magnetic \(\frac{dI}{dV}\) contrast vs \(\vec{H}\)-field loop is then compared to a \(\vec{M}\)-\(\vec{H}\) loop (±30 kOe) taken of the same sample with a superconducting quantum interference device (SQUID). The changes in magnetic \(\frac{dI}{dV}\) contrast versus \(\vec{H}\)-field at L-He temperature between different regions with \textit{out-of-plane} separation indicate the presence of a spin-valve, which is formed from overlapping Ising domains within a single crystal, within an ultrathin sample. Changes in magnetic \(\frac{dI}{dV}\) contrast versus \(\vec{H}\)-field at L-He temperature are attributed to the domain boundary between these overlapping Ising domains moving toward and away from the surface with increasing and decreasing \(\vec{H}\)-field respectively. The model presented for this system (an \(\varepsilon\)-Mn\(_4\)N ultrathin film) at L-He temperature indicates that two conductive regions, which each possess anti-aligned spin populations and are separated \textit{out-of-plane} by an energy barrier, together with quantized
peaks in LDOS are present when there is no $\hat{H}$-field applied. Each of these features is among the hallmarks of samples, which exhibit the anomalous quantum Hall effect [86, 87].

Two $\varepsilon$-Mn$_4$N thin films (samples 4.A and 4.B) are taken through a minor hysteresis loop while MFM images are recorded at various $\hat{H}$-field values between -0.165 and 0.170 kOe at room temperature. Magnetic domain motion is observed during these $\hat{H}$-field loops at room temperature. Using the method described in Section 2.2, the changes in the magnetic polarization localized to the surface ($P_S$) during the minor hysteresis loop are measured from the MFM images and show a range of polarizations from -53±5% to +58±5%. In contrast, room temperature VSM measurements of the total magnetic polarization of a sample is ±3% for the same minor $\hat{H}$-field loop. In this way, a switching of the $P_S$, which does not significantly affect the total magnetic polarization of the sample, with small $\hat{H}$-field ($\sim$0.17 kOe) is observed at room temperature. As well, a several tens of minutes delay (20 to 40 min) before reaching equilibrium is observed for the $P_S$ after changing the $\hat{H}$-field at room temperature. In contrast, room temperature VSM measurements show the total magnetization reaches equilibrium almost immediately (<<1 sec) after changing the $\hat{H}$-field.

5.2 Single Crystal Spin Valve Observed with Spin-Polarized Scanning Tunneling Microscopy in $\varepsilon$-Mn$_4$N Thin Films Grown on MgO(001)

5.2.1 Procedure

This experiment is performed in a custom designed UHV facility, which combines MBE with LT-SP-STM to allow study of as grown samples without external contamination (e.g. atmospheric) [4]. Two $\varepsilon$-Mn$_4$N ultrathin films (~9 nm) (samples 4.C and 4.D from Chapter 4), which were grown using the growth procedure for $\varepsilon$-Mn$_4$N ultrathin films laid out in Chapter 4, are used in this study. $\vec{M}$-$\hat{H}$ hysteresis loops are taken for each sample with in- and out-of-plane $\hat{H}$-fields as seen in Figs. 4.2(c) and (d). The in- and
out-of-plane remnant magnetization ($M_r$) as well as the $\vec{H}$-field needed to saturate each sample is determined from these SQUID measurements. In turn, the angle of the easy-axis with respect to the surface normal ($\Theta$) of each sample is calculated from these $M_r$:

$$\Theta = \tan^{-1}(\frac{M_r \parallel}{M_r \perp}) \ [2].$$

A Stanford Research System lock-in amplifier is used to extract a $\frac{dI}{dV}$ signal related to a 5 mV amplitude oscillation, which is provided by the lock-in amplifier, of the bias voltage of the STM at a frequency of 4.5 kHz during scanning. The $\frac{dI}{dV}$ value for a given area of the surface is determined by taking the average value within a $\frac{dI}{dV}$ map of that area. The $\frac{dI}{dV}$ value for a given point is determined using scanning tunneling spectroscopy (STS). The extracted $\frac{dI}{dV}$ signal is used to determine information about the local density of states (LDOS) and magnetization of the samples. A set point of $\sim$30 pA is used for the tunneling current for all STM images. Uncoated W tips are used to investigate the LDOS of the samples. As well, W tips coated with $\sim$50 monolayers (ML) of Fe are used to observe the effect of an external out-of-plane $\vec{H}$-field on the magnetization of the samples. The deposition of Fe on the W tips is calibrated in situ using an Inficon oscillating quartz crystal film thickness deposition monitor.

5.2.2 SP-STM Contrast during Major Hysteresis of Ultrathin ε-Mn₄N

Fig. 5.1 shows the $\frac{dI}{dV}$ contrast mapped over sample areas using uncoated and Fe-coated W tips with a -4 V bias while maintaining a current of $\sim$30 pA when 0 and 20 kOe is applied out-of-plane at L-He temperature. No $\frac{dI}{dV}$ contrast is found with a W tip between the mesa-like islands and box canyon-shaped valleys of the samples when either 0 or 20 kOe is applied out-of-plane. The only $\frac{dI}{dV}$ contrast observed with an uncoated W tip is associated with an artificial enhancement during the rapid rise of the tip as it travels over island edges. This contrast is identified as unrelated to LDOS because it switches polarity between left and right scans.
The $\varepsilon$-Mn$_4$N unit cell is composed of 4 Mn atoms in a face-centered cubic structure (1 corner atom and 3 face-centered atoms) with 1 N at the body center [39, 40]. Surface theory performed by Guerrero-Sánchez and Takeuchi indicates that the surface of a given $\varepsilon$-Mn$_4$N sample is expected to favor one of two surfaces depending on the N concentration of that sample [88]. Therefore, the observed lack of $\frac{dI}{dV}$ contrast due to differences in LDOS is expected because all the islands and valleys should possess the same surface for a single sample, in which the growth conditions were homogenous across the entire sample.

![Figure 5.1: SP-STM images taken of an ultrathin sample (∼9 nm) with a ∼30 pA tunneling current and a -4 V bias voltage at L-He temperature. Each row shows the topography of an area as well as the corresponding $\frac{dI}{dV}$ maps for the left and right directional scans. The top and bottom two rows show results from a demagnetized sample under 0 kOe and a fully magnetized sample under 20 kOe (out-of-plane), respectively. Both the top and bottom two rows contain one scan taken with an uncoated W tip and one scan taken with an Fe-coated W tip.](image)

Due to this lack of LDOS contrast with an uncoated W tip, the first term in Eq. 2.2 $[n_t(z, V)n_s(z, V)]$ can be treated as constant across different regions of an $\varepsilon$-Mn$_4$N sample when scanning with a single tip while maintaining a ∼30 pA current with a -4 V bias. In turn, any $\frac{dI}{dV}$ contrast seen while maintaining ∼30 pA current with a -4 V bias and using a single Fe-coated W tip is due to differences in the magnetic LDOS within the $\varepsilon$-Mn$_4$N sample.
It is known from MFM measurements [Figs. 4.5(c) and (d)] that the mesa-like islands and box canyon-shaped valleys of these ultrathin ε-Mn₄N samples (4.C and 4.D) have opposing out-of-plane aligned magnetizations when the samples are demagnetized. In agreement, a $\frac{dI}{dV}$ contrast is observed in a demagnetized ultrathin ε-Mn₄N sample between the mesa-like islands and box canyon-shaped valleys when using an out-of-plane magnetized Fe-coated W tip as seen in Fig. 5.1. In addition, this $\frac{dI}{dV}$ contrast goes away when the sample is magnetized by a 20 kOe out-of-plane $\vec{H}$-field, which would fully magnetize the sample, as seen in Figs. 4.2(c)/(d) and 5.1.

Electrons are predicted to strongly align in ε-Mn₄N with the magnetization of the material [59, 58, 60]. As well, only three alignments of magnetization [one alignment (in small abundance) has atoms with zero to nearly zero out-of-plane net-magnetization and the other two alignments (the majority of the total states) have atoms with magnetizations possessing significant out-of-plane components] are expected for an ε-Mn₄N sample based on a previous neutron diffraction experiment by Fruchart et al. [40]. Therefore, from Eq. 2.2, discrete differences in the $\frac{dI}{dV}$ signal between different ε-Mn₄N sample regions (e.g. islands and valleys) are expected to be proportional to a change in $\cos \alpha$ between different sample regions when at -4 V bias, where $\alpha$ is the angle between the magnetization of a sample region (potentially different between regions) and the magnetic LDOS vector of the tip (constant at single $\vec{H}$-field). In this way, the contrast in $\frac{dI}{dV}$ signal seen in Fig. 5.1 (with an Fe-coated W tip using these tunneling conditions) between valleys and islands of a demagnetized sample is attributed to these sample regions possessing anti-aligned and highly out-of-plane magnetizations.

SP-STM measurements shown in Fig. 5.2(b), in which $\frac{dI}{dV}$ contrast between islands and valleys is obtained with an out-of-plane magnetized tip over an initially demagnetized sample using the same tunneling conditions at L-He temperature, are consistent with this attribution. Starting with a demagnetized sample, five SP-STM images are taken over the
same area when the \textit{out-of-plane} $\mathbf{H}$-field is at 0 kOe, 0.165 kOe, 0.3 kOe, 0.5 kOe and 0.7 kOe (field increased between images) as shown in Figs. 5.2(c) to (f) respectively. The $\frac{dI}{dV}$ signals from the circled areas in Fig. 5.2(a) all show increasing $\frac{dI}{dV}$ with $\mathbf{H}$-field, which is consistent with the expected increase in alignment with $\mathbf{H}$-field as the $\mathbf{H}$-field increases.

Figure 5.2: (a) Topographic STM image of an ultrathin $\varepsilon$-Mn$_4$N sample at L-He temperature. (b) to (f) $\frac{dI}{dV}$ maps of the area shown in a). Starting with a demagnetized sample, the $\mathbf{H}$-field is increased between images from (b) 0 kOe, (c) 0.165 kOe, (d) 0.3 kOe, (e) 0.5 kOe, to (f) 0.7 kOe in the \textit{out-of-plane} direction. Circles in a) show areas, which switch magnetization as field increases.
As seen in Fig. 5.2, the valleys and islands maintain opposing polarization under small changes in $\vec{H}$-field ($<0.7$ kOe). This continued overlap of domains, leads to the question of whether the out-of-plane overlap of opposing domains is maintained throughout larger changes in field (e.g. a major hysteresis loop). In order to investigate this possibility, the $\frac{dI}{dV}$ response is observed in an $\varepsilon$-Mn$_4$N ultrathin film (4.D) for both valleys and islands during a major hysteresis loop ($\pm$20 kOe) while scanning with an Fe-coated W tip at L-He temperature as shown in Fig. 5.3.

Figure 5.3: Average value of $\frac{dI}{dV}$ for several islands and valleys of an $\varepsilon$-Mn$_4$N ultrathin sample (4.D) at various field values during a $\pm$20 kOe hysteresis loop when the field is being (a) increased (forward) and (b) decreased (reverse) at L-He temperature.
Each point on the graph in Fig. 5.3 corresponds to the average $\frac{dI}{dV}$ signal found across either multiple islands or multiple valleys when at a particular $\vec{H}$-field value. For example, the red and white boxes in Figs. 5.4(a) and (c) indicate areas sampled in order to determine the average $\frac{dI}{dV}$ value at a particular $\vec{H}$-field for islands and valleys respectively. Flat regions are chosen for the red boxes in order to minimize topography artifacts in the $\frac{dI}{dV}$ signal. As well, the red boxes sample the tallest portions of the mesa-like islands in order to sample regions with the furthest vertical separation from the box canyon-shaped valleys. The white boxes are positioned away from the edges of the box canyon-shaped valleys in order to avoid topography artifacts in the $\frac{dI}{dV}$ signal coming from valley edges.

First, in order to plot Fig. 5.3, the average $\frac{dI}{dV}$ value is found across the area within each box. Then, the values from each box of a given color (i.e. islands or valleys) are averaged in order to find the average $\frac{dI}{dV}$ signal (the data points in Fig. 5.3) for each $\vec{H}$-field. A splitting between the $\frac{dI}{dV}$ signals is observed between valleys and islands when moving towards 0 kOe at both -5 and 5 kOe as seen Figs. 5.4(c) and (d), which correspond to the topographic images shown in Fig. 5.4(a) and (b) respectively. From SQUID measurement, the magnetization of the sample is 80% of $M_S$ at 5 kOe following full magnetization at 20 kOe.
Figure 5.4: (a) and (b) Topographic STM images of an \( \varepsilon \)-Mn\(_4\)N ultrathin sample (4.D) at L-He temperature. (c) and (d) \( \frac{dI}{dV} \) maps corresponding to a) and b) respectively. (c) A -5 kOe \( \mathbf{H} \)-field is applied \textit{out-of-plane} after fully magnetizing the sample with a -20 kOe \textit{out-of-plane} \( \mathbf{H} \)-field. (d) A 5 kOe \( \mathbf{H} \)-field is applied \textit{out-of-plane} after fully magnetizing the sample with a 20 kOe \textit{out-of-plane} \( \mathbf{H} \)-field. Red and white boxes in c) indicate examples of areas over islands and valleys, which are sampled in order to find the average \( \frac{dI}{dV} \) signal across multiple valleys and islands, respectively.

Based on previous experiment, the magnetic tips used here are expected to have an \( H_C \) well below 5 kOe [89, 90]. Therefore, the magnetization of the Fe-coated W tips during the splitting are expected to remain almost fully \textit{out-of-plane} because \( H_C \) is expected to be significantly exceeded for both before and after the splitting. From this, it can be concluded that the splitting is due to a change in the sample and not the tip because the state of the tip should not change significantly. The \( \frac{dI}{dV} \) contrast between the two antiparallel domains aligned with the easy-axis (7° from surface normal) would be proportional to \( \cos(173° - 0°) - \cos(7° - 0°) \), which is 99% of the alignment with maximum possible contrast (tip and antiparallel domains all on the same axis).
As well, the remnant magnetization after *out-of-plane* magnetization reported for W tips coated with similar thicknesses of Fe is neither completely *in-* or *out-of-plane* [91, 92]. Assuming a tip magnetization at $\sim 45^\circ$, the calculation of the $\frac{dI}{dV}$ contrast in this case [the two antiparallel domains aligned with the easy-axis ($7^\circ$ from surface normal)] is reduced ($\frac{\cos(173^\circ - 45^\circ) - \cos(7^\circ - 45^\circ)}{2} = 70\%$ of optimal alignment) compared to the value calculated for the conditions at $\pm 5$ kOe (99%). This serves as an explanation for the reduction in $\frac{dI}{dV}$ contrast seen in Fig. 5.3 when going from -5 kOe to 0 kOe as well as from 5 kOe to 0 kOe.

The remnant magnetization of the sample (4.D) is found with SQUID measurements to be 30\% of the saturation magnetization, which indicates the difference between the amount of up and down states in the sample is 30\% of the total states. In addition, the amount of the sample (4.D) in the base (40\%) and islands (60\%) is known from Chapter 4. Therefore, if the magnetic domains continue to overlap *out-of-plane*, there should be reduced $\frac{dI}{dV}$ contrast at 0 kOe between the valleys and islands in the forward and reverse directions due to the domain boundary beginning to cross the surface of the valleys as depicted in Figs. 5.5(c) and (g). In agreement, $\frac{dI}{dV}$ contrast is found at 0 kOe in the forward direction and not the reverse direction as seen in Figs. 5.3(a) and (b) respectively.
Figure 5.5: Schematic of the expected spin valve under various fields at L-He temperature. (a) to (f) show the expected magnetization of the tip and the position of the domain boundary in this spin valve at various applied $\mathbf{H}$-fields. (a) to (d) correspond to an increasing $\mathbf{H}$-field going from (a) -20 kOe, (b) -5 kOe, (c) 0 kOe to (d) 2.5 kOe. (e) to (h) correspond to a decreasing $\mathbf{H}$-field going from (e) 20 kOe, (f) 5 kOe, (g) 0 kOe to (h) -2.5 kOe.
At ±2.5 kOe after passing 0 kOe, the $\frac{dI}{dV}$ contrast between the valleys and islands is expected to be even more reduced after the $\vec{H}$-field passes 0 kOe as depicted in Figs. 5.5(d) and (h) because of the further increasing magnetizations at these $\vec{H}$-fields. In agreement, no $\frac{dI}{dV}$ contrast larger than a standard deviation of the $\frac{dI}{dV}$ signals can be resolved at these $\vec{H}$-fields (an increasing absolute value ≥2.5 kOe) as shown in Fig. 5.3. Due to the absence of clear contrast, the domain boundary is expected to reach the surface of the mesa-like islands and the bottom of the base as depicted in Figs. 5.5(d) and (h).

A wider standard deviation is observed for the $\frac{dI}{dV}$ signal of the valleys compared to the islands when the $\vec{H}$-field is at ±5 kOe and going to zero as seen in Fig. 5.3. This larger standard deviation is explained by some of the smaller isolated islands within the valleys not sharing the same $\frac{dI}{dV}$ signal as the rest of the valleys at this point in the hysteresis as seen in Fig. 5.4 and depicted in Figs. 5.5(b) and (f). The standard deviation is expected to reduce as the $\vec{H}$-field continues toward zero due to the $\frac{dI}{dV}$ signal valleys becoming more consistent as depicted in Figs. 5.5(c) and (g).

In agreement, the standard deviation of the $\frac{dI}{dV}$ signal from the valleys reduces as $\vec{H}$-field continues toward zero as seen in Fig. 5.3. In this way, the $\vec{H}$-fields, over which this reduction in standard deviation takes place, match the $\vec{H}$-fields when the boundary between out-of-plane overlapping magnetic domains are expected to pass the surface of the valleys based on the values of sample magnetization from SQUID. Together, the contrasts and standard deviations in $\frac{dI}{dV}$ seen during a major hysteresis loop (±20 kOe) are consistent with a boundary between two out-of-plane overlapping magnetic domains being moved towards and away from the surface with increasing and decreasing out-of-plane $\vec{H}$-fields respectively.

The magnetic domains extend laterally beyond the range of 40 µm wide areas in the ε-Mn$_4$N ultrathin samples (4.C and 4.D) as demonstrated with MFM measurements in Chapter 4. It follows that the primary direction available for such a domain to expand is
expected to be *out-of-plane* because the domain already occupies much of the lateral space. In this way, the *out-of-plane* domain motion is attributed to the shape of magnetic domains, which in turn is attributed to an *out-of-plane* shape anisotropy in Chapter 4.

5.2.3 Quantized Local Density of States in Ultrathin $\varepsilon$-Mn$_4$N at Low Temperature under Zero $\vec{H}$-Field

There is a clear $\frac{dI}{dV}$ contrast between anti-aligned domains observed with SP-STM. Further, if two anti-aligned domains are overlapping *out-of-plane* in these ultrathin films, there should be a giant magnetoresistive (GMR) effect in these samples related to the spin-polarized current from one domain having an increased resistance associated with entering an anti-aligned domain. This indicates that when the system is demagnetized at low temperature there are two layers, which are separated by an energy barrier (GMR effect), with highly polarized spins oppositely aligned *out-of-plane* without any external $\vec{H}$-field applied. These parameters match many of the hallmarks (two conductive regions with spin populations anti-aligned *out-of-plane* that are separated by an energy barrier when under no external $\vec{H}$-field) of systems, which exhibit the anomalous quantum Hall effect (AQHE) [86, 87].

It should be noted, that chromium telluride based ultrathin films have shown properties similar to those of $\varepsilon$-Mn$_4$N ultrathin films: namely; a large *out-of-plane* PMA and AMR [93, 94]. In addition, AQHE has been observed in chromium telluride based ultrathin films [94]. Due to the similarities between the two systems and the presence of the AQHE in chromium telluride based films, further investigation of the potential presence of the AQHE in $\varepsilon$-Mn$_4$N ultrathin films is of interest.

Another hallmark of the AQHE, which can be investigated, is the quantization of the LDOS of a sample at specific energy levels without any external $\vec{H}$-field applied [86, 87]. In order to investigate the LDOS of a demagnetized $\varepsilon$-Mn$_4$N ultrathin sample, a series of STM
images of atomically flat terraces on such a sample are taken at a series of bias voltages and a constant tunneling current (~30 pA) while using an uncoated W tip at low (LHe) temperature under zero applied \( \vec{H} \)-field. The average \( \frac{dI}{dV} \) signal corresponding to each of these voltages was then taken from the \( \frac{dI}{dV} \) map corresponding to these terraces. The \( \frac{dI}{dV} \) values obtained from this measurement are shown in Fig. 5.6. This method results in the distance between the tip and the sample varying with bias voltage.
Figure 5.6: (a) $\frac{dI}{dV}$ values of the surface of a mesa-like island on an $\varepsilon$-Mn$_4$N ultrathin sample (9 nm thick) using an uncoated W tip with a $\sim$30 pA tunneling current at various bias voltages when at L-He temperature. (b) A zoom-in of a), which better shows the smaller peaks in $\frac{dI}{dV}$. 
Peaks, which are symmetrically positioned around an enormous central peak (located between ±5 mV), in the $\frac{dI}{dV}$ signal are found as seen in Fig. 5.6. The symmetric positioning of the peaks around the central peak suggests that the peaks are at quantized values. Also indicating quantization, the positions of these peaks relative to the central peak appear to be increasing by factors that are the square roots of integers ($\pm 1.2 \text{ V, } \pm \sqrt{6} \times 1.2 \text{ V } = 2.9 \text{ V, } \pm \sqrt{12} \times 1.2 \text{ V } = 4.2 \text{ V, } \ldots$). The areas under the peaks relative to the enormous central peak for the -2.9 V, -1.2 V, 1.2 V, and 2.9 V peaks are found to be 30%, 35%, 15% and 60% respectively. In addition, the enormous central peak [seen in Fig. 5.6(a)] agrees with a similar enormous peak at the 0th peak position seen by Spielman et al. in a system exhibiting the quantum Hall effect [86].

On the other hand, no such enormous central peak is found with low temperature scanning tunneling spectroscopy measurements [$\sim 100 \text{ pA and 0.4 V bias initial set point (i.e constant tip height)}$] on an $\varepsilon$-Mn$_4$N thin sample (103 nm thick) as seen in Fig. 5.7. In addition, the shoulder seen near 0.1 V in Fig. 5.7 has no analogous shoulder or peak opposite the central $\frac{dI}{dV}$ valley. This indicates that the $\frac{dI}{dV}$ peaks (enormous central and smaller symmetric) of the ultrathin film are related to the lower thickness of the ultrathin sample (9 nm compared to 103 nm). In agreement with the interpretation that the ultrathin films may be showing signs of AQHE, quantized peaks, which are associated with AQHE, are typically seen in 2D materials and not thicker materials [95].
Figure 5.7: Average LT-STS of 312 spectra (2nd order polynomial Savitzky-Golay with 10 point smoothing) on the surface of an $\varepsilon$-Mn$_4$N thin sample (103 nm thick) using an uncoated W tip with a $\sim$100 pA current and 0.4 V bias initial set point.

It should be noted, the anomalous Hall effect has been observed previously in $\varepsilon$-Mn$_4$N thin films [63, 79, 85]. Therefore, it is reasonable that this effect may be quantized at ultrathin thickness and low temperatures. Landau lines, which are associated with the quantum Hall effect, are generally related to the energies of cyclotron oscillations, which are induced by an out-of-plane $\vec{H}$-field, of electrons in 2D materials [86]. A potential explanation for the quantized $\frac{dI}{dV}$ peaks observed for the $\varepsilon$-Mn$_4$N ultrathin film is as follows: a substantial magnetic field interaction between two dipole layers, which are oppositely magnetized out-of-plane in the film, induces a cyclotron oscillation in the quasi-2D ($\sim$45 mL thick) layers of the film and hence Landau lines.

Further theory is needed to determine if the quantized levels seen in Fig. 5.6(b) match the expected Landau levels of such a system. These calculations may be non-trivial due to what appears to be a quasi-2D nature for these $\varepsilon$-Mn$_4$N ultrathin films ($\sim$45 monolayers thick) because $\frac{dI}{dV}$ peak quantization related to the quantum anomalous Hall effect is usually associated with 2D systems (a few monolayers or less) [95]. As well, additional
measurements probing the \( \frac{dl}{dV} \) peak positions under different \( \vec{H} \)-fields should provide more information in order to determine if the peaks are related to Landau levels in these \( \varepsilon \)-Mn\(_4\)N ultrathin films [96, 97].

As discussed in Chapter 4, the energy of the dipole-dipole interaction, which is attributed to an internal (molecular) magnetic field interaction between the overlapping domains, scales linearly with thickness. Therefore, it should be possible to scale the magnetic field between the overlapping dipoles in an \( \varepsilon \)-Mn\(_4\)N ultrathin film by adjusting the thickness of the samples. In this way, the potential relationship between the dipole-dipole interaction and the quantized \( \frac{dl}{dV} \) peaks observed here for \( \varepsilon \)-Mn\(_4\)N ultrathin films may be investigated by probing the peak positions at various film thicknesses. For example, the \( \frac{dl}{dV} \) peak positions are more than an order of magnitude (10\( \times \)) larger than the positions observed in QHE systems (<0.2 V) under large external \( \vec{H} \)-fields (100 kOe) [96]. Therefore, the peak positions observed here may indicate the internal magnetic field interaction is very large [on the order of \( 10^2 \times 100 \) kOe]. This seems unreasonable. For this reason, an explanation of the peak position, which is much larger than a typical QHE system, besides a huge internal magnetic field is being pursued.

### 5.2.4 Conclusions

SP-STM contrast, which is in agreement with the MFM data from Chapter 4, of \( \varepsilon \)-Mn\(_4\)N ultrathin films is obtained. Based on the known sample magnetizations from SQUID, the changes in \( \frac{dl}{dV} \) contrast between the box canyon-shaped valleys and mesa-like islands during a major hysteresis loop (\( \pm 20 \) kOe) are consistent with a boundary between two out-of-plane overlapping magnetic domains being moved towards and away from the surface with increasing and decreasing out-of-plane \( \vec{H} \)-fields. This organization of magnetic domains would be expected to produce a GMR effect, which can be turned on
and off with external $\vec{H}$-field, in single crystals of $\varepsilon$-Mn$_4$N. In this case, a single crystal of this versatile spin-contact would be able to serve as a spin-valve by itself.

In addition, a quantization of $\frac{dI}{dV}$ peaks is observed in $\frac{dI}{dV}$ maps of an $\varepsilon$-Mn$_4$N ultrathin film (9 nm). A comparable quantization is not observed in thicker films (103 nm) using STS. Further resistivity measurements versus thickness and $\vec{H}$-field are needed on these $\varepsilon$-Mn$_4$N ultrathin films in order to determine how out-of-plane overlapping magnetic domains and $\frac{dI}{dV}$ peak quantization may be related to the anomalous Hall effect previously observed in $\varepsilon$-Mn$_4$N thin films [63, 79, 85]. As well, further magnetic microscopy investigations are needed to determine if out-of-plane overlapping domains may be related to the AMR and AQHE observed in ultrathin films of any other materials (e.g. chromium telluride based materials) [93, 94].

5.3 Polarity Switching of Ising Domain Overlap in $\varepsilon$-Mn$_4$N Thin Films under Low $\vec{H}$-field

5.3.1 Procedure

Atomic (magnetic) force microscopy is performed using a Park Scientific CP AFM/MFM head retrofitted with a new controller system by Anfatec Inc., which is operated ex situ to obtain information about the topographical and magnetic properties of samples 4.A and 4.B at RT. The surface magnetic polarization is determined using our variation of the Park et al. technique as described in Section 2.2 [25]. A Fisher Scientific FS60 Ultrasonic Cleaner was used to vibrate the samples for $\sim$10 min intervals in order to remove any net magnetic polarization in the samples when necessary. The $\vec{H}$-field during MFM measurements is supplied by a permanent magnet and calibrated using a gauss meter at the position of the sample to within $\pm$5 Oe. Total magnetization versus $\vec{H}$-field is measured for the samples using a RT-VSM. The diamagnetic contribution of the MgO substrate to
the magnetization is subtracted out using the RT-VSM measurement of a blank MgO as a reference.

5.3.2 Magnetic Force Microscopy during a Minor Hysteresis Loop

Magnetic domain motion is observed across multiple images taken at a single $\vec{H}$-field value over time spans of multiple minutes (20 to 40 min) as seen in Fig. 5.8. It can be seen in Fig. 5.8(a) (a down scan) that in the first image ($\sim$20 min to scan one image) after changing the $\vec{H}$-field from 120 Oe to 130 Oe there are several lines where an instance of sudden domain motion has occurred. The second image taken at the same $\vec{H}$-field immediately following the first can be seen in Fig. 5.8(b) (an up scan). Figure 5.8(b) can be seen to contain domains with an increased surface area compared to domains in Fig. 5.8(a). As well, Fig. 5.8(b) has no lines where a sudden domain motion occurs. This reduction in lines with sudden domain motion is attributed to the sample reaching equilibrium over time (20 to 40 min).
Figure 5.8: Two ∼15 μm MFM images of sample 4.A, which are taken over the same area at RT after changing the $\vec{H}$-field to 130 Oe and take ∼20 minutes each to acquire. (a) Down scan. (b) Up scan immediately following a).

This domain motion at constant $\vec{H}$-field indicates a time delay of multiple tens of minutes before the overlapping of magnetic domains in an $\varepsilon$-Mn$_4$N sample reaches equilibrium for each new $\vec{H}$-field value. In contrast, VSM measurements (not shown here) of the magnetization of the entire sample (sample 4.A) after switching the $\vec{H}$-field on the initially demagnetized sample from 0 to 165 Oe show a magnetization of ∼3% of $M_S$ is reached in a time span negligible compared to the MFM measurement ($<<1$ s) and then
the magnetization remains constant for over 25 minutes. In this way, the surface magnetic polarization is continuing to change over large timescales (20 to 40 min) when the magnetic polarization of the entire sample is known to be static. Therefore, it is observed that the surface magnetic polarization of the sample can change without significantly affecting the magnetic polarization of the sample as a whole.

The magnetic domains over a single area of sample 4.A during an $\vec{H}$-field loop (-165 Oe to 170 Oe) are shown in Fig. 5.9. The corresponding changes in $P_S$ are measured and show a range of from -53±5% to +58±5% as shown in Fig. 5.10. In contrast, room temperature VSM measurements of the total magnetic polarization of a sample is ±3% for the same $\vec{H}$-field loop as seen in Figs. 5.10(b) and (c). Therefore, sample 4.A is at nearly zero (<3%) magnetization during this minor hysteresis (-165 to 170 Oe) and the substantial changes in $P_S$ are nearly all due to domain motion.
Figure 5.9: MFM images numbered 1-10 each taken over the same area (topography seen in bottom left) taken when sample 4.A (310 nm thick) is under various out-of-plane fields during a minor hysteresis loop (∼±165 Oe) at RT. MFM image 2 not shown.
Figure 5.10: (a) The magnetization distributions for MFM images numbered 1-10 seen in Fig. 5.9. (b) A comparison of the magnetization values obtained with RT-VSM (black) and the surface polarization values obtained with RT-MFM (red and numbered). (c) Zoom-in of VSM measurement in b).
The fact that the change in surface polarization is due nearly entirely to domain motion leads to the model depicted in Fig. 5.11. In this model, the center of the domains are stationary and the polarity of the regions of overlap switches as depicted in the change between Fig. 5.11(a) and (c). As seen in Fig. 5.11(b), this model predicts that at one point during the domains flipping their overlap, the interiors of the domains no longer have an anti-aligned dipole above or below them. Due to this, the interior of the domains are expected to lose the PMA contribution from the dipole-dipole shape anisotropy. After losing this PMA contribution, the polarization of the interior of the domains would become much less \textit{out-of-plane} due to the loss of a substantial amount of \textit{out-of-plane} anisotropy as depicted in Fig. 5.11(b). In agreement, at the point in the minor hysteresis where samples 4.A and 4.B are near zero surface polarization the interior of the domains have a greatly reduced \textit{out-of-plane} MFM signal compared to the edges of the domains, which are expected to still overlap with anti-aligned dipoles, as seen in Fig. 5.12.
Figure 5.11: Diagram depicting the magnetic domain motion of an $\varepsilon$-Mn$_4$N thin film during minor hysteresis at RT. Solid lines indicate domain boundaries. Whereas, dotted lines indicate the transition point between strong and weak dipole-dipole interaction. (a) Sample at the negative end of the minor hysteresis loop. (b) Sample at zero surface polarization. (c) Sample at the positive end of the minor hysteresis loop.
Figure 5.12: RT-MFM data from samples 4.A and 4.B when they are at zero magnetic surface polarization during minor hysteresis loops. (a) 15 μm MFM image of 4.A. (b) 12.5 μm MFM image of 4.B. (c) The distribution of magnetization values taken from a) and b). (d) Line profile taken across b).
As well, at this transition point it is expected that some of the domain boundaries have up domains overlapping down domains and others have down domains overlapping up domains as depicted in Fig. 5.11(b). In agreement, the domain boundaries observed in Fig. 5.12 having brighter and darker regions is interpreted as the transition occurring at some parts of the domain boundary before others. In this way, MFM and VSM measurements are consistent with a small $\vec{H}$-field ($\pm 165$ Oe) flipping the surface magnetization of $\varepsilon$-Mn$_4$N thin films at RT. This flipping of the surface magnetization in the films is attributed to anti-aligned overlapping domains in the films undergoing domain motion, which results in the overlapping domains becoming the underlying domains and vice versa.

From these MFM images taken near zero surface polarization, the distance of the dipole-dipole interaction can be measured by looking at the width at the edges of the domains in which there is still strong out-of-plane alignment. In order to measure the typical width, the average distance of 20 widths is taken from an image of sample 4.B near zero surface polarization [Fig. 5.12(b)]. In agreement with Chapter 4, the width of the dipole-dipole interaction measured here ($510 \pm 170$ nm) is larger and of the same order as the sample thickness at which the second term of shape anisotropy is expected to dissipate ($\sim 360$ nm). The change in the polarity of the out-of-plane overlap of the domains is seen in $\varepsilon$-Mn$_4$N thin films at room temperature and not observed in $\varepsilon$-Mn$_4$N ultrathin films with SP-STM at L-He temperature.

A likely explanation for this difference is that the $P_5$ switching is frozen out at L-He temperatures. Potentially related to this, a temperature dependence on the magnetoresistive effects (AHE and AMR) found in $\varepsilon$-Mn$_4$N thin films has been observed [85]. Speculatively, if out-of-plane dipole overlap in $\varepsilon$-Mn$_4$N thin films is related to these magnetoresistive effects then a dependence of the domain flipping on temperature would be anticipated. Further study in which $\varepsilon$-Mn$_4$N ultrathin films are taken through a minor hysteresis loop at room temperature are needed in order to test this potential temperature dependence on
domain flipping and check if the temperature dependence of the observed magnetoresistive effects may be related.

Another potential explanation for this difference in $P_S$ switching is that the sample shape of the ultrathin films confines the domain motion such that $P_S$ switching is limited. It is shown in Chapter 4 that the domains are pinned by sample shape. As well, the domains appear to become pinned along trench structures, which are attributed to the MgO substrate based on previous AFM showing similar trench structures on bare MgO substrates from the same batch, in sample 4.A during a minor hysteresis loop as seen when comparing images 5 and 10 to the topographic image (bottom left) from Fig. 5.9. Therefore, it is reasonable to expect that the domains would have greater pinning along the box canyon-shaped valleys of the ultrathin samples. For this reason, additional study of thin and ultrathin samples is needed at room and L-He temperatures in order to determine the cause(s) (temperature or shape) of the $P_S$ switching under small $\vec{H}$-field.

### 5.3.3 Conclusions

In summary, a significant change to the magnetic surface polarization of the film ($-53\pm5\%$ to $+58\pm5\%$) is observed when taking a $\varepsilon$-Mn$_4$N thin film through a minor hysteresis (-165 Oe to 170 Oe). The change in total magnetization of the same sample over the same field range is found to be much less significant ($\pm3\%$). This agrees with the presented model of domain motion, in which the polarity of the out-of-plane overlap of domains switches under small $\vec{H}$-fields ($\sim\pm200$ Oe) without significant changes to the magnetization of the entire sample ($<3\%$). Based off of this model, the distance at which the dipole-dipole interaction is significant is estimated ($510\pm170$ nm) to be larger and of the same order as the film thickness at which the dipole-dipole interaction is predicted in Chapter 4 to become insignificant (360 nm). This model indicates that small $\vec{H}$-fields ($\pm170$ Oe) can switch the magnetic polarity of the surface of these $\varepsilon$-Mn$_4$N thin films.
between two orientations (positive and negative collinear states with large *out-of-plane* components) with some unknown less *out-of-plane* state(s) as an intermediary orientation. In this way, these $\varepsilon$-Mn$_4$N thin films exhibit ternary switching under small $\vec{H}$-fields. Further investigation (neutron diffraction, SP-STM ...) of the magnetic ordering of atoms in the intermediary orientation are needed in order to determine the nature of the less *out-of-plane* state(s).
6 GROWTH AND MAGNETIC PROPERTIES OF $\gamma$-TYPE $\zeta$-PHASE

Mn$_{10}$N on MgO(001)

This chapter includes a portion of a published paper, which discusses the growth of $\zeta$-phase Mn$_{10}$N on MgO(001) [50]. As well, evidence, which partially supports the coexistence of ferromagnetic and antiferromagnetic properties in $\zeta$-phase Mn$_x$N$_y$, is presented in this chapter.

6.1 High Phase-Purity Growth of $\gamma$-type $\zeta$-phase Mn$_{10}$N on MgO(001)

Single phase $\zeta$-Mn$_{10}$N thin films are grown on MgO(001) using molecular beam epitaxy. The films are identified and characterized using reflection high-energy electron diffraction, x-ray diffraction, atomic/magnetic force microscopy and Rutherford backscattering spectrometry. These films are found to be highly smooth with root-mean-squared roughnesses of ~0.8 nm. Measurements of the $\zeta$-phase detail the structure of the material as high Mn content (Mn$_{10}$N) $\gamma$-type $\zeta$-phase with a regular surface corrugation along the [100]-direction of the MgO substrate.

6.1.1 Introduction

Transition metal (TM) nitrides such as (Mn,Fe,Co)$_x$N$_y$ have been demonstrated to possess a wide range of magnetic properties with tunability between different types of magnetism (e.g. ferromagnetic, antiferromagnetic, non-magnetic, or ferrimagnetic) via phase control of each material [1, 51, 52, 53]. Giant magnetoresistance (GMR) devices depend on the controlled organization of magnetic properties (e.g. alternating layers with different magnetism). Therefore, the growth of all the phases of a single TM nitride (e.g. Mn$_x$N$_y$) on a single type of substrate [e.g. MgO(001)] is of interest for GMR device fabrication because it would maximize the options of magnetic properties available in a single growth environment [e.g. Mn$_x$N$_y$ on MgO(001)].
The antiferromagnetic $\zeta$-phase of $\text{Mn}_x\text{N}_y$ is typically grown through incorporation of some gaseous form of N into solid Mn (e.g. reactive annealing) [3, 14, 64, 98]. Additionally, $\zeta$-phase $\text{Mn}_x\text{N}_y$ has been grown epitaxially on a hexagonal substrate (sapphire) [99]. It has been proposed that the $\zeta$-phase does not grow on MgO(001) due to the hexagonal versus tetragonal nature of the $\zeta$-phase versus MgO [1, 99]. Unlike the other phases of $\text{Mn}_x\text{N}_y$, which each fall within a narrow range of Mn percentage (Mn%) values ($\pm \sim 2\%$), the $\zeta$-phase has been found to be stable within a wide range from 64% to 92% [14].

A growth study is performed on $\zeta$-phase $\text{Mn}_x\text{N}_y$ grown on MgO(001). The growth is characterized using RHEED, XRD, Rutherford backscattering spectrometry (RBS) and AFM/MFM. The application of these characterization techniques reveals the Mn% can be raised above the stability limit of $\varepsilon$-Mn$_4$N ($\sim 81.5\%$), which results in an upper stability limit $\zeta$-phase on MgO(001) ($\sim 92\%$). This high Mn:N ratio identifies the sample as $\gamma$-type $\zeta$-phase $\text{Mn}_{10}\text{N}$. XRD and RHEED measurements are found to be in agreement with this identification. High phase-purity is present in these $\gamma$-type $\zeta$-phase $\text{Mn}_{10}\text{N}$ samples. However, the crystal growth direction is mixed. A stripe-like superstructure with stripes running parallel to the MgO [100]-direction ([100]$_{\text{MgO}}$) is observed on the $\gamma$-type $\zeta$-phase $\text{Mn}_{10}\text{N}$ grown on MgO(001) surface. This is the fourth and final phase of $\text{Mn}_x\text{N}_y$ to be grown on MgO(001) [1, 3, 50]. Following the original publication of this project, growth of a single crystal direction was achieved for the $\zeta$-phase on MgO(001) by Wang et al. [16, 50].

### 6.1.2 Procedure

All samples were prepared in a custom designed ultra-high vacuum molecular beam epitaxy system [4]. The $\text{Mn}_x\text{N}_y$ samples were grown on MgO(001) substrates. Beforehand, the substrates were cleaned ex situ using solvent, first with acetone and then with isopropyl-
alcohol. Additional in situ cleaning of the substrate was performed by annealing at a temperature of 1000 °C with nitrogen plasma incident for ~1 hr. Manganese flux was provided by a custom designed effusion cell operated at temperatures of ~1200 °C, whereas N flux was supplied by an RF N Plasma Source (SVT Associates) with a forward power of 450 W and N₂ as the source gas. The Mn flux is measured using a quartz crystal thickness monitor giving readings in Å/s, while the effective N flux is determined by finding the crossover point between Ga- and N-rich GaN growth [23].

RHEED is actively used in situ during growth with a 20 keV incident electron beam energy in order to monitor the phase of growth based on the observation of phase specific surface structure/reconstruction; this is determined by measuring, for example, the characteristic RHEED streak spacings and from these determining the in-plane lattice constant(s) by means of the RHEED calibration. The calibration is performed for each growth using the MgO substrate post-annealing streak spacings as a reference. XRD is applied ex situ employing Cu Kα x-rays in order to determine the bulk crystal structure normal to the substrate surface including atomic spacings prevalent in the samples. The bulk Mn:N ratios in the samples are determined using RBS. Atomic/magnetic force microscopy is performed using a Park Scientific CP AFM/MFM head retrofitted with a controller system by Anfatec Inc., which is operated ex situ to obtain information about the topographical and magnetic properties of the samples. The MFM is performed in phase contrast mode, giving a picture of the stray field map of the samples at a certain height z above the sample plane. Analysis of the obtained stray field maps is used to infer sample domain structure.

6.1.3 Growth Summary

Control of the sample growth parameters in this study enabled the synthesis of high-phase purity ζ-phase thin films on MgO(001). Although growth of η-phase is typically
achieved at sample temperatures up to 450 °C, and the growth of ε-phase can be achieved at sample temperatures above 450 °C, growth of ζ-phase favors not only temperatures of ~480 °C or higher but also requires a growth interrupt to trigger this less common phase to appear; this is achieved by temporarily closing the plasma shutter to interrupt N-flux during growth [50].

Figure 6.1(a) shows the RHEED pattern characteristic of the post-annealing MgO substrate on which each of the samples were grown. The bright uniform streaks together with the sharp Kikuchi lines within the characteristic RHEED pattern of these substrates shows that the substrate surface was highly-smooth, well-ordered MgO suitable for RHEED calibration. Figures 6.1(b) and 6.2 present the RHEED and XRD patterns, respectively, for the samples to be focused on in this study with all associated values tabulated in Table 6.1. The presentation begins with a discussion of the diffraction (RHEED and XRD) data for the ζ-phase samples and then follows with a discussion of the RBS data.
Figure 6.1: RHEED taken *in situ* along the [100]-direction relative to the MgO substrate during the growth of a $\zeta$-Mn$_{10}$N sample. (a) Taken of an annealed MgO substrate. (b) Taken of a $\zeta$-Mn$_{10}$N sample.

Figure 6.2: *Out-of-plane* XRD taken of a $\zeta$-Mn$_{10}$N sample.
Table 6.1: Comparisons of out-of-plane XRD and in-plane RHEED data for a $\zeta$-Mn$_{10}$N sample with values from literature for a $\gamma$-type $\zeta$-phase sample [3]. All RHEED measurements were taken along the MgO [100]-direction.

<table>
<thead>
<tr>
<th>Growth plane (h k l)</th>
<th>Observed (Å)</th>
<th>Expected (Å)</th>
<th>Observed (Å)</th>
<th>Expected (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRD</td>
<td>out-of-plane</td>
<td>RHEED</td>
<td>in-plane</td>
</tr>
<tr>
<td>$\gamma$-type $\zeta$-phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 0 1)</td>
<td>2.15±0.01</td>
<td>2.16</td>
<td>5.23±0.15</td>
<td>5.36</td>
</tr>
<tr>
<td>(3 0 4)*</td>
<td>4.53±0.01</td>
<td>4.55</td>
<td>4.95±0.10</td>
<td>4.91</td>
</tr>
<tr>
<td>(0 0 2)</td>
<td>2.43±0.01</td>
<td>2.45</td>
<td>5.23±0.15</td>
<td>5.36</td>
</tr>
<tr>
<td>*This plane is 7.79° off (101) and associated with a facet, which would be formed at the surface between Mn atoms in nearest (101) Mn-planes of different bases.</td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

The presentation finishes with a discussion of the microscopy data (AFM and MFM) of the $\zeta$-phase samples. The requirement of a substrate temperature over 450 °C for growth of the $\zeta$-phase samples is consistent with Yang et al., in which at 450 °C the growth of $\zeta$-phase on MgO(001) was unobserved [1]. Samples in this project were not intentionally annealed for any significant times, although it has been shown that $\theta$, $\eta$, $\zeta$, and $\epsilon$ (up to as high as 4:1 Mn:N) can be achieved by successively increasing annealing temperatures which results in increasing levels of N loss [64].

6.1.4 Crystallography

The RHEED and XRD taken from a 510 °C $\zeta$-phase sample are shown in Fig. 6.1 and Fig. 6.2, respectively. The RHEED pattern shown in Fig. 6.1 shows split 1st and 2nd order streaks, which together indicate two in-plane spacings of 4.95±0.10 Å (bottom arrow dotted) and 5.23±0.15 Å (bottom arrow solid). There is also a streak (bottom arrow dotted)
with an associated spacing of 9.87±0.22 Å, which is close to 2× the 4.95 Å spacing. As well, there is a 1st order streak (top arrow) showing a 3.80±0.24 Å \textit{in-plane} spacing with a chevron, which is observed in the angular splitting at the bottom of the streak. Such chevron features can be characteristic of refraction effects due to surface faceting \cite{100}. However, the observed chevrons are too weak and apex location too unclear to obtain an accurate measurement of the angle between the facet and the growth plane.

X-ray diffraction in Fig. 6.2 shows no \(\epsilon\)-, \(\eta\)-, or \(\theta\)-phase peaks, but instead a sizeable 101 \(\zeta\)-phase peak corresponding to a \(d\)-spacing of 2.15 Å, and two additional \(\zeta\)-phase peaks (002 and 100) corresponding to \(d\)-spacings of 4.53 Å (002) and 2.43 Å (100). These measured \(d\)-spacings agree with known values for \(\gamma\)-type \(\zeta\)-phase \(\text{Mn}_x\text{N}_y\) presented by Leineweber \textit{et al.} and are shown in Table 6.1 \cite{3}. Corresponding to the three \(\zeta\)-phase peaks seen in the XRD are three planes within the perspective view of the \(\gamma\)-type \(\zeta\)-phase model shown in Fig. 6.3. The 002 XRD peak corresponds to the interplanar distance between \(c\)-planes in the \(\gamma\)-type \(\zeta\)-phase structure with known \(c\)-spacing 4.55 Å. The 101 XRD peak corresponds to (101) planes of the zeta structure which have known interplanar spacings of 2.15 Å. Finally, the 100 XRD peak corresponds to (100) zeta structure planes which have interplanar spacings of \(2.83 \times \cos(30^\circ) = 2.45\) Å. Based on these agreements between measured XRD spacings and known \(\zeta\)-phase interplanar spacings, we conclude that there are at least three different orientations of \(\zeta\)-phase grains within the film.
The measured RHEED pattern spacings can be seen to correspond to \textit{in-plane} spacings of the three \(\zeta\)-phase grain orientations found from XRD. Corresponding to (001) \(c\)-planes, the long diagonal along \([1\bar{1}0]\) is \(2.83 \, \text{Å} \times \sqrt{3} = 4.91 \, \text{Å}\), agreeing well with the RHEED spacing of \(4.95\pm0.1 \, \text{Å}\). Corresponding to the (101) planes, the atomic spacing along the \([10\bar{1}]\)-direction is \(\sqrt{(2.83 \, \text{Å})^2 + (4.55 \, \text{Å})^2} = 5.36 \, \text{Å}\), which is within error of the measured RHEED spacing of \(5.23\pm0.15 \, \text{Å}\). Corresponding to the (100) \(a\)-planes, the relevant atomic spacing along the \([011]\)-direction is \(\sqrt{(2.83 \, \text{Å})^2 + (4.55 \, \text{Å})^2} = 5.36 \, \text{Å}\), which also agrees with the measured RHEED spacing \(5.23\pm0.15 \, \text{Å}\) within error. Finally, if we assume (304) facets, which are slightly off of (101) planes, we get an inter-atomic spacing of \(3.99 \, \text{Å}\) along \([\frac{2}{3} \frac{7}{3} \frac{1}{3}]\), which is in reasonable agreement with the measured \(3.80\pm0.24 \, \text{Å}\) spacing seen in RHEED. In total, all the RHEED and XRD spacing measurements are consistent with a film having (101), (001), and (100) orientations of the \(\zeta\)-phase structure with possible (304) oriented facet planes.

Further evidence for the \(\gamma\)-type \(\zeta\)-phase identification of the \(\zeta\)-phase sample is obtained by measuring stoichiometry with RBS. A wide range of potential stoichiometries are associated with the \(\zeta\)-phase [3, 14]. RBS taken on the \(\zeta\)-phase samples grown on MgO(001) in this experiment indicates an approximately 10:1 Mn:N ratio (90.9\% Mn).
This 90.9% Mn concentration approaches the highest Mn% observed for the ζ-phase (92%), which suggests either ε-type (hexagonal with ordered N-site occupation) or γ-type (hexagonal with disordered N-site occupation) ζ-phase, the two most Mn-rich types, was grown [3, 14].

The ε-type ζ-phase unit cell contains 8 Mn and 6 N-sites [3]. This means a 10:1 Mn:N ratio would require a unit cell to have less than one N-atom on average (0.8). Therefore, the size of the ε-type ζ-phase unit cell is too small to contain well-ordered N-site occupation at this Mn:N ratio. It follows that a 10:1 Mn:N ratio indicates primarily disordered N-vacancies, which identifies the majority of the ζ-phase sample as γ-type ζ-phase.

The model in Fig. 6.3 shows the N-sites fully occupied. Randomly-incorporated N-vacancies can be added to the model until the stability limit is reached [3, 14]. This can allow agreement with the measured 90.9% Mn concentration. Clearly, growth of hexagonal ζ-phase MnₓNᵧ on a tetragonal MgO (001)-oriented substrate is favored over the tetragonal MnₓNᵧ phases at high Mn concentrations such as that shown here.

6.1.5 Morphology and Magnetism

AFM/MFM results from a ζ-phase sample are shown in Fig. 6.4, in which a stripe-like pattern with stripes running parallel to [100]MgO is observed. Line section measurements across the stripe-like pattern, as shown in Fig. 6.4(d), indicate a typical corrugation width and height of ~70–90 nm and ~1–3 nm, respectively. The observation of corrugation dimensions being semi-periodic suggests that the surface is faceted and may agree with the observation of weak chevrons seen in the RHEED pattern in Fig. 6.1(d). The AFM measured width and height correspond to a slope of \( \arctan \left( \frac{1\text{ nm}}{45\text{ nm}} \right) = 1.27^{\circ} \) to \( \arctan \left( \frac{3\text{ nm}}{35\text{ nm}} \right) = 4.90^{\circ} \) with respect to the growth plane, which is below the 7.79° separation between the (304)- and (101)-planes. This angular difference suggests that the
slope is a mixture of (304) and (101) facets, which agrees with the observation of both 3.80 Å and 5.23 Å spacings in RHEED.

![AFM image of ζ-phase surface](image1)

![MFM image over the same area shown in (a)](image2)

![Zoom-in of region from (a)](image3)

![Topographic line profile across line shown in (c) and the corresponding magnetic line profile](image4)

Figure 6.4: (a) AFM image of ζ-phase surface (b) MFM image over the same area shown in a) (c) Zoom-in of region from a) (d) Topographic line profile across line shown in c) and the corresponding magnetic line profile

No grains boundaries were observed in the AFM images of the ζ-phase sample despite RHEED and XRD results both indicating the sample contains a mix of grains. This discrepancy may be explained by the scale of the grain size being too large to observe grain boundaries with this AFM. Occasionally, some macrosteps having heights of ~2–3 nm and running perpendicular to [100]_{MgO}, as seen in Fig. 6.4(a), are also observed. Roughness
analysis of Fig. 6.4(a) gives an RMS roughness of 0.84 nm and a height range of 4.62 nm across the 2 µm sized image. The sample is therefore highly smooth while at the same time faceted.

The MFM image in Fig. 6.4(b) shows the localized stray field of the ζ-phase sample over the area observed in Fig. 6.4(a). Contrast features of the MFM image match quite closely to the features in the AFM image. This comparison suggests that the magnetic image contains no magnetic stray field signal with only the remnant topographic signal coming through [37]. As seen in comparing the topographic (dotted) and magnetic (solid) line profiles in Fig. 6.4(d), the MFM signal does not exactly match the height variation. However, the agreement is good enough that the presence of stray field in the sample is doubted. This measurement is consistent with an uncertainty as to whether the ζ-phase thin film is antiferromagnetic or ferromagnetic.

**6.1.6 Conclusions**

In conclusion, with an increased growth temperature (510 °C compared to 480 °C for ε-Mn₄N growth) and when deprived sufficiently of N, upper Mn:N ratio stability limit hexagonal γ-type ζ-phase can be grown epitaxially on a tetragonal MgO(001) substrate with a stripe-like superstructure. A dominant (101) growth orientation is achieved, but with limited orientational purity. Following the original publication of this project, growth of a single crystal direction was achieved for the ζ-phase on MgO(001) by Wang et al. [16, 50].

**6.2 Evidence for the Coexistence of Ferromagnetic and Antiferromagnetic Properties in ζ-phase MnₓNᵧ**

A semi-periodic stripe-like superstructure ~70-90 nm wide and ~1-3 nm high that is oriented along the [100]-direction is observed in Section 6.1 using AFM. Initial SP-STM results are taken for a grain embedded in a majority ε-Mn₄N sample, which possesses this
\(\zeta\)-phase associated stripe-like morphology. These results show \(\frac{dI}{dV}\) contrast aligned with the adjacent stripes of the pattern. Applying a magnetic field to the tip and sample is found to alter the contrast between stripes. This provides potential insight into how ferromagnetic and antiferromagnetic properties might coexist in a \(\zeta\)-phase sample; specifically, regions with net magnetization (a property of ferromagnetism) present in individual stripes of the morphology of a material that is generally considered antiferromagnetic.

### 6.2.1 Introduction

The three metal-rich phases (\(\eta\), \(\epsilon\) and \(\zeta\)) in Mn\(_x\)N\(_y\) system have shown evidence of net magnetization and hence spin-polarization [14, 15, 16]. Of these three, \(\epsilon\) and \(\zeta\) have shown evidence of net magnetization in ambient conditions (i.e. room temperature and atmospheric pressure) [14, 16]. The ferromagnetic behavior of the \(\zeta\)-phase is attributed to a strain related effect inducing the simultaneous presence of both ferro- and antiferromagnetic properties in \(\zeta\)-phase thin films [16]. However, the manner in which these two different magnetic properties might be present in the same thin film has not yet been visualized. For this reason, a SP-STM study of the magnetic structure of the \(\zeta\)-phase is of interest.

A grain with the same stripe-like pattern, which is observed with AFM on a high-phase purity \(\zeta\)-Mn\(_{10}\)N sample in Section 6.1, is found embedded in a mostly \(\epsilon\)-Mn\(_4\)N sample. SP-STM measurements of this embedded grain find evidence for regions with net magnetization. This result agrees with the observation of the coexistence of ferromagnetic and antiferromagnetic properties in \(\zeta\)-phase thin films on MgO(001) by Wang et al. [16]. However, VSM measurements of a majority \(\zeta\)-Mn\(_{10}\)N thin film showed a small magnetization roughly matching the expected magnetization due to the quantity of \(\epsilon\)-Mn\(_4\)N impurities measured with XRD (10±2%). Ultimately, these results are inconclusive, but
may give insight into the manner in which ferro- and antiferromagnetic properties could exist simultaneously in the same thin film.

6.2.2 Procedure

A comparison of the area under the peaks, which are the signature of particular Mn$_x$N$_y$ phases, is used to measure the phase composition between the $\zeta$- and $\epsilon$-phases within a few percent error. SP-STM in conjunction with a varied *out-of-plane* $\vec{H}$-field ($\pm 5$ kOe) are used to identify the presence of regions with net magnetization. Each STM image was taken at a -9.3 V bias and a 900 pA set point. A Stanford Research System lock-in amplifier is used to extract a $\frac{dI}{dV}$ signal related to a 5 mV amplitude oscillation, which is provided by the lock-in amplifier, of the bias voltage of the STM at a frequency of 4.5 kHz during scanning. The extracted $\frac{dI}{dV}$ signal is used to determine information about the local density of states (LDOS) and magnetization of the samples. A W tip coated with $\sim$50 mL of Fe is used for SP-STM measurements. RT-VSM is used to determine the $\vec{M}$ versus $\vec{H}$ dependence of samples. The diamagnetic contribution of the MgO substrate to the magnetization is subtracted out using the RT-VSM measurement of a blank MgO as a reference. RBS is used for thickness calibration and determining the Mn:N ratio composition of samples.

6.2.3 Growth Summary

Sample 6.2.A is a 205 nm thick sample grown on MgO(001). Sample 6.2.A was grown in two layers ($\sim$100 nm thick) using the procedure for $\epsilon$-Mn$_4$N outlined in Chapter 3 for each layer with a $\sim$24 hour break at room temperature in between. Sample 6.2.B is a 130 nm thick sample grown on MgO(001) using the procedure for $\zeta$-Mn$_{10}$N outlined in the previous section (Section 6.1).

Figures 6.5(a) and (b) show the XRD of samples 6.2.A and 6.2.B respectively. X-ray diffraction in Fig. 6.5(a) shows a 002 $\epsilon$-phase peak among MgO peaks (002 and 111) with a very small 101 $\zeta$-phase peak ($0.4 \pm 0.1\%$ of the sum of the Mn$_x$N$_y$ peak areas). X-ray
diffraction in Fig. 6.5(b) shows a sizeable 101 $\zeta$-phase peak (81±8% of the sum of the Mn$_x$N$_y$ peak areas), two additional $\zeta$-phase peaks [002 (4±1% of total) and 100 (5±1% of total)], and a small (10±2% of total) 002 $\epsilon$-phase peak. RBS identifies a 10:1 Mn:N ratio in sample 6.2.B. Therefore, sample 6.2.B is a mostly $\zeta$-Mn$_{10}$N sample based on the arguments of Section 6.1.

![Figure 6.5: Out-of-plane XRD taken of samples (a) 6.2.A and (b) 6.2.B.](image)

### 6.2.4 Results and Discussion

During the STM scanning of sample 6.2.A a region with a morphology matching the stripe-like pattern, which is associated with the $\zeta$-Mn$_{10}$N thin films described in Section 6.1, is observed embedded within the mostly flat-square terrace morphology of the sample as shown in Figs. 6.6 and 6.7(a). In agreement, XRD shows a very small 101 $\zeta$-phase peak
as seen in Fig. 6.5(a). For this reason, this grain is likely a $\zeta$-phase grain embedded in the mostly $\varepsilon$-$\text{Mn}_4\text{N}$ sample.

Figure 6.6: A LT-STM image of the grain boundary between stripe-like and square-flat terrace morphologies on the surface of sample 6.2.A at a -9.3 V bias and a 900 pA set point.
Figure 6.7: LT-SP-STM data taken on 6.2.A at a -9.3 V bias and a 900 pA set point. (a) Topographic image of a grain with $\zeta$-phase morphology embedded in an $\varepsilon$-phase sample. (b) Line profiles, which are perpendicular to the [100]$_{\text{MgO}}$ orientation of the stripe-like morphology, corresponding to the line shown in a) for the left [(c) and (e)] and right [(d) and (f)] scanned $\frac{dI}{dV}$ maps with external $\vec{H}$-fields of -5 kOe [(c) and (d)] and 5 kOe [(e) and (f)].

Figures 6.7(c) and (e) show the $\frac{dI}{dV}$ signal of the left scans of the stripe-like pattern with a -5 and 5 kOe out-of-plane $\vec{H}$-field respectively. Whereas, Figs. 6.7(d) and (f) show the right scans corresponding to Figs. 6.7(c) and (e) respectively. Fig. 6.8 shows the distributions of the $\frac{dI}{dV}$ signal of these four images. A shift in $\frac{dI}{dV}$ signal is evident due to the change in $\vec{H}$-field (-5 to 5 kOe) in that $\sim 13\%$ of the signal above $\frac{dI}{dV}=0$ in the -5 kOe distributions (top two) goes to below $\frac{dI}{dV}=0$ in the 5 kOe distributions (bottom two).
Figure 6.8: The distributions of \( \frac{dl}{dV} \) values for the \( \frac{dl}{dV} \) maps shown in Fig. 6.7(c) to (f). Both the left and right scans show a \( \sim -13\% \) shift in polarization when increasing the external \( \vec{H} \)-field from -5 to 5 kOe.

Line profiles across the same line section of these four \( \frac{dl}{dV} \) maps are shown in Fig. 6.7(b). It is evident in Figs. 6.7(b)-(f) that the changes in \( \frac{dl}{dV} \) signal, which are due to changing \( \vec{H} \)-field, align with the stripe-like pattern when looking at these profiles along with the corresponding images. This indicates that there is a net magnetization across the surface of some of these stripe-like features.

These magnetic tips are expected to have an \( H_C \) well below 5 kOe [89, 90]. Therefore, the magnetization of the tip is flipping between -5 to 5 kOe. The fact that the tip changing magnetization results in a shift in the \( \frac{dl}{dV} \) signal across entire areas much larger than a unit cell (tens of nm wide stripes and hundreds of nm wide areas) indicates that areas with
net magnetization (a ferromagnetic property) are present in a sample, which is expected to be antiferromagnetic. In this way, this SP-STM evidence may indicate a way in which ferromagnetic and antiferromagnetic properties coexist in a sample.

It is proposed by Wang et al. that the ferromagnetism present in $\zeta$-phase grown on MgO(001) is induced by strain [16]. It is reasonable to expect that the semi-periodic nature of the stripe-like pattern is related to a strain reduction due to the lattice mismatch between a $\zeta$-phase and the surrounding material ($\varepsilon$-phase and MgO). In this case, there would be a semi-periodic pattern to the strain, which is aligned with the stripe-like pattern and therefore the observed net magnetization. In this way, the results of this study are in agreement with a strain induced ferromagnetic property due to the pattern of strain and net magnetization overlapping.

Fig. 6.9 shows $\mathbf{M} - \mathbf{H}$ loop of sample 6.2.B with the $\mathbf{H}$-field applied in- and out-of-plane. The saturation magnetization of this sample ($11 \text{ emu/cm}^3$) is in agreement with the amount of $\varepsilon$-Mn$_4$N impurity found with XRD (10±2%) because $11 \text{ emu/cm}^3$ is 9% of the saturation magnetizations common in $\varepsilon$-Mn$_4$N thin films from Chapter 4 ($\sim 120 \text{ emu/cm}^3$). In addition, a small PMA is observed due to the mismatch in coercivity between the in- (0.2 kOe) and out-of-plane (1.1 kOe) loops. This observed PMA is in agreement with the identification of this magnetization as being due to $\varepsilon$-Mn$_4$N, which is known to exhibit PMA [54]. As well, a large vertical shift is observed for the out-of-plane loop. This is consistent for ferrimagnetic grains (e.g. $\varepsilon$-Mn$_4$N) embedded in an antiferromagnetic sample (e.g. $\zeta$-Mn$_{10}$N) because vertical shifts are a commonly observed feature in ferri-/antiferromagnetic core/shell systems [101, 102, 103]. In this way, the XRD and VSM of sample 6.2.B both indicate the magnetization of this thin film is due to $\varepsilon$-Mn$_4$N impurities in a mostly $\zeta$-Mn$_{10}$N sample. This VSM data does not support the observation of net magnetization in a $\zeta$-phase thin film. However, this film is thicker (130 nm thick) than those of Wang et al.
(45 nm thick), in which net magnetization was observed and attributed to a strain related to the film thickness [16].

![VSM of ζ-phase sample with 10% ε-phase impurity](image)

Figure 6.9: RT-VSM taken on ζ-Mn₁₀N sample 6.2.B with the \( \vec{H} \)-field applied in- and out-of-plane.

### 6.2.5 Conclusions

Based on the measurements of this study, it is unclear whether the ferromagnetic properties observed with SP-STM are inherent in the ζ-phase or simply due to the ε-Mn₄N found in sample. The only means of identifying the grain embedded in an ε-Mn₄N thin film as ζ-phase is by the morphology of the grain. XRD shows that this identification is plausible due to the presence of ζ-phase XRD peaks. Ultimately, this study can only present evidence, which suggests that this embedded grain is ζ-phase, as opposed to a verification...
of its identity. Additional SP-STM and VSM measurements of phase-pure $\zeta$-Mn$_x$N$_y$ thin films are needed in order to make a more definitive conclusion on the magnetism present in $\zeta$-Mn$_{10}$N thin films on MgO(001). However, the magnetization observed with SP-STM (net magnetization along single stripes) serves as a potential example of strain induced ferromagnetic properties existing in a material that is expected to be generally antiferromagnetic.
7 Interfacial Properties of Ga-Rich GaN Reconstructions

GaN was first developed for use in light emitting diodes, which later resulted in the Nobel Prize in Physics in 2014 [104, 105, 106, 107, 108]. Following the original development of GaN, the functionality of GaN has spread into a variety of applications (spintronics, transistors, and optoelectronics) [6, 107, 109, 110]. The applications of optoelectronics and spintronics depend on interfacial quality for low loss transmission of optical and spin data [13, 110]. Ga-rich growths of GaN are known to produce the highest quality interfaces [17]. For this reason, studies of Ga-rich GaN interfaces are of particular interest. In this chapter, two Ga-rich surfaces [the pseudo-1×1+\frac{1}{12} reconstruction on GaN(0001) and GaN grown on Al2O3(0001) under Ga saturation] are investigated.

7.0.6 Procedure

All GaN sample growths were performed in a custom designed ultra-high vacuum molecular beam epitaxy system [4]. In situ reflection high energy diffraction (RHEED) measurements use a 20 keV energy incident beam to identify features of the in-plane structure (e.g. spacings, periodicity ...) of the surface of these GaN samples. Scanning tunneling microscopy is performed in situ in order to further characterize the GaN surfaces (structure and LDOS) without contamination. The flux of the elemental sources are measured in situ using an Inficon oscillating quartz crystal film thickness deposition monitor. The N-plasma flux is determined by identifying the transition between N- and Ga-rich growth of GaN when using a known Ga-flux [26]. Scanning electron microscopy measurements in conjunction with energy dispersive x-ray spectroscopy (EDX) are used to compare the chemical composition of separate regions of the GaN samples.
7.1 Pseudo-1×1+1/12 Reconstruction on GaN(0001)

Two samples possessing the pseudo-1×1+1/12 reconstruction on a GaN(0001) surface are grown using molecular beam epitaxy and identified using reflection high-energy electron diffraction measurements. The surfaces of both samples are found to consist of atomically flat ~25-100 nm wide terraces with scanning tunneling microscopy. Atomic resolution, which shows a 9×12 unit cell, is obtained of the ground (low temperature) state of the pseudo-1×1+1/12 reconstruction on the GaN(0001) surface.

7.1.1 Introduction

In previous work, multiple surface reconstructions composed of Ga have been observed on GaN surfaces through RHEED and STM measurements [47, 111, 112]. The two c-plane surfaces of GaN [Ga-polar (0001) and N-polar (000\overline{1})] are on opposite crystal faces (crystal directions are flipped by 180°). The ”1×1”+1/12 reconstruction is the most Ga-rich reconstruction on the Ga-polar GaN surface, has a unique RHEED signature, and has fluid-like properties at room temperature [24]. However, the structure of the ”1×1”+1/12 reconstruction in the ground state (at low-temperature) remains an open question. For this reason, this study investigates the ground (low temperature) state of the pseudo-1×1+1/12 reconstruction using scanning tunneling microscopy.

7.1.2 Growth Summary

In this project, two GaN samples (samples 7.A and 7.B) were grown on commercially available MOCVD grown GaN(0001) substrates. Before deposition the samples were cleaned for ~5 min with a N-plasma beam at the growth temperature of 730±30 °C. Samples 7.A and 7.B are 160 nm and 60 nm thick respectively.
7.1.3 Results and Discussion

A RHEED measurement characteristic of these samples, which is taken along the [11\overline{2}0]-direction of the GaN(0001) substrate at room temperature, is shown in Fig. 7.1. This RHEED pattern matches the unique RHEED signature of the "1×1"+\frac{1}{12} surface reconstruction along the [11\overline{2}0]-direction (i.e. 1× streaks with 12× streaks at the \frac{13}{12}th position) at room temperature [113]. Additionally, this RHEED pattern is highly streaky with easily visible Kikuchi lines, which indicates a highly-smooth and well-ordered surface. Therefore, these samples are identified from RHEED measurement as highly-smooth and well-ordered GaN(0001) with a "1×1"+\frac{1}{12} surface reconstruction.

Figure 7.1: RHEED image taken along the [11\overline{2}0]-direction of the "1×1"+\frac{1}{12} reconstruction on GaN(0001).

STM measurements of samples 7.A and 7.B, which are shown in Figs. 7.2(a) and (b) respectively, were taken in situ at liquid helium temperatures (~4.2 K) using separate W tips. Atomic resolution images were obtained of the surface. Extensive scanning revealed a homogenous surface with only a single type of surface reconstruction on atomically flat terraces, which are ~25-100 nm wide. The unit cell of this surface reconstruction, which is marked by the red parallelogram seen in Fig. 7.2(b), is found to be 9×12 the in-plane lattice spacing (a = 3.19 Å) of GaN with sides forming a ~60° angle.[48]. The corrugation of the 9×12 surface reconstruction is found to be ~0.2-0.5 Å tall.
Figure 7.2: (a) and (b) LT-STM images taken of the "1×1"+1/12 reconstruction with a ∼100 and ∼15 pA tunneling current respectively. The image in a) is taken of sample 7.A with a 150 mV bias voltage. The image in b) is taken of sample 7.B with a 5 mV bias voltage.

Translational domain boundaries (marked with green dotted lines) are seen in Fig. 7.2(a) where the reconstruction is translationally shifted along the domain boundary. In addition, round impurities (marked by red circles) are shown in Figs. 7.2(a) and (b). These impurities formed on the surface during scanning and were only observed on areas that had already been scanned. From this, it is concluded that these round impurities are due to interactions between the surface and the STM tip as opposed to being as grown features.
or due to vacuum contamination. In this way, the only observed as grown features are atomically flat terraces with a 9×12 surface reconstruction.

Therefore, the STM images are in agreement with RHEED measurements because STM images show a highly-smooth (∼25 to 100 nm wide terraces) and well-ordered (a single type of surface reconstruction) surface. As well, a 12× periodicity, which is indicated in the RHEED by the 12× streaks at the $\frac{13}{12}$th position, is found along one of the sides of this 9×12 reconstruction. Based on RHEED measurements at room temperature, the solely observed reconstruction at L-He temperature (9×12) is identified as the ground (low temperature) state of the $"1\times1"+\frac{1}{12}$ surface reconstruction on GaN(0001).

7.1.4 Conclusions

In summary, atomic resolution images of the $"1\times1"+\frac{1}{12}$ reconstruction reveal the ground state of the reconstruction to consist of a 9×12 structure. Good agreement is found in separate measurements using two different W tips on the two different samples. This observation allows the identification of this reconstruction on other GaN samples (e.g. GaN samples with multiple reconstructions and/or mixed polarity) with STM when RHEED measurements on such samples would be inconclusive due to the mix of periodicities present on those types of samples. However, a model for the ground state of the $"1\times1"+\frac{1}{12}$ reconstruction based on these STM results remains to be developed.

7.2 Interfacial Properties of GaN on Al$_2$O$_3$(0001) under Ga Saturation

Two GaN samples are grown on the Al$_2$O$_3$(0001) surface under Ga saturation. A combination of c(6×12) and pseudo-$1\times1+\frac{1}{12}$ reconstructions as well as Ga-droplets are observed on the surface of these samples using scanning tunneling microscopy and scanning electron microscopy in conjunction with energy dispersive x-ray spectroscopy. Reflection high-energy electron diffraction measurements show a 3× symmetry is present on the surface. Evidence is found for Ga diffusing on the pseudo-$1\times1+\frac{1}{12}$ surface in the
gas phase. This evidence includes the observation that the typical diffusion length of Ga adatoms across the GaN(0001) surface is greater than 12 μm. A direct comparison is made between the LDOS of the c(6×12) and pseudo-1×1+$\frac{1}{12}$ reconstructions at multiple positive voltages. Contrast between the LDOS of these reconstructions is found to vary with voltage.

7.2.1 Introduction

Ga droplet formation during MBE growth of GaN is a commonly observed phenomenon, in which an excess Ga flux is used during growth [17]. As well, a previous observation of a frozen out gas-phase of Ga on a GaN surface at liquid helium temperatures (∼ 4.2 K) suggests that Ga is present on the surface of GaN during growth in an equilibrium between liquid and gas phases [23]. The different atomic ordering of each potential surface structure (i.e. droplets and types of surface reconstructions) can be expected to result in different diffusion pathways (growth mechanisms) for Ga. In addition, growths of GaN, which employ excess Ga, have been found to produce the highest quality surfaces in the GaN system [17]. Therefore, studying the formation of different types of surface structures (e.g. gaseous Ga adatoms and liquid Ga droplets) during Ga-rich GaN growth can provide insight into the growth mechanisms, which produce the highest quality surfaces, of GaN.

The c(6×12) reconstruction is the most Ga-rich reconstruction on the N-polar surface (stability limit 1/4 ML of Ga) [23]. Exceeding this stability limit on the N-polar surface should induce the formation of additional surface structures (e.g. Ga-gas and -droplets), which are related to Ga-rich GaN growth. Therefore, insight into the growth mechanisms, which are related to the growth of the highest quality GaN surfaces, can be developed by investigating the surface structures grown when exceeding this stability limit ($>>\frac{1}{4}$ ML of Ga) on the N-polar surface.
7.2.2 Growth Summary for GaN Samples Grown on Al$_2$O$_3$(0001) under Ga Saturation

In this project, two GaN samples (GaN samples 7.C and 7.D) are grown on Al$_2$O$_3$(0001) substrates using a Ga flux, which would result in Ga at the surface far exceeding the stability limit ($>\frac{1}{4}$ ML) of the c(6×12) reconstruction. In order to achieve this, a Ga to N flux ratio of $\sim$1.35:1 was used for these samples with the Ga flux on the order of $10^{14} \frac{n}{cm^2 \ sec}$. Samples 7.C and 7.D consist of 30 nm and 20 nm thick GaN, respectively, each with an excess of $\sim$25 monolayers of Ga. These samples were grown in order to investigate the surface structures formed under Ga saturation.

The substrate of each sample (7.C and 7.D) was annealed ($T = 700 \ ^\circ C$) under N-plasma for $\sim$30 min prior to growth. Following this, a 2 nm thick buffer layer was deposited at a temperature of $T = 620 \ ^\circ C$. This buffer layer is grown at a lower temperature in order to introduce defects, which are intended to relax the strain induced by the lattice mismatch between the substrate and the sample [49]. After relaxing the strain across an ultrathin buffer layer, the main GaN sample can be grown at higher temperature ($T = 700 \ ^\circ C$) with less strain and fewer defects.

A characteristic RHEED image, which is taken along the [1120]-direction, of samples 7.C and 7.D is shown in Fig. 7.3. This RHEED image along the [11\bar{2}0]-direction has 3× streaks in the primary Laue zone and no additional Laue zones. In this way, the RHEED image contains one aspect of the expected pattern of the N-polar 3×3 reconstruction (3× streaks), but does not possess another key aspect of the 3×3 reconstruction (an additional Laue zone) [47].
7.2.3 Results and Discussion for Mixed Polarity (N-polar and Ga-polar) Surfaces on GaN

For samples 7.C and 7.D, two types of regions were observed at the surface using scanning electron microscopy (SEM) as seen in Fig. 7.4. One region consists of a highly-smooth surface (region A) and the other consists of micron scale droplets (region B).
Figure 7.4: (a) and (b) SEM images taken over the surface of GaN grown on Al$_2$O$_3$(0001) under Ga saturation. Brighter (more conductive) small droplets seen on a darker (less conductive) flat surface.

EDX measurements taken over regions A and B are shown in Figs. 7.5(a) and (b) respectively. The peaks in Fig. 7.5 match the L$_\alpha$ or K$_\alpha$ lines of the elements expected to be observed in the EDX measurement. The Cu peak is associated with the tape, which is used to mount the samples for measurement, at the base of the substrate. The substantial Al peak and the O peak, which is just over the background, match the expected contribution from the Al$_2$O$_3$ substrate. Whereas, the substantial Ga peak and the N peak, which is just over the background, are related to the grown sample (GaN) on top of the substrate.
Figure 7.5: EDX taken over (a) the GaN surface (region A) and (b) a Ga Droplet (region B).

Every EDX peak besides Ga is greatly reduced in the case of the substantial peaks (Cu and Al) or completely obscured in the case of the peaks, which are just over the background, (N and O) for the measurement of the droplets (region B) compared to the EDX measurement of region A. At the same time, the Ga peak is greatly enhanced in the EDX measurement of the droplets (region B) compared to the EDX measurement of region A. Clearly, the signal from the droplets, which obscures the signal from the substrate and shows no N peak, is due to the droplets being predominantly Ga. In this way, the EDX measurements of the grown droplets are consistent with the Ga droplets, which are common in GaN growths with excess Ga [17].

Figures 7.6(a) and (b) show the distributions of the distances between and the diameters of the Ga droplets, respectively, which are contained within a 1220 μm-sided square from the left side of SEM image in Fig. 7.4(a). The average distance between the
208 droplets measured is 620 µm with a standard deviation of 300 µm. In 1965, Shapiro and Wilk devised a means for calculating the probability that a given data set was produced by a system, which follows a normal distribution [114]. A Shapiro-Wilk value of $8.6\times10^{-12}$ was found for the distribution of the distances between 30 of these droplets, which indicates a higher than 6.5-σ certainty that the distances between droplets are normally distributed, in a smaller patch [114]. A smaller number of droplets (30 droplets) was used for this calculation because otherwise the data size would be too large to perform the analysis [114]. The average diameter of the 208 droplets measured is 26 µm with a standard deviation of 3.9 µm. Clearly, the droplets are uniform in diameter. Additionally, a Shapiro-Wilk value of 27% for the distribution of droplet diameters indicates a 73% probability, which is not significant enough for confirmation, that the diameters are normally distributed [114].
Figure 7.6: (a) Distribution of the distance between Ga droplets seen in Fig. 7.4(a). (b) Distribution of the diameters of the Ga droplets seen in Fig. 7.4(a). Each distribution is fit to a normal distribution (black curves).

In agreement with SEM, two types of areas are observed in STM. First, atomically flat areas, which agree with the high smoothness found in region A using SEM, are observed as seen in Figs. 7.7 and 7.8. These atomically flat areas consist of both the c(6×12) and "1×1"+$\frac{1}{12}$ reconstructions. In agreement, the RHEED of the surface along [1120] shows a 3× symmetry, which is the common symmetry shared by these two reconstructions along this direction, as seen in Fig. 7.3. As well, the c(6×12) and "1×1"+$\frac{1}{12}$ reconstructions are the most Ga-rich reconstructions of the N-polar and Ga-polar surfaces of GaN respectively
Having reconstructions, which are the most Ga-rich, present at the surface is in agreement with the fact that the samples were grown under Ga-saturation.

Figure 7.7: LT-STM images taken over the surface of GaN grown on Al$_2$O$_3$(0001) under Ga saturation using a $\sim$30 pA tunneling current. (a) Image of both the "1×1"+$\frac{1}{12}$ and c(6×12) surfaces using a 1 V bias voltage. (b) Image of the "1×1"+$\frac{1}{12}$ reconstruction using a bias voltage of 0.15 V.
The common presence of "1×1"+$\frac{1}{12}$ along with the c(6×12) reconstruction on a sample surface indicates that inversion (180° flipped) domains are common at the surface of samples 7.C and 7.D. In fact, the c(6×12) and "1×1"+$\frac{1}{12}$ occupy 25±2% and 75±2% respectively. Further, no domains of either polarity [(0001) or (0001)] are observed to extend more than ~200 nm across in any direction as seen in Fig. 7.8.

Second, an amorphous and often highly sloped surface is observed in STM with atomic resolution as seen in Fig. 7.9. The surface in Fig. 7.9 matches the surface of the Ga droplets seen in region B with SEM, which is also highly sloped across most of the droplet. As well, the Ga droplets formed during growth are liquid [17]. Therefore, the initially liquid droplets, which are quenched when put into the L-He cooled microscope, are expected to assume a disordered structure. Due to this, the amorphous and often highly sloped structure observed with STM in Fig. 7.9 matches well with the expected characteristics of the Ga balls observed in region B. Therefore, the first and second surfaces observed with STM are identified as regions A and B respectively.
The smallest 5 distances between the 208 Ga droplets measured in Fig. 7.6 are 7, 14, 21, 22 and 24 µm. To put another way, at least ~98% of the droplets are 24 µm or further from the nearest neighbor. Secondly, the areas across region A consist of atomically smooth reconstructions. This indicates there is no build up of Ga beyond a couple monolayers in region A because these reconstructions have Ga-concentrations 2 monolayers and below [23, 24]. Further, the vapor pressure of Ga at the growth temperature of 700 C° is on the order of $10^{-6}$ atm [115]. Using Langmuir’s evaporation equation ($\frac{dN}{dt} = \frac{P}{\sqrt{2\pi mnkT}}$), this vapor...
pressure at such a growth temperature corresponds to an outward Ga flux rate \( a \) on the order of \( 10^{17} \frac{n}{cm^2 sec} \) from the Ga droplets whereas a much smaller flux of Ga on the order of \( 10^{14} \frac{n}{cm^2 sec} \) is supplied from the effusion cell. In comparison, an extrapolation from the vapor pressures at higher temperatures (1170 to 1425 °C) gives a vapor pressure of GaN at 700 °C, which is orders of magnitude smaller than that of Ga at the same temperature (on the order of \( 10^{-8} atm \)) [116]. These vapor pressures for Ga and GaN indicate that Ga from region A is supplying the Ga droplets during growth in order for the Ga droplets to form. Therefore, large transport distances are expected for Ga across region A.

At the same time, ~25 monolayers of excess Ga are known to be on the surface and region A covers the majority of the surface. Therefore, the majority of Ga adatoms, which are deposited evenly across the surface during MBE, must travel more than 12 µm (half of 24 µm) in order to reach the nearest droplet. In this way, the Ga-adatoms are demonstrated to have a very large diffusion length (>12 µm) across both the c(6×12) (25±2% of region A) and ”1×1”+\( \frac{1}{12} \) (75±2% of region A) reconstructions. Diffusion lengths on GaN greater than 10 µm indicate gas phase diffusion [117]. Therefore, the large diffusion lengths (>12 µm) observed here indicate gas-phase transport on the c(6×12) and ”1×1”+\( \frac{1}{12} \) reconstructions.

7.2.4 Growth of c(6×12) Reconstruction Dominant GaN Samples on Al₂O₃(0001)

GaN grown on Al₂O₃(0001) substrates is expected to have a predominately N-polar surface [118]. However, small inversion domains (~20×20 nm²) with a 12×12 reconstruction have been observed by Feenstra et al. in small concentrations embedded in N-polar surfaces at room temperature [112]. In contrast, inversion domains are found to be common in region B of GaN samples 7.C and 7.D, which are grown on Al₂O₃(0001) substrates. Additional samples (GaN samples 7.E and 7.F) without large concentrations of inversion domains are grown near the stability limit (1/4 ML) of the c(6×12) reconstruction for comparison with samples 7.C and 7.D, which possess large concentrations of inversion
domains. In order to achieve this, a Ga to N flux ratio of $\sim 1.002:1$ was used for these samples with the Ga flux on the order of $10^{14} \ \text{n/cm}^2\text{sec}$. Each sample (7.E and 7.F) is annealed ($T = 1000 \ ^\circ\text{C}$) under N-plasma for $\sim 30$ min prior to growth. A $\sim 2$ nm buffer layer is grown at $\sim 630 \ ^\circ\text{C}$. The samples were then grown at a temperature of $\sim 730 \ ^\circ\text{C}$. Samples 7.E and 7.F are each $\sim 70$ nm thick.

A RHEED measurement, which is characteristic of samples 7.E and 7.F, taken along the [11\overline{2}0]-direction is shown in Fig. 7.10. The RHEED image in Fig. 7.10 matches the RHEED image in Fig. 2.3(d), which is determined to be characteristic of the c(6×12) reconstruction in Section 2.5. Therefore, the surfaces of 7.E and 7.F are determined to predominately be the c(6×12) reconstruction.

![Figure 7.10: A RHEED measurement, which is characteristic of c(6×12) dominant samples 7.E and 7.F, taken along the [11\overline{2}0]-direction.](image)

7.2.5 Results and Discussion for c(6×12) Reconstruction Dominant Samples on Al₂O₃(0001)

STM measurements at liquid helium temperature ($\sim 4.2 \ \text{K}$) show that GaN samples 7.E and 7.F have surfaces covered predominately with the c(6×12) reconstruction and therefore are predominately N-polar surfaces as seen in Fig. 7.11(a). Small domains (circled) with a 9×12 reconstruction are observed in samples 7.E and 7.F at $\sim 4.2 \ \text{K}$ as seen in Fig. 7.11(b). The unit cell (red parallelogram) of this 9×12 reconstruction, which is shown
in Fig. 7.11(b), agrees with the ”1×1”+ $\frac{1}{12}$ unit cell seen in Fig. 7.7(b). The differences between the STM images of the ”1×1”+ $\frac{1}{12}$ reconstruction in Fig. 7.7(b) compared to Fig. 7.11(b) is explained by the different bias voltages, which are used to obtain the images (1 V vs. 0.15 V), corresponding to different LDOS for the same structure. These small domains are identified as inversion domains because they possess a reconstruction (”1×1”+ $\frac{1}{12}$) associated with the inverted surface [GaN(0001)]. These inversion domains are similar to the inversion domains (12×12 reconstructions) observed at room temperature by Feenstra et al. [112]. The discrepancy in the size of the reconstructions (9×12 instead of 12×12) may be due to the measurement in this study being made at ∼4.2 K instead of room temperature.
Figure 7.11: LT-STM images taken over a c(6×12) reconstruction dominant sample grown on Al₂O₃(0001). (a) A 215 nm STM image taken with a bias voltage of 1.5 V and a tunneling current of 46 pA was used. Three inversion domains are each circled. (b) STM image taken over an inversion domain embedded in the c(6×12) reconstruction dominant sample grown on Al₂O₃(0001). A bias voltage of 1 V and a tunneling current of 10.7 pA was used. The 9×12 unit cell of the surface reconstruction on the inversion domain is marked by a red parallelogram.

### 7.2.6 Comparison of Mixed Polarity and c(6×12) Dominant Surfaces

The frozen out Ga gas-phase is visible on the c(6×12) reconstructions in region A of samples 7.C and 7.D as well as the c(6×12) surfaces of samples 7.E and 7.F. The densities
of the Ga adatoms are lower [12% compared to 33% of the c(6×12) unit cells] on the c(6×12) reconstructions of the mixed polarity samples (7.C and 7.D) compared to those of the majority c(6×12) samples (7.E and 7.F). A lower Ga-gas density is present despite the much larger excess Ga deposition during growth (∼25 ML compared to ∼1/4 ML). The only distinguishing factor between these c(6×12) surfaces is the amount of neighboring Ga droplets and inversion domains. The amount of neighboring Ga droplets and/or inversion domains must be responsible for this difference in Ga-gas density. Therefore, the explanation for the difference in Ga-gas density between these two types of samples is that the neighboring Ga droplets and/or inversion domains trap a disproportionate amount of Ga-gas compared to c(6×12) surfaces. The Ga droplets are known to be liquid during growth [17]. Liquid transport would result in shorter diffusion lengths compared to gas transport on GaN [117]. Therefore, the Ga droplets are expected to behave as Ga-gas traps during sample cooling and would reduce the Ga-gas density in Region A.

Unlike the Ga droplets, the inversion domains (75±2% of region A) must share a similarly large diffusion length with the c(6×12) reconstruction (25±2% of region A) because of the large diffusion lengths observed across Region A, in which domains of a single polarity do not extend beyond ∼200 nm in any direction and the majority of the surface is inversion domains. Therefore, if the inversion domains trap a disproportionate amount of Ga-gas during sample cooling compared to c(6×12) surfaces, then a greater density of Ga-gas sites on the "1×1"+1/12 reconstruction compared to the c(6×12) reconstruction is expected. Future studies may test whether Ga-gas density on the c(6×12) reconstructed terraces is also dependent on the relative occupation of inversion domains on the surface, which would determine if the "1×1"+1/12 have a greater density of Ga-gas sites than the c(6×12) reconstruction.

The increased number of inversion domains in samples (7.C and 7.D) compared to samples (7.E and 7.F) may be due to either the higher Ga:N flux ratios during growth
(~1.35:1 compared to ~1.002:1) or the lower annealing temperature (700 °C compared to 1000 °C). Further growth of GaN samples using a high Ga:N flux ratio (~1.35:1) on Al₂O₃(0001) substrates annealed at a higher temperature (1000 °C) can determine if the inversion domains are related to annealing temperature or flux ratio.

### 7.2.7 Direct Comparison of the $\frac{dI}{dV}$ of Pseudo-1×1+$\frac{1}{12}$ and c(6×12) Reconstructions

The presence of adjacent c(6×12) and ”1×1”+$\frac{1}{12}$ reconstructions in GaN samples 7.C and 7.D allows for the direct comparison of the $\frac{dI}{dV}$ contrast of the two surfaces using the same STM tip as seen in Fig. 7.12(b). The $\frac{dI}{dV}$ contrast of each reconstruction was taken across multiple positive voltage biases as shown in Fig. 7.13. Contrast between the $\frac{dI}{dV}$ maps of the two reconstructions is found to vary with voltage bias under a constant current set point of ~30 pA.
Figure 7.12: LT-STM images taken over the surface of GaN grown on Al$_2$O$_3$(0001) under Ga saturation. (a) A topographic and (b) a $\frac{dI}{dV}$ map taken using a $\sim$30 pA tunneling current and a bias voltage of 2 V.

Figure 7.13: $\frac{dI}{dV}$ values (avg. $\frac{dI}{dV}$) of the c(6×12) and ”1×1”$+\frac{1}{12}$ reconstructions at the surface of GaN grown on Al$_2$O$_3$(0001) under Ga saturation using a $\sim$30 pA tunneling current at L-He temperature.
The (6×12) reconstruction (\(\frac{1}{4}\) monolayers of Ga) is less metal-rich than the ”1×1”+\(\frac{1}{12}\) reconstruction (2 monolayers of Ga) [23, 24]. Despite being less metal-rich, the (6×12) reconstruction has a higher LDOS than ”1×1”+\(\frac{1}{12}\) at many voltages as seen in Figs. 7.12(b) and 7.13. As well, a peak is observed near 0.15 V for both reconstructions. Further investigation of this peak, which employ greater voltage and spatial resolution (e.g. isolating the signal of individual adatoms), may provide more information on the cause of this peak [e.g. fermi level, lowest unoccupied molecular orbital (LUMO)] [23].

In addition, a shoulder in the \(\frac{dI}{dV}\) of each reconstruction is found around \(\sim 1\) V. The voltage value of this shoulder is near a previously observed LUMO peak of the frozen out Ga-gas on the c(6×12) reconstruction [23]. Further investigation is needed to determine if the \(\frac{dI}{dV}\) shoulder observed in this study corresponds to a unique signal from Ga-gas on the GaN surface.

Ga-gas transport is present across the ”1×1”+\(\frac{1}{12}\) reconstruction based on the large diffusion length (>12 \(\mu\)m) found in region A [117]. If the \(\frac{dI}{dV}\) shoulder is a unique signature of this gas, the higher shoulder of the ”1×1”+\(\frac{1}{12}\) reconstruction would indicate the presence of Ga-gas on this reconstruction with a greater density than the c(6×12) reconstruction. The ”1×1”+\(\frac{1}{12}\) reconstruction having a greater density of Ga-gas would determine that the reduced Ga-gas concentration, which is found on the c(6×12) surfaces in the mixed polarity samples compared to single polarity samples in Section 7.2, is dependent on the amount of inversion domains as well as the amount of Ga droplets on the surface. Further investigation of the \(\frac{dI}{dV}\) contrast is needed to determine the nature of the Ga-gas adatoms on this mixed polarity surface.

7.2.8 Conclusions

In conclusion, GaN samples grown under Ga saturation on Al\(_2\)O\(_3\)(0001) substrates, which are annealed at lower temperature (700 °C), are seen to consist of a mix of
GaN(0001) and GaN(000$\overline{1}$) as well as Ga droplets. Whereas, GaN samples grown near the Ga stability limit of c(6×12) ($\frac{1}{4}$ ML) on Al$_2$O$_3$(0001) substrates, which are annealed at higher temperature (1000 °C), are seen to consist predominately of the c(6×12) reconstruction on GaN(000$\overline{1}$). The large separation (typically >24 µm) between Ga droplets on the mixed polarity surface indicates that Ga diffuses in a gas phase across both the c(6×12) and ”1×1″+$\frac{1}{12}$ reconstructions. Further study is needed in order to determine if the higher occurrence of domain inversion in the mixed polarity samples compared to the predominately c(6×12) samples is due to a higher Ga:N flux ratio during growth (∼1.35:1 compared to ∼1.002:1), a lower annealing temperature of the substrate (700 °C compared to 1000 °C), or both.

In addition, contrast is found between the LDOS of the (6×12) and ”1×1″+$\frac{1}{12}$ reconstructions. A peak in LDOS is found for both surfaces near 0.15 V. Further study is needed to map out the differing LDOS with greater voltage resolution in order to determine the origin of this peak and to locate any potential unresolved peaks. As well, further study is needed to determine if the differences in LDOS at certain voltages are related to a difference in the density of available Ga-gas sites.
8 CONCLUSIONS

8.1 Summary

In conclusion, several studies investigating the magnetic and interfacial properties of the metal-rich Mn$_x$N$_y$ phases and GaN reconstructions were performed. Growth studies of the metal-rich Mn$_x$N$_y$ phases ($\eta$, $\epsilon$, and $\zeta$) on MgO(001) found that beyond the Mn:N flux ratio the growth temperature is also important for controlling the phase purity. Controlling these growth parameters during the nucleation step is found to be particularly important for phase control of Mn$_x$N$_y$. High quality [smooth (RMS roughness < 4.1 nm) and phase pure] Mn$_x$N$_y$ ($\epsilon$ and $\zeta$) samples are grown. As well, Mn$_x$N$_y$ grains of different phase ($\eta$ and $\epsilon$) are shown to grow side by side in high quality films, which may prove useful for patterning magnetic properties (ferrimagnetic vs antiferromagnetic) in devices. The final Mn$_x$N$_y$ phase ($\zeta$) is grown on MgO(001) under Mn rich conditions. These $\zeta$-Mn$_{10}$N samples are found to have a semi-periodic stripe-like superstructure aligned along the MgO [100]-direction. Following the original publication of this project, growth of a single crystal direction was achieved for the $\zeta$-phase on MgO(001) by Wang et al. [16, 50].

Additionally, several investigations into the magnetic properties of the metal-rich phases of Mn$_x$N$_y$ are performed. Ising domains are observed in $\epsilon$-Mn$_4$N samples, which are estimated to roughly maintain a volume of $\sim$30 $\mu$m$^3$ across various thicknesses of single crystal $\epsilon$-Mn$_4$N. These domains are found to overlap out-of-plane as the sample thickness decreases in relation to the width of the $\epsilon$-Mn$_4$N grains. A large out-of-plane shape component of PMA is attributed to a dipole-dipole interaction, which has an effective range measured to be 510±170 nm, between these Ising domains. Based on a negative linear relationship observed between $t$ and the large out-of-plane shape component of PMA, this shape component is predicted to lose significance in high-phase purity $\epsilon$-Mn$_4$N films.
thicker than 360 nm. The scaling factor $[\frac{3}{2} \lambda_{100}(C_{11} - C_{12})]$ between the tetragonal strain in $\varepsilon$-Mn$_4$N and the subsequent strain component of PMA is measured to be $193 \pm 60 \ \text{Merg cm}^3$.

Measurements of $\varepsilon$-Mn$_4$N ultrathin films at low temperature are consistent with a spin valve, in which the boundary between two magnetic domains overlapping out-of-plane is moved towards and away from the sample surface with increasing and decreasing out-of-plane $\mathbf{H}$-field respectively. Measurements of $\varepsilon$-Mn$_4$N thin films at room temperature indicate that the polarity of the out-of-plane overlap of the Ising domains can be switched with small $\mathbf{H}$-fields (~0.2 kOe). Further investigations, which measure the $\mathbf{H}$-field dependence of the resistivity of these samples in conjunction with magnetic microscopy measurements of magnetic domain structure of these samples, are desired in order to determine how the out-of-plane overlap of the Ising domains affects resistivity in $\varepsilon$-Mn$_4$N thin films. Further study is needed to determine if Ising domains overlapping out-of-plane contribute to PMA, microwave absorption or magnetoresistance in other systems with similar properties to $\varepsilon$-Mn$_4$N such as chromium telluride based thin films and LuFe$_2$O$_4$ [67, 93, 94].

Inconclusive evidence is found, which supports the existence of ferromagnetic properties in $\zeta$-phase Mn$_x$N$_y$. However, the observed magnetization (net magnetization in single stripes) may provide insight into how ferromagnetic properties might exist in a $\zeta$-phase Mn$_x$N$_y$ sample.

Finally, investigations of the metal-rich reconstructions on GaN surfaces provide information on surface structure and diffusion on high quality GaN surfaces. Atomic-scale resolution, which shows a 9×12 unit cell, is obtained of the ground (low temperature) state of the "1×1"$+\frac{1}{12}$ reconstruction on the GaN(0001). Atomic-scale resolution, which shows a mixture of "1×1"$+\frac{1}{12}$ and c(6×12) reconstructions as well as Ga droplets, is obtained of the surface of GaN grown on Al$_2$O$_3$(0001) substrates under Ga-saturation. The typical distance between Ga droplets on the surface (>12 µm) indicates that Ga diffuses across "1×1"$+\frac{1}{12}$
and c(6×12) reconstructions in a gas phase. Further microscopy study may determine the
density and location of Ga-gas sites on the ”1×1”+$\frac{1}{12}$ reconstruction. A difference between
the LDOS of ”1×1”+$\frac{1}{12}$ and c(6×12) reconstructions is found. Further investigation of$
\frac{dl}{dV}$ contrast between these reconstructions is needed to further understand the cause and
implications of this difference in LDOS (e.g. fermi level, Ga-gas site density ...).

8.2 Future Work

Control of magnetic properties, which include $M_S$ and the type of magnetism
(antiferromagnetism versus ferrimagnetism), in the Mn$_x$N$_y$ system has been achieved
through control of the Mn:N ratio [14, 72]. Due to this, magnetic properties may be
patterned in Mn$_x$N$_y$ devices by patterning regions with different Mn:N ratios in such
devices. As shown in Chapter 3, vertical layering of phases with differing Mn:N ratios
is limited in the Mn$_x$N$_y$ system due to the greater favorability of side by side growth of
grains of different phase (i.e. different Mn:N ratio) compared to overgrowth of grains of
different phase. As well, the means for patterning the sites of nucleation for different phases
remains an open question as discussed in Chapter 3. This suggests that lateral organization
as opposed to vertical layering is favored in the Mn$_x$N$_y$ system and the means to control
lateral organization are unknown.

However, another approach, which controls the Mn:N ratio in ultrathin/thin films
following the initial nucleation, is demonstrated in Chapter 4; namely, high temperature
annealing a film of uncertain phase into a single phase of $\varepsilon$-Mn$_4$N by increasing the Mn:N
ratio. This result suggests that if temperature annealing could be localized and patterned,
then a template with patterned magnetic properties could be created and a film sharing the
same lateral pattern could be grown on top of said template. Preexisting photo-annealing
techniques, such as using a mask to flash anneal certain areas at the surface of Mn$_x$N$_y$ thin
film, may provide a method to laterally pattern regions with increased Mn:N ratio at the surface of a film in order to provide a template for further growth.

The fabrication of layered magnetic heterojunctions with large PMA is of high interest for use in magnetic tunnel junction devices (MTJs) [119]. However, the use of a temperature based annealing technique alone would limit the number of alternating ferrimagnetic and antiferromagnetic layers because this type of technique only enables an increase in the Mn:N ratio in successive Mn\textsubscript{x}N\textsubscript{y} layers through the release of nitrogen. For this reason, a method for incorporating nitrogen back into a sample surface would be of interest.

Fortunately, Mn\textsubscript{x}N\textsubscript{y} powder preparation techniques, which are used to incorporate nitrogen into Mn\textsubscript{x}N\textsubscript{y} samples, have already been demonstrated [120, 121]. These powder techniques work under the principle of supplying a nitrogen source to powders while at the same time activating nitrogen absorption into the powders by controlling certain parameters, such as microwave exposure and/or temperature [120, 121]. Further, it has been demonstrated by Kabara \textit{et al.} that this principle employed in powder techniques works for thin films as well [72]. Therefore, these techniques should be able to be modified further for use in thin film and device preparation by using established photoresist techniques in order to pattern regions in thin films and devices with and without nitrogen exposure during the nitridation process, which would in turn pattern regions with different magnetic properties at the surface.

In summary of the discussion of these two types of potential patterning techniques, lateral organization and vertical layering of magnetic properties could be achieved by combining patterned photo-annealing/nitridation of the surface of Mn\textsubscript{x}N\textsubscript{y} thin films/devices with existing growth techniques. Further, epitaxial growth of $\varepsilon$-Mn\textsubscript{4}N on GaN, Si, Al and Cu has been demonstrated [12, 54, 78]. In addition, in Chapter 4 the main factor controlling the PMA in $\varepsilon$-Mn\textsubscript{4}N is indicated to be shape in nanoscale systems as opposed to strain. As
well, Mn$_x$N$_y$ is suitable for use as a diffusion barrier [75, 122]. Therefore, major concerns in heterostructures such as the introduction of strain due to heteroepitaxial growth and material diffusion across interfaces are unlikely to be major concerns for the incorporation of Mn$_x$N$_y$ based MTJs into semiconductor based devices. Therefore, Mn$_x$N$_y$ thin films and devices should readily incorporate as MTJs in material systems, which are popular across the semiconductor industry.

Ising domain formation has been related to domain pinning [25, 67]. Further, there is a suspected causal relationship between Ising domain pinning and a large coercivity [25]. Based on the observations of Chapters 3 and 4, the likely source of pinning, which introduces Ising domain formation in ε-Mn$_4$N, is grain shape. Based on the suspected causal relationship between Ising domain pinning and large coercivity, it is reasonable to expect that controlling domain pinning in ε-Mn$_4$N should in turn control the coercivity of the material. Due to this, controlling the vertical layering and lateral organization of grain boundaries within a sample composed of alternating layers of ε-Mn$_4$N and an antiferromagnetic phase(s) (i.e. controlling the shape of ε-Mn$_4$N) by using the patterning techniques discussed earlier in this section should in turn control the coercivity of the ε-Mn$_4$N in the sample. Freely controlling the coercivity would potentially enable ε-Mn$_4$N to be tuned between a hard and a soft magnetic material, which would mean it can be tuned across a huge range of potential applications involving permanent magnets (e.g. loudspeakers) to those involving soft magnets (e.g. data storage/processing) [123]. For this reason, a study of the coercivity of ε-Mn$_4$N in relationship to various grain shapes (i.e. various sizes and patterns of ε-Mn$_4$N grains embedded in antiferromagnetic phases of Mn$_x$N$_y$) would be of interest.

Another property of interest is the dipole-dipole interaction, which encourages vertical layering of Ising domains, in ε-Mn$_4$N. In Chapter 5, it is observed that a small $\vec{H}$-field (i.e. small change in energy) is able to flip the domain overlap in a ε-Mn$_4$N thin
film at room temperature. If this alternating order of magnetization is maintained and flipping on one end can propagate through successive alternating ferrimagnetic $\varepsilon$-Mn$_4$N and antiferromagnetic Mn$_x$N$_y$ layers, this dipole-dipole interaction could potentially be used as a means for the transfer of information using a small initial energy without the radiative loss of traditional conducting interconnects. Further investigations, which employ MFM techniques, of how Ising domain order propagates through a sequence of alternating ferrimagnetic $\varepsilon$-Mn$_4$N and antiferromagnetic Mn$_x$N$_y$ layers is of interest in order to assess potential applications of Mn$_x$N$_y$ based devices as low power loss interconnects.

In conclusion, potential techniques for patterning magnetic properties (e.g. types of magnetism and $M_S$) in the Mn$_x$N$_y$ system are discussed. The control of Mn$_x$N$_y$ grain shape, which would be allowed by these techniques, has the potential to tune the coercivity as well as PMA in $\varepsilon$-Mn$_4$N. Control of these parameters indicates a huge range of potential applications for the material, which include applications as permanent magnets, MTJs, spin injection contacts, and low power consumption interconnects [56, 119, 123]. For this reason, further growth studies and characterization are desired of Mn$_x$N$_y$ heterostructures. Due to the functional spin-lifetimes in GaN and the suitability for heteroepitaxial growth of $\varepsilon$-Mn$_4$N on GaN, further study of the potential for incorporation of such magnetic devices into GaN based semiconductor devices is of particular interest [8, 9, 12].
REFERENCES


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APPENDIX A: RHEED OF HIGH PHASE-PURITY $\varepsilon$-Mn$_4$N(001) AND $\eta$-Mn$_3$N$_2$(010) THIN FILMS GROWN ON MgO(001)

This appendix is intended to serve as a reference that aids in the discussion of RHEED patterns in the preceding chapters. RHEED was taken for samples of high phase-purity $\varepsilon$-Mn$_4$N(001) and $\eta$-Mn$_3$N$_2$(010). The features of these RHEED patterns, which are the signature of these metal-rich Mn$_x$N$_y$ phases, are shown and described. As well, these RHEED patterns contain examples of RHEED patterns with periodicity, which is caused by periodicities in non-degenerate atoms. Further, an example with a second Laue zone is among these RHEED patterns. How this second Laue zone relates to surface structure is discussed. These examples are a useful reference when analyzing RHEED patterns, which possess similar features to Mn$_x$N$_y$ RHEED patterns, of the metal-rich GaN surface reconstructions. In this way, this appendix serves as a reference guide to RHEED features found in both the metal-rich phases and surface reconstructions of Mn$_x$N$_y$ and GaN.

Figures A.1(a) to (e) show RHEED patterns taken along the [100]-direction of the MgO(001) surface as well as along the [100]-, [310]-, [210]-, and [110]-directions, respectively, on a high phase-purity $\varepsilon$-Mn$_4$N(001) surface. Two key changes, which are observed after deposition of high phase-purity $\varepsilon$-Mn$_4$N on MgO(001), are the appearance of 2$\times$ steaks and an increase in the distance between the 1st order streaks as seen when comparing Fig. A.1(a) to Fig. A.1(b). The appearance of 2$\times$ steaks results from the 2$\times$ periodicity of the $\varepsilon$-Mn$_4$N surface as described in Chapter 3. The increase in the distance between the 1st order streaks is due to the decrease in lattice spacing at the surface along [100] (4.21 Å to 3.86 Å) [1]. In this way, the spacing between the 1st order streak is indicative of the atomic spacing perpendicular to the RHEED beam.
Figure A.1: (a) RHEED patterns of the surface of an annealed MgO substrate along [100]. As well, RHEED patterns of high phase-purity $\varepsilon$-Mn$_4$N(001) surface taken along (b) [100], (c) [310], (d) [210], and (e) [110].
A second Laue zone can be seen along the [310]-direction in Fig. A.1(c) with streaks at the 2/3rd and 1/3rd positions to the left and right of the 0th order streak respectively. Additional Laue zones are caused by a change in atomic periodicity (perpendicular to the RHEED direction) between rows, which are separated from each other parallel to the RHEED beam direction [124].

Figures A.2 and A.3 show the RHEED patterns mapped onto the corresponding imaginary lattices of the $\varepsilon$-Mn$_4$N and $\eta$-Mn$_3$N$_2$(010) surfaces, respectively, with an example of the corresponding real and imaginary unit cells at the bottom of each figure. Each imaginary lattice is based on the ideal real lattices for these samples, which are described by Yang et al.[1]. In the depictions of real lattices, red and blue atoms correspond to the corner and the other atoms, which are non-degenerate with the corner atoms, respectively. In the depictions of the imaginary lattices, red atoms on top of blue atoms indicate locations in the imaginary lattice where a corner atom and another atom overlap whereas blue atoms indicate locations where only the other atoms (center or edge) are present within the imaginary lattice.
Figure A.2: RHEED patterns of a high phase-purity $\varepsilon$-Mn$_4$N(001) surface from Fig. A.1 are mapped to an imaginary lattice. Illustration of the real space unit cell (left) of the (001)-surface of $\varepsilon$-Mn$_4$N is shown next to the corresponding imaginary space unit cell (right).
Figure A.3: RHEED patterns of a high phase-purity $\eta$-Mn$_3$N$_2$(010) surface are mapped to an imaginary lattice. Illustration of the real space unit cell (left) of the (010)-surface of Mn$_3$N$_2$ is shown next to the corresponding imaginary space unit cell (right). Splitting between $\eta$-Mn$_3$N$_2$ [001]- and [100]-directions is observed upon close inspection.

The imaginary unit cells, which the RHEED images are mapped to in Figs. A.2 and A.3, are each scaled based on a RHEED image of an MgO [like the one seen in Fig. A.1(a)]. As well, the RHEED images, which are mapped to these imaginary lattices, share the same scale as these MgO RHEED images. Due to this, mapping these RHEED images to these
imaginary lattices shows how well each sample matches with the corresponding expected lattice.

Good agreement is found between all the features (such as the lattice spacings, periodicity and additional Laue zones) of these RHEED images and the expected imaginary lattice. A 2\times periodicity appears for the directions ([100] and [210]), in which 2\times periodicity is expected, as seen in Fig. A.2. As well, an expected second Laue zone, which is due to the row behind the primary row being shifted \frac{1}{3}rd the lattice spacing perpendicular to the RHEED beam, is found along the [310]-direction for the \( \varepsilon \)-Mn\(_4\)N sample in Fig. A.2.

For the \( \eta \)-Mn\(_3\)N\(_2\)(010) sample, an expected splitting, which is due to both \( \frac{c}{3} = 4.04 \ \text{Å} \) and \( a = 4.21 \ \text{Å} \) lattice spacings being present together at the sample surface, (010), along the [100]-direction of the MgO substrate ([100]\(_{\text{MgO}}\)), is observed in the 1st order peaks along [100]\(_{\text{MgO}}\) in Fig. A.3. As well, the expected 3\times peaks, which are caused by the corner atoms (separated by 12.12 \ Ä along the \( c \)-direction) being non-degenerate with the rest of the atoms (separated by \( \frac{12.12}{3} \ Ä = 4.04 \ \text{Å} \) along the \( c \)-direction), are found along [100]\(_{\text{MgO}}\) in Fig. A.3.

In summary, this appendix shows various RHEED features. These features include streak spacings related to atomic spacings, periodicity due to non-degenerate atoms, and Laue rings due to non-degenerate rows of atoms. These features are mapped to their corresponding reciprocal lattices in order to illustrate the relationship between these RHEED features and the real lattices to which the reciprocal lattices correspond.
 Appendix B: Annealed $\varepsilon$-Mn$_4$N on MgO(001)

A Mn$_x$N$_y$ sample (sample B.A) is annealed into $\varepsilon$-Mn$_4$N using a temperature of 772 °C while under vacuum. Then, sample B.A was annealed further using the same temperature until a RHEED pattern resembling MgO(001) was observed as seen in Fig. B.1. This produced a transparent surface, which was found to be insulating using a multimeter. All known Mn$_x$N$_y$ phases are conductive [14]. From this, it is concluded that the majority of the sample annealed down to the MgO(001) substrate. This was done to directly show that material is removed during the annealing process outlined in Chapter 4.

![Figure B.1: A RHEED pattern taken along the MgO [100]-direction for sample B.A.](image)

In addition, AFM/MFM images were taken in order to further characterize the surface of sample B.A as shown in Fig. B.2. Two distinct morphologies (A and B) can be seen in Fig. B.2(a). Using MFM, the majority of the sample is found to consist of areas without net-magnetization (morphology A). However, some regions (in small abundance) with net-magnetization (morphology B) were found.
Figure B.2: AFM/MFM data of an $\varepsilon$-Mn$_4$N sample (B.A) annealed until the RHEED pattern nearly matches that of MgO. (a) AFM image showing two distinct morphologies with an inset showing a zoom-in as well as the AFM line profile shown in c). (b) MFM image corresponding to a) with an inset showing a zoom-in as well as the MFM line profile shown in c). (c) Topographic (solid green) and magnetic (dotted orange) line profiles from a) and b), respectively, taken across two distinct morphologies.
Both morphologies (A and B) appear as triangular shaped islands of similar size (~0.25 \( \mu \)m across) in Fig. B.2(a). The triangular shape is likely an artifact due to tip shape and not the actual shape of the islands. This same effect is seen in a larger scale image (15 \( \mu \)m) in Fig. 4.6, in which square-shaped islands and valleys appear to be more triangular compared to those seen in smaller scale images [Figs. 4.5(a) and (b)], taken over an ultrathin \( \varepsilon \)-Mn\(_4\)N sample.

In morphology A the islands are tightly packed. If any valleys are present in morphology A, they are difficult to distinguish with our instrument (< 0.1 \( \mu \)m). Morphology A is found to cover the majority of the sample. Unlike morphology A, morphology B contains measurable valleys between the islands (~0.25 \( \mu \)m across).

The AFM/MFM measurements in Fig. B.2 are taken over a demagnetized sample. Magnetic contrast between adjacent regions is seen in Fig. B.2(b) for morphology B, but not morphology A. The magnitude of the magnetic signal along a line profile in Fig. B.2(a) is shown in Fig. B.2(c). For morphology B the magnetic signal is primarily at one of two values, one higher and one lower. On the other hand, the magnetic signal for morphology A is in between the two primary values of morphology B with roughly a ninth the difference in signal from the lower value compared to the higher value. In morphology B the islands typically have a negative magnetic signal while the valleys typically have a positive magnetic signal. These two magnetic signals of different magnitude and sign are consistent with *out-of-plane* overlapping domains, in which the signal from the domain near the base cancels out some of the signal from the islands.

The presence of this magnetic contrast indicates that the material in morphology B has \( \mu \)m-scale magnetic domains while demagnetized. MgO(001) and the Mn\(_4\)N\(_y\) phases are the only materials that could be at the surface of sample B.A because only Mn and N were deposited on the MgO(001) substrate. Of these potential options, only the ferrimagnetic \( \varepsilon \)-Mn\(_4\)N is known to have \( \mu \)m-scale magnetic domains when demagnetized.
Therefore, the presence of $\mu$m-scale magnetic domains in morphology B suggests it is composed of ferrimagnetic $\varepsilon$-$\text{Mn}_4\text{N}$.

MgO streaks are responsible for the primary streak intensity in Fig. B.1, in which the $\varepsilon$-$\text{Mn}_4\text{N}$ streaks are not distinguishable. In comparison, the MgO related streaks in Fig. 4.1(c) are just visible among the $\varepsilon$-$\text{Mn}_4\text{N}$ streaks. The morphology that dominates the surface when MgO dominates the RHEED (morphology A) should correspond to MgO and not any Mn$_x$N$_y$ phases. For this reason the primary morphology (morphology A) is readily identified as MgO. In addition, the lack of magnetic domains when demagnetized agrees with the identification of morphology A as the diamagnetic MgO.

No Mn$_x$N$_y$ phases besides $\varepsilon$-$\text{Mn}_4\text{N}$ were identified within this annealed sample. It can be concluded that after the annealing step the sample surface consists primarily of MgO and a small abundance of $\varepsilon$-$\text{Mn}_4\text{N}$. Further, the annealing step does not introduce significant amounts of other Mn$_x$N$_y$ phases. This is in agreement with the observation of Suzuki et al., in which annealing Mn$_x$N$_y$ phases always resulted in an increase in the Mn:N ratio with $\varepsilon$-$\text{Mn}_4\text{N}$ as the terminal phase [64].
Appendix C: Growth of GdN Thin Films on Mn$_x$N$_y$

GdN is a ferromagnet, which has been investigated for potential spintronics and optoelectronics applications [125, 126, 127, 128]. Multiple growth studies, which demonstrate epitaxial growth of GdN on a wide range of substrates including Si and GaN, but not as of yet Mn$_x$N$_y$ phases, have been conducted [127, 129, 130, 131, 132, 133].

Two samples (samples C.A and C.B) are grown, in which GdN is deposited on metal-rich Mn$_x$N$_y$, using MBE. Sample thickness was determined based on material flux, which was measured in situ with an Inficon oscillating quartz crystal film thickness deposition monitor. The Mn$_x$N$_y$ layers for samples C.A and C.B were each $\sim$30 nm thick. The GdN layers of C.A and C.B were both $\sim$120 nm thick. These samples demonstrate epitaxial growth of GdN on Mn$_x$N$_y$ phases.

The RHEED images shown in Fig. C.1 are taken of samples C.A and C.B along the MgO [100]-direction during MBE growth. The RHEED image of sample C.A, which is taken directly before deposition of GdN, seen in Fig. C.1 has streaks associated with an $\eta$-Mn$_3$N$_2$(010) surface (primary streaks with corresponding 3$\times$ streaks) as well as streaks associated with an $\varepsilon$-Mn$_4$N surface (primary streaks with corresponding 2$\times$ streaks). Whereas, the RHEED from sample C.B, which is taken directly before deposition of GdN, seen in Fig. C.1 only has streaks associated with an $\varepsilon$-Mn$_4$N surface (primary streaks with corresponding 2$\times$ streaks). Clearly, the surface of sample C.A is a mix of $\eta$-Mn$_3$N$_2$(010) and $\varepsilon$-Mn$_4$N based on RHEED. However, as demonstrated in Chapter 3, further measurements beyond RHEED are needed to verify the $\varepsilon$-Mn$_4$N phase purity of sample C.B.
Figure C.1: RHEED data from GdN samples taken along the MgO [100]-direction. (a) RHEED from the Mn$_x$N$_y$ substrate of sample C.A (b) RHEED from the Mn$_x$N$_y$ substrate of sample C.B (c) RHEED from sample C.A (d) RHEED from sample C.B

XRD data of samples C.A and C.B are shown in Fig. C.2. These XRD data show a clear switching in the GdN peaks without noticeable changes to the position of the MgO and ε-Mn$_4$N peaks. The primary GdN peak for sample C.A is the 333 peak while the primary GdN peak for sample C.B is the 002 peak. Temperature changing the directional favorability of GdN is not expected because growth in the [111]- and [001]-directions have both been observed at high temperatures and appear to be dependent on the substrate as opposed to the temperature [127, 130, 133]. The XRD of each sample only shows peaks associated with ε-Mn$_4$N, GdN and the MgO substrate. However, any η-Mn$_3$N$_2$ 020-peak is known to be obscured by the MgO 002-peak [1].

The thicknesses of the Mn$_x$N$_y$ and GdN layers of each sample are roughly equal. However, the area under the XRD 002-peak ε-Mn$_4$N for sample C.A is 2.4 times as large as the area of sample C.B. Due to this large difference in peak area, it follows that sample C.A has significantly more ε-Mn$_4$N material than in sample C.A. Therefore, due
to these samples sharing roughly the same Mn$_x$N$_y$ and GdN layer thicknesses, sample C.A possesses significantly higher ε-Mn$_4$N phase purity.

Figure C.2: *Out-of-plane* XRD data from GdN samples (a) C.A and (b) C.B.

Based on these XRD measurements, control of the growth direction ([111] or [001]) of GdN was accomplished on Mn$_x$N$_y$. Growth of GdN in the [111]-direction occurred on a sample of mixed η-Mn$_3$N$_2$ and ε-Mn$_4$N phases (sample C.A) at 440±30 °C. Conversely, growth of GdN in the [001]-direction occurred on a sample with lower ε-Mn$_4$N phase-purity (sample C.B) at 700±50 °C. Phase is known to effect the size of lattice constants in the Mn$_x$N$_y$ system [1]. In addition, RHEED of Mn$_x$N$_y$ substrates of samples C.A and C.B indicate different spacings at the surface of the Mn$_x$N$_y$ substrates. Therefore, it is reasonable to expect that a difference in phase purity/surface spacings between these two
Mn$_x$N$_y$ substrates results in the change in direction of GdN crystal growth between [111] and [001].

However, higher temperatures (such as 700±50 °C) are known to change the phase of Mn$_x$N$_y$ samples [64]. For this reason, further investigation, in which both lower and higher temperatures are used to grow GdN on both mixed phase and phase pure Mn$_x$N$_y$ with different surface spacings, is needed to verify the cause of the change in growth direction of GdN between samples C.A and C.B. It can be concluded that GdN can be grown epitaxially on two of the metal-rich Mn$_x$N$_y$ phases ($\eta$-Mn$_3$N$_2$ and $\epsilon$-Mn$_4$N).
Appendix D: Supernumerary Ga Exclusion from Gd-Doped GaN Grown on Al$_2$O$_3$(0001)

Significant interest has been placed on GaN:Gd as a means for introducing dilute ferromagnetism into GaN at room temperature [134, 135]. However, poor reproducibility of the magnetic properties of GaN:Gd samples has lead to further study, which suggests crystal defects may play an important role in the magnetic properties of GaN:Gd [136]. Ga incorporation into GaN is a key aspect for limiting defects during GaN growth. For this reason, a growth study into the effect of Gd doping on the incorporation of Ga into GaN is of interest.

In this study, five Gd-doped GaN (GaN:Gd) samples were grown, in which Gd was doped into GaN seeking (Gd+Ga):N ratios equal to 1:1 across a range of Gd:Ga ratios (3.5:96.5 to 1:99). The flux of the elemental sources are measured in situ using an Inficon oscillating quartz crystal film thickness deposition monitor. The N-plasma flux is determined by identifying the transition between N- and Ga-rich growth of GaN when using a known Ga-flux [26]. A 1.4 \( \frac{\text{n}}{\text{cm}^2\text{sec}} \) N-plasma flux was used in each case. For each sample, an initial GaN layer was deposited with Ga:N=1:1. Following this, the growth was interrupted by closing the source shutters (Ga and N). The Ga and Gd flux were then adjusted so that (Gd+Ga):N=1:1 before opening all three source shutters (Ga, Gd, and N).

During GaN growth the Ga:N ratio is known to equal 1:1 at the transition point between spotty RHEED streaks and a dimming in the RHEED pattern when at a growth temperature, which is suitable for Ga incorporation [26]. This transition can be interpreted as follows: (1) The RHEED streaks become spotty due to the amount of Ga being insufficient to fill all the available Ga sites in GaN. (2) The RHEED dims due to excess Ga at the surface obscuring the signal from the GaN crystal structure [26]. In this study,
before Gd doping the growth temperature, which is used, is determined to be sufficient for Ga incorporation because a streaky RHEED pattern could be generated with sufficient Ga.

RHEED images are taken on the GaN:Gd samples along the [11\overline{2}0]-direction immediately before and after the initial deposition of the GaN:Gd layer as seen in Fig. D.1. Figs. D.1(a) and (b) are taken immediately before and after the initial deposition of the Gd-doped layer, respectively, with Gd:Ga = 2.5:98.5. Figs. D.1(c) and (d) are taken immediately before and after the initial deposition of the Gd-doped layer, respectively, with Gd:Ga = 1:99. For the samples with higher Gd doping concentrations (Gd:Ga ≥ 2.5\%) there was an immediate response in the RHEED, in which the streaks became more spotty, as seen in Fig. D.1(b). Similarly, a spotty RHEED pattern was observed by Dhar et al. when doping GaN with Gd [137]. After sufficiently reducing the Gd doping concentration (Gd:Ga = 1\%), the immediate response in the RHEED, in which the streaks became more spotty, was greatly reduced as seen in Fig. D.1(d).
Figure D.1: RHEED images from GaN:Gd samples along the [11\bar{2}0]-direction. (a) and (b) are taken immediately before and after the initial deposition of the Gd-doped layer, respectively, with a Gd:N flux ratio 2.5:98.5. (c) and (d) are taken immediately before and after the initial deposition of the Gd-doped layer, respectively, with a Gd:N flux ratio 1:99.

In every GaN:Gd sample, excess metal (Ga or Gd) was observed at the sample surface either in droplets (visible by eye) and/or metal-rich surface reconstructions (additional periodicity in RHEED) despite seeking a 1:1 (Gd+Ga):N ratio as seen in Figs. D.2(a) and (b) respectively. The observed excess droplets did not show signs of Gd oxidation (transition from reflective grey to powdery white). This lack of Gd oxidation suggests that the metal being segregated to the surface is Ga and not Gd.
Figure D.2: (a) A 1 cm GaN:Gd sample showing extensive Ga droplet coverage (bright dots covering the majority of the surface) after growth. (b) RHEED images from a GaN:Gd sample along the [11\overline{2}0]-direction, which shows a c(6\times12) reconstruction.

One explanation for the excess Ga at the surface despite seeking a (Gd+Ga):N ratio equal to 1 is that the flux of Gd was systematically underestimated. However, the immediate RHEED response, in which streaks become spotty following the start of Gd-doped growth in the more Gd-rich samples, together with the substantial amount of excess Ga at the surface of each sample indicate that Gd-doping leads to a reduction in Ga incorporation significantly greater than a 1:1 displacement. Further study, in which the Gd flux used is more precisely determined, is desired in order more accurately measure the effect of Gd flux on reducing Ga incorporation into GaN.