INVESTIGATION AND MANIPULATION OF FERROMAGNETIC PROPERTIES
OF GaMnAs AND GaMnAsP NANOSTRUCTURES

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Abstract

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Ferromagnetic properties are investigated in GaMnAs and GaMnAsP diluted magnetic semiconductors by multiple experimental techniques, including magnetometry, magnetotransport, and ferromagnetic resonance (FMR), with emphasis on magnetic anisotropy and its manipulation by nano-patterning, strain, and interfacial exchange between layers of dissimilar materials.

Studies of temperature dependence of ac magnetic susceptibility in GaMnAs films revealed a single peak along the [110] crystallographic direction occurring close to the Curie temperature, which is attributed to paramagnetic-to-ferromagnetic phase transition; and another single peak occurring at lower temperatures and seen along [100] direction, which signals the onset of biaxial domain structure in GaMnAs induced by the competition between uniaxial and cubic anisotropy. In lithographically-patterned GaMnAs nanostructures this intrinsic magneto-crystalline anisotropy was observed to compete with shape-induced magnetic anisotropy that occurs in such nanostructures due to their geometry. Interestingly, the effects due to nanostructure shape can be remarkably
reduced by low-temperature annealing of the nanostructures, which thus provides an approach for controlling magnetic anisotropy on the nano-scale.

A series of thin films of the quaternary alloy GaMnAsP with various phosphorus concentrations (up to 30%) was also fabricated and investigated in detail. X-ray diffraction and reciprocal space mapping confirmed that the strain in GaMnAsP films grown on GaAs (100) substrates undergoes a transition from compressive to tensile as P concentration increases in GaMnAs. This was followed by magnetometry and magnetotransport measurements, which clearly show that as the tensile strain increases, the easy axis in the GaMnAsP films shifts from the in-plane [100] orientation to the out-of-plane [001] direction. These experiments also revealed a dropping trend in T_C and steady increase of sheet resistivity as with increasing mole fraction of P. For completeness, anomalous Hall effect and anisotropic magnetoresistance were also observed in the GaMnAsP, attesting to its excellent ferromagnetic characteristics.

A further study on GaMnAsP/GaMnAs bilayer nanostructures revealed an entirely new interfacial exchange interaction between the two magnetic layers, that occurs as a result of orthogonal easy axis orientations in the two alloys. This interfacial coupling revealed itself as a horizontal shift of the hysteresis loops of the GaMnAs layer in weak-field-cooled magnetization measurements, thus representing a novel form of exchange bias. Under favorable conditions, this effect holds promise of applications in magnetic memory devices.

Finally, the same lithographic patterning techniques used for GaMnAs nanostructures were adopted to fabricate GaMnAsP nano-squares. Experimental results unambiguously show that perpendicular magnetic anisotropy is strongly affected by the
size of the ferromagnetic nano-scale elements, while their in-plane anisotropy remains unchanged in the range studied. The analysis of the spin-wave resonance (SWR) measurements reveals the importance of surface anisotropy in determining the properties of nanoscale magnets.
This is for my parents and my fiancée.

In memory of my grandparents
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CHAPTER 1:
INTRODUCTION AND BACKGROUND

1.1 Motivation

In the past three decades, diluted magnetic semiconductors (DMSs) have continuously drawn much research interest due to their potential for applications in spintronic devices [1]. Among these materials, ferromagnetic III-Mn-V alloys, and especially GaMnAs, have been the subject of very intense investigation [2].

A great deal of work has already been done to investigate the magnetic properties of this important alloy. Presently we know that GaMnAs makes a transition from paramagnetic to ferromagnetic phase as the temperature decreases below the Curie temperature ($T_C$). The highest reported $T_C$ observed so far in ultra-thin films of this alloy is about 200 K [3], while $T_C$ in thicker (~100 nm) GaMnAs films is around 60 K to 70 K. When grown on a (001) GaAs substrate, the total magnetic moment of the GaMnAs thin film mainly lies in the plane parallel to the film surface and displays angular magnetic anisotropy within the plane.

In addition to understanding the magnetic properties of GaMnAs, much research has focused on controlling these properties by varying growth parameters of GaMnAs, post-growth annealing, doping, manipulation of lattice-mismatch-induced strain, and other processes [2]. On nanometer scale, the complex magnetism of GaMnAs is also expected to depend on the actual dimensions of the specimen, especially when the
specimen size becomes comparable to such length scales as magnetic exchange length, the size of individual magnetic domains, or the domain wall width [4]. Research interests have also been attracted to the study on the quaternary alloy GaMnAsP, which provides a promising approach for manipulating magneto-crystalline anisotropy by controlling strain within in this material [5-8].

Motivated by the need of further systematic investigation to understand the physics manifested by GaMnAs films and its structures at the nanoscale, and inspired by the prospects of device application that require magnetic anisotropy manipulation in GaMnAs and GaMnAsP nanostructures, my thesis focuses on the effects of scale and geometry on ferromagnetic properties of GaMnAs nanostructures, and partially also to structures involving the closely related quaternary alloy GaMnAsP. The outline of the thesis is provided in the next section.

1.2 Outline of Thesis

This thesis is organized in seven chapters. In the remaining part of Chapter 1, the background of the research on GaMnAs and GaMnAsP will be briefly introduced, including a review of DMSs, a brief discussion of the origin of ferromagnetism in III-Mn-V semiconductors and of its magnetic anisotropy in GaMnAs, and a basic introduction to the related quaternary alloy GaMnAsP.

Chapter 2 will describe sample fabrication techniques and the experimental methods involved in this thesis, including molecular beam epitaxy (MBE) used for growing the samples, nanofabrication techniques, X-ray Diffraction measurements, superconducting Quantum Interference Device (SQUID) measurements, and procedures used for magnetotransport measurements.
Chapter 3 presents the results of anisotropic \textit{ac} magnetic susceptibility in GaMnAs films. The theory of \textit{ac} magnetic susceptibility will be introduced first, followed by a discussion of different mechanisms behind low temperature and high temperature susceptibility peaks observed in GaMnAs films.

Chapter 4 will discuss temperature-dependent shape anisotropy in patterned ferromagnetic (Ga,Mn)As films with low Mn concentration. Here I will describe how the GaMnAs films were fabricated into nanostripes. I will then present measurements carried out on the nanostripes, along with the analysis of these measurements in terms of shape anisotropy and its dependence on temperature.

Chapter 5 will introduce the topic of GaMnAsP alloys. I will discuss the MBE growth of nanoscale films of this alloy with various P concentrations, and the characterization of their strain profiles by XRD and reciprocal space mapping (RSM). I will then present measurements of the Curie temperature $T_C$ of this material, its magnetic anisotropy, carrier density, and the behavior of the anomalous Hall effect (AHE) for various concentrations of P in this quaternary alloy.

In Chapter 6, we integrated GaMnAsP and GaMnAs thin films together to make the bilayer nanostructures. The strong but abnormal exchange coupling at the interfaces between two layers observed by SQUID and FMR will be described and a phenomenological model will be proposed to explain the effect.

In the last chapter (Chapter 7) we patterned the GaMnAsP films into nanoscale squares using the same fabrication techniques as in Chapter 4, in order to discuss the effects of physical dimensions on the behavior of magnetic anisotropy in these lithographically-patterned specimens measured by SQUID and FMR. Additionally,
observation and analysis of spin-wave resonances (SWRs) generated by surface anisotropy will be presented.

The appendices at the end of this dissertation will provide details of the special handling required for phosphorus in the MBE process, as well as the step-by-step instructions of the standard protocol for performing the patterning processes used in this thesis, for future reference.

1.3 Background

1.3.1 Review of Diluted Magnetic Semiconductors

Diluted magnetic semiconductors (DMSs) were first introduced in mid-1970s [9][10] by alloying magnetic ions into non-magnetic semiconductors, thus combining localized magnetic moments with bulk semiconductor properties via exchange interaction. The II-Mn-VI DMSs, in which part of the group-II atoms are randomly replaced by Mn ions, were extensively investigated by the 1980s. It was discovered that in bulk crystals the substitution of Mn in these materials could as high as 50% or more in CdMnTe or HgMnTe alloys [10]. Although remarkable magnetic properties, such as giant Faraday rotation and giant Zeeman splitting, were observed in these II-VI DMSs [11]-[13], II-Mn-VI alloys do not display ferromagnetic behaviors, as the magnetic interaction in these alloys is usually dominated by antiferromagnetic super-exchange. The exceptions are heavily p-doped II-Mn-VI DMSs and (Pb,Sn,Mn)Se, in which ferromagnetism at low temperature were reported [14][15].

The new era came in 1989, when Munekata et al. [16] successfully grew InMnAs using low temperature molecular beam epitaxy (LT-MBE) growth, with Mn content up to
10^{21} \text{ cm}^{-3}, \text{ which is two magnitudes higher than the usual concentration limit obtainable in equilibrium crystal growth. Ferromagnetism was observed in p-type InMnAs epilayers below 10 K [17]. Utilizing the LT-MBE technique, with the similar or higher Mn concentration, growth was extended to GaMnAs by several groups in 1996 [18][19]. The most important advantage of GaMnAs over InMnAs is that the Curie temperature (ferromagnetic phase transition temperature) is much higher for GaMnAs [20], exceeding 150K in the thin film structures [21][22].

1.3.2 Ferromagnetism in III-Mn-V Semiconductors

Magnetic ordering in III-Mn-V systems (e.g., GaMnAs or InMnAs) was discovered to be mediated by holes [23][24], which originate from the presence of substitutional Mn ions in the system, as discussed at the end of this subsection. The interaction between localized spins and carrier spins is governed by the $p$-$d$ kinetic exchange [23][25]. The Hamiltonian for this exchange interaction is given by [9]

$$H = H_h + J_{pd} \sum_{i,j} S_j \cdot s_i \delta(r_i - R_j). \quad (1.1)$$

where $H_h$ is the Hamiltonian of the band carriers that includes the $k \cdot p$ Hamiltonian and the interaction among holes. The second term represents the sum of $p$-$d$ exchange coupling between local Mn spins $S_j$ from d-orbitals and hole spins $s_i$ from the valence band p-orbitals [26]. Due to the strong $p$-$d$ exchange, the hole spins couple anti-ferromagnetically with the localized Mn spins, leading to ferromagnetic ordering of the localized Mn spins. The Curie temperature of ferromagnetism in such DMSs is given by the Zener mean field model as [23]

$$T_c = Cxp^{1/3}. \quad (1.2)$$
Thus the Curie temperature is proportional to the mole fraction of substitutional Mn ions \( x \), and the power of 1/3 of the hole concentration \( p \).

In GaMnAs specifically, considering a substitutional Mn ion at Ga site, the local moment is formed by three occupied \( sp-d \) bonding states with spins of all five electrons in the Mn \( d \)-shell aligned in the same direction, leading to an \( S = 5/2 \) local moment. The Landé g-factor for Mn ion is \( g = 2 \). The holes come from the absence of an electron in the \( 4p \) orbital of a substitutional Mn ion [27]. STM experiments [28][29] and infrared (IR) spectroscopy [30] have confirmed that Mn acts as a shallow acceptor in GaAs. Thus the substitutional Mn ion is not only the source of magnetic ions, but also provides the carriers which mediate the ferromagnetic ordering of these ions.

In addition to replacing the Ga atom in GaAs, Mn ion can also enter spaces between the lattice sites, referred as the interstitial Mn [31][32]. In that situation Mn ions on GaMnAs act as double donors, thus compensating a fraction of the substitutional Mn ions, and lowering the number of carriers needed for ferromagnetic order. Moreover, the two types of Mn ions can form antiferromagnetic pairs [33], thus canceling a fraction of magnetic ions involved in ferromagnetic ordering and resulting in a significant reduction of ferromagnetism in GaMnAs. Post-growth annealing treatment was found to be effective in eliminating these interstitial Mn, and thus in restoring the carrier concentration, total magnetization, and as a consequence also the Curie temperature [34][35].

1.3.3 Magnetic Anisotropy of GaMnAs

The band structure of GaAs (and therefore also of GaMnAs), and particularly the Fermi surface of the holes in these material, is anisotropic. Since holes mediate
ferromagnetic properties of GaMnAs, that will automatically lead to anisotropy of magnetic properties [24]. Since the understanding to magnetic anisotropy in GaMnAs is crucial to applications of this material in spintronic devices [36]-[38], intensive studies on this topic were performed both theoretically [24][39] and experimentally [40][43]. It is now well established that the magnetic anisotropy in GaMnAs thin films grown on (001) GaAs substrates by LT-MBE has a strong temperature and angular dependence, and the directions of the easy axes of magnetization also depend on Mn concentration [44] and on sample thickness [45].

To describe magneto-crystalline anisotropy, one typically uses magnetic free energy, which is expressed as [38]

\[ E = K_U \sin^2 \theta + \left( \frac{K_C}{4} \right) \cos^2 2\theta - MH \cos(\theta - \theta_H), \] (1.3)

where \( K_U \) and \( K_C \) are the lowest-order uniaxial and cubic anisotropy constants, \( M \) is the magnetization, \( H \) is the external magnetic field, and \( \theta \) and \( \theta_H \) represent, respectively, the orientations of magnetization and of the applied magnetic field measured from the \([1\bar{1}0]\) crystallographic axis. At temperatures lower than \( T_C \) the in-plane magnetization is under competing effects of cubic and uniaxial anisotropy. Importantly, as temperature decreases, the cubic anisotropy increases so as to almost dominate the behavior of total magnetization at lowest temperatures [46]. Detailed investigation and manipulation of the magnetic anisotropy in GaMnAs alloys will be discussed in Chapter 3 and Chapter 4.

1.3.4 Introduction to GaMnAsP Material

As noted above, it is desirable to develop reliable approaches for manipulating the magnetic anisotropy in GaMnAs, both because of its scientific interest and its importance in spintronic device applications. Magnetization easy axis oriented perpendicular to the
film plane in a device has recently drawn particular interest, as this property provides important prospects for increasing information storage density in non-volatile magnetic memory devices [47].

Incorporating phosphorus into GaMnAs material is an effective method to fulfill the demands stated above, since the presence of P reduces the lattice parameter of the resulting alloy [7][5]. As the lattice constant is reduced below that of GaAs, GaMnAsP grown epitaxially on a GaAs (001) substrate is under tensile strain [5], instead of compressive strain experienced by GaMnAs films grown in this way [18]. As a result, the easy axis in GaMnAsP will be reoriented from an in-plane direction to out-of-plane, normal to the film surface [5]. Alongside with the changing strain profile, the Curie temperature, carrier density and other physical properties have also been reported to vary with phosphorus concentration [5][8]. While some preliminary work has already been done on this material on specimens with relatively low concentrations of P, GaMnAsP alloys with mole fraction of P higher than 20% is currently unexplored, and requires detailed study to gain further understanding of this relatively new ferromagnetic semiconductor. In addition to investigating the basic properties of this quaternary alloy itself, we will extend our studies of this material to different methods, such as integrating layers of GaMnAsP with other magnetic layers, or to lithographically patterning GaMnAsP films into nanoscale structures, to manipulate their out-of-plane magnetic anisotropy for in ways that may be of interest in device applications.
1.4 References


CHAPTER 2:

SAMPLE FABRICATION AND METHODS OF CHARACTERIZATION

2.1 Synopsis

In this chapter, the sample growth and fabrication techniques are described, as well as different methods to perform structural, magnetic and electrical characterizations on materials. The growth procedure used in the preparation of (Ga,Mn)As and (Ga,Mn)AsP samples by molecular beam epitaxy (MBE) will be briefly presented in section 2.2, including a description of key MBE components. Nanofabrication processes for patterned samples will be introduced in section 2.3. Structural characterization by X-ray diffraction (XRD) is discussed in section 2.4. In the following sections 2.5, introduction to magnetic characterization methods, including superconducting quantum interference device (SQUID) and ferromagnetic resonance (FMR), will be provided. Finally, I will present magnetotransport apparatus and measurement setup in section 2.6.

2.2 Film Growth by Molecular Beam Epitaxy (MBE)

2.2.1 Introduction

Most semiconductor alloys are composed of constituent elements which are volatile. When one attempts to grow compound semiconductors such as III-V alloys from the vapor state, one needs to consider that the constituent elements generally have vapor pressures that differ by several orders of magnitude, which can result in a
nonstoichiometric decomposition 0 [2]. In a pioneering work of Günther [3], this
difficulty was first overcome by using different temperatures of the group-III and
group-V elemental sources and of the substrate in order to control the vapor pressure
independently in the crystal growth chamber. Although subsequent methodology of
growth techniques had been rapidly developed, an especially spectacular landmark
success in the pursuit of high quality crystalline samples was achieved with the
development of molecular beam epitaxy (MBE) utilizing cryogenic panels, developed in
early 70s [4][5]. In this technique, a unidirectional beam of atoms or molecules can be
effused from heated sources and travels under an ultra-high vacuum (UHV) condition
(below $10^{-9}$ torr) almost without interactions among these atoms or molecules, until they
react with the surface of the substrate. The reaction allows an ordered growth of one
crystalline layer upon another, i.e., the formation of successive epitaxial layers whose
crystallographic structure replicates that of the substrate.

The advantages of MBE for producing high quality crystal samples are numerous.
A few important advantages are briefly highlighted below [6]:

Non-equilibrium Growth: In the MBE chamber, the surface of the new epitaxially
grown layer can never achieve the global equilibrium between the incident atomic or
molecular flux and the growing crystal surface, quite unlike bulk crystal growth
conditions. During such non-equilibrium growth, the surface structure is determined by
the competition between two processes: the surface diffusion, which tries to flatten the
surface by seeking lattice vacancies; and the surface deposition process caused by
incident particles, that tends to make the surface rough. These two competing processes
can be tuned under certain conditions, such as a lower substrate temperature, allowing
fabrication of compositions and phases of materials that could not be fabricated by natural equilibrium crystal growth processes. For example, despite the low solubility of Mn in GaAs (less than $10^{19}$ cm$^{-3}$), which allows no more than 0.002 mole fraction of Mn atoms to be incorporated into the host in an equilibrium growth, the ferromagnetic semiconductor $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ alloys [6] [7] (with $x$ up to 0.1) can be grown successfully by low-temperature MBE technique. It will be discussed in following chapters how this non-equilibrium growth technique is extended to the growth of $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y$ quaternary alloys.

Crystalline Heterostructures: One of the unique advantages of MBE is the ability to grow monolithic crystalline structures of high crystalline perfection and an arbitrary compositional profile, which means grow a “single crystal” composed of layers of different materials. This is made possible by the precise atomic-layer-by-atomic-layer growth that characterizes this method. For example, by using MBE it is possible to produce multilayer structures that consist of alternating layers of, e.g., $(\text{Ga,Mn})\text{As}$ and $(\text{Ga,Mn})\text{AsP}$, with arbitrary layer thickness and various dopant concentrations. Generally, the atomic precision of MBE has made possible many semiconductor devices, including high-speed integrated circuits, light-emitting diodes, quantum cascade lasers [8], optical detectors, etc.
2.2.2 Basics of MBE Apparatus

Fig. 2.1: Schematic diagram of the MBE system used for growing III-V-based semiconductors alloys [6]. (Definition of abbreviations: RHEED - reflection high energy electron diffraction; CAR - continuous azimuthal rotation; and BEP - beam equivalent pressure.)

A schematic of the MBE chamber (model RIBER 32 R&D) used for growing III-V-based heterostructures is shown in Fig. 2.1. The III-V chamber is equipped with elemental Ga, Mn, In, Al, As, Sb, and Be sources. Growth of phosphide alloys such as (Ga,Mn)AsP will also be required for this work, but the P source cannot be incorporated as a simple effusion cell directly into the III-V MBE chamber like other sources due to the specificity of phosphorous. For completeness, we will discuss the details of the special handling required for phosphorus in the MBE process in Appendix A.
At the Notre Dame MBE facility we have a sister MBE which is used to grow II-VI compounds. These two MBE chambers are interconnected by an ultra-high vacuum (UHV) transfer line, allowing in situ transfer of wafers without exposure to atmosphere, as shown in Fig. 2.2. The UHV environment in the chamber is typically achieved by a series of pumping systems, including ion pumps, titanium sublimation pumps, cryopumps, and turbo-molecular pumps. In the cryogenic pumping process, liquid nitrogen shielding surrounding the source cells is used to reduce outgassing from the heated effusion cells, leading to a further reduction in the gas pressure within the chamber. The pressures of residual gases and of the molecular streams are determined by ionization gauges.

Fig. 2.2: Schematic diagram of the dual-chamber MBE system at Notre Dame [6].
The effusion cells are made of pyro-boron nitride (PBN), and produce their respective elemental beams by thermally evaporating the elements placed inside the cells. The vapor escapes from the cell through an aperture in the form of a collimated beam, traveling ballistically with almost no collisions due to the UHV environment after it emerges from the cell. The quality of crystal growth depends critically on three main conditions: (i) the flux of the atoms of the beam; (ii) the purity of the sources; and also (iii) the UHV environment.

To maintain appropriate flux ratios between the various elemental sources, the corresponding effusion cell must be thermally well controlled. In the MBE system, thermocouples are used to provide feedback by standard proportional-integral-derivative (PID) control loop that can regulate the temperatures of the cells within ±1°C, regulating the flux to within 5%. Such control of the flux conditions makes possible highly accurate deposition of the epitaxial layers, to within a fraction of an atomic monolayer.

2.2.3 MBE Growth Process

A brief description on MBE growth process will be given in this subsection. In general, epitaxial growth of III-V-based or II-VI-based compounds by MBE involves a series of events, as follows [2]:

- Adsorption of the constituent atoms or molecules;
- Surface migration and dissociation of the adsorbed atoms or molecules;
- Incorporation of the atoms in the epitaxial film atop the substrate, resulting in nucleation and growth of succeeding layers.

In the first process, when the atoms arrive at the substrate, condensation of the atoms occurs. Next, these atoms begin to migrate along the substrate surface, with some fraction re-evaporating. Since this process requires a slower growth rate, a typical layer
growth in MBE depends on the precise steady control of the temperatures of both the effusion cells (which controls the elemental fluxes) and the substrate (which controls the rate of condensation). The final step leads to the desired construction of a crystallographic structure that resembles the profile of the underlying substrate.

![Schematic phase diagram](image)

Fig. 2.3: Schematic phase diagram for the relation between the substrate temperature and Mn concentration in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ grown by molecular beam epitaxy. (reprint from Ref. [7])

In this study, the III-Mn-V samples were grown at low substrate temperature. This condition, usually termed as low temperature (LT)-MBE growth, enhances the non-equilibrium character of MBE growth, and has been successful in producing remarkable ferromagnetic III-Mn-V thin films. For example, in the LT-MBE growth of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, the non-equilibrium growth condition allows the incorporation of a significantly larger number of Mn atoms (up to $x \sim 0.1$) into the GaAs host [7], as compared to $x \sim 0.0003$ that corresponds to the equilibrium solubility of Mn in GaAs. A
A schematic diagram showing the relation between substrate temperature and the Mn concentration in the corresponding (Ga,Mn)As alloy is shown in Fig. 2.3.

A generic LT-MBE growth of (Ga,Mn)As samples typically involves the following sequences. After growing a crystalline GaAs buffer layer on a semi-insulating (001) GaAs substrate at 590°C, the substrate temperature $T_S$ is allowed to cool to 200-300°C, and a LT-GaAs buffer is deposited to a thickness usually between 3 and 100 nm. Epitaxial films of $\text{Ga}_1-x\text{Mn}_x\text{As}$ with various Mn concentration $0 < x < 0.10$ are then grown on the thin LT-GaAs buffer at a typical growth rate of about 0.8 $\mu$m/h. The various details describing the growth of specific III-Mn-V samples used in this work will be presented in the relevant sections of the chapters that follow.

2.3 Nanofabrication Techniques

Nanostructures of materials can have distinctly different properties from their bulk forms, which represents an important component of this thesis. Especially for diluted magnetic semiconductor materials such as the III-Mn-V series of alloys, restricting the dimension of samples to nanometer scale can lead to significant changes in their magnetic and electrical properties, and yield important application potential for information storage technologies.

In this work, we have developed a solid nanofabrication procedure to fabricate MBE-grown III-Mn-V films into nanostripe and nanosquare structures. All of the nanofabrication processes which we use are carried out in facilities available in the Center for Nano Science and Technology at the University of Notre Dame, including Notre Dame Nanofabrication Facility (NDNF) and Notre Dame Integrated Imaging Facility (NDIIF).
The NDNF and NDIIF facilities feature with advanced nanofabrication and characterization equipment, such as: electron beam lithography (EBL) system, contact photolithography system, electron beam evaporator, reactive ion etching (RIE) system, scanning electron microscope (SEM) and transmission electron microscope (TEM). The step-by-step details of the standard protocol for performing the patterning processes used in this thesis will be presented in Appendix B.

2.4 Structural Characterization

2.4.1 X-ray Diffraction (XRD)

In this work, knowledge of the crystal structure of Ga$_{1-x}$Mn$_x$As and Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ materials is essential for determining the crystal quality of the films and the real concentrations of elemental constituents (values of x and y), as well as for determining the strain profiles in the samples.
X-rays are used as an electromagnetic probe of the crystal structure of a solid due to the fact that their wavelength (1 ~ 2 angstrom) are comparable to typical interatomic distances in a solid. In X-ray diffraction, for certain sharply defined wavelengths and incident directions, intense peaks of scattered radiation (known as Bragg peaks) are observed. The relation between the X-ray wavelength and the incident direction obeys the Bragg’s Law:

$$n\lambda = 2d \sin \theta,$$

where $n$ is an integer, $\lambda$ is the wavelength of the incident X-rays, and $d$ is the distance between adjacent parallel scattering planes in the crystal. As an illustration, X-rays reflected from the lattice planes are shown in Fig. 2.4. An X-ray incident on the atoms of a crystal will elastically scatter off the electrons of those atoms, producing secondary circular waves emanating from the scattering sites. An array of spherical waves is produced by the array of atoms in a crystal. Destructive interference causes these waves
to cancel out one another in most directions, but in a few specific directions, given by Eq. (2.1), these waves add constructively, leading to so-called Bragg peaks. These peaks are then used to identify specific atomic layers where scattering leads to reflection. For a known X-ray wavelength, one can measure the incident angle $\theta$ at the Bragg conditions to obtain the value of $d$, which will yield the information on the lattice constants of the solid. Additionally, peak widths give information on lattice disorder.

Fig. 2.5: Schematic of Bruker D8 Discover X-ray diffractometer in triple-axis configuration [9].

In our specific work, a Bruker D8 Discover high-resolution X-ray diffractometer is utilized to perform the structural characterization of the films used in our experiments. A typical method of measuring the XRD diffraction spectrum is to perform $2\theta$-$\omega$ (or $\omega$-2$\theta$) coupled scans with a triple-axis configuration shown in Fig. 2.5. X-rays generated from a Cu source tube are reflected by the Goebel mirror, then they go through a rotary absorber (which can reduce the intensity of the X-ray by different levels), and are incident onto the...
monochromator crystal (first crystal) to eliminate the Cu K\textsubscript{α2} emission wave. The monochromatic X-rays are then incident on our sample crystal (the second crystal) and get diffracted toward the analyzer crystal (third crystal); finally the diffraction beam is received by a scintillation detector. There is an alternative optic path after diffraction called the double-axis configuration, in which the X-rays pass through a variable slit instead of an analyzer crystal before hitting the detector. The advantage of the triple-axis setup is that the analyzer crystal removes the diffuse scattering and fluorescence, thus providing a higher angular resolution in 2\(θ\), although at the price of reducing the intensity.

In a 2\(θ\)-\(ω\) (or \(ω\)-2\(θ\)) coupled scan, 2\(θ\) (the angle between the extension of incident ray and the diffracted ray) is moving at twice the speed as \(ω\) (the angle between the incident ray and the horizontal plane) simultaneously, which means the X-ray tube and the detector will move at the same speed, since the sample stage remains fixed during the measurements. As we sweep 2\(θ\), an XRD spectrum of diffracted beam intensities at various angles is obtained. At the Bragg condition, a sharp peak will appear in the spectrum. By combining the Bragg’s law and the plane spacing equation for a cubic crystal, we can calculate the lattice constant \(a\) in the c-axis of the crystal:

\[
a = d\sqrt{h^2 + k^2 + l^2},
\]

where \(h\), \(k\), and \(l\) are the Miller indices of the Bragg plane.

Figure 2.6 shows a typical X-ray 2\(θ\)-\(ω\) scan for a (Ga,Mn)As film grown on a GaAs (001) substrate. Note that the vertical axis is in logarithmic scale. Here the most intense, narrow peak is the GaAs substrate (004) Bragg peak, and the second highest peak on the left is the (Ga,Mn)As (004) Bragg peak. The oscillating satellite peaks on the two
sides of the film Bragg peak are so-called Pendellösung fringes. These arise from multiple reflections arising from interference from the x-ray wave reflected from the film surface and from the interface between the substrate and the film. The period of the Pendellösung fringes can be used to determine the thickness of the thin film of interest.

![Graph showing X-ray 2θ-ω scan](image)

**Fig. 2.6:** A typical X-ray 2θ-ω scan of (Ga,Mn)As film grown on a GaAs substrate.

2.4.2 Reciprocal Space Mapping (RSM) Measurement

The reciprocal space mapping measurement by an X-ray diffractometer records diffraction intensity distributions by scanning both the diffraction angle and sample rotation axes, and plots the result in reciprocal space. The reciprocal lattice map can provide information on the crystal structure, crystal orientation relationships, crystallinity,
and the preferred orientation of the sample. The central coordinates, shapes, and positional relationships of the reciprocal lattice points appearing in a 2D (or 3D) data plotted in reciprocal space provide a wide range of information on crystal structure. So, this is the method which obtains two dimensional distribution maps with the scanning scattering vector $\mathbf{K}$ (Fig. 2.7).

![Fig. 2.7: Vector notation of the reciprocal space mapping measurement [10].](image)

Shown in Fig. 2.7, the incident and scattered (or diffracted) X-ray beams are represented by the wave vectors $\mathbf{k}_0$ and $\mathbf{k}$ in the reciprocal space, respectively, as follows:

$$\mathbf{K} = \mathbf{k} - \mathbf{k}_0,$$

(2.3)

where $\mathbf{K}$ is the scattering vector and its length $|\mathbf{K}|$ equals to the inverse of lattice spacing $d_{hkl}$. In a conventional $2\theta$-$\omega$ measurement, the incident angle and the exit angle are kept equal so that the direction of the scattering vector $\mathbf{K}$ is fixed, and only the length of $\mathbf{K}$ is changed. If the measured lattice planes are parallel to the sample surface, the incident X-ray beam is diffracted by the lattice planes, normal direction of whom matches the scattering vector. In a RSM measurement, distribution of reciprocal points can be
observed either from a radial spread, representing changes in lattice constant, or a tangential dispersion, suggesting variation of orientation of lattice planes. Lattice constants and the condition of strain can then be extracted from the information of the positional relationships and the shape of reciprocal lattice points [11][12].

![Fig. 2.8: Reciprocal space map of (Ga,Mn)As grown on GaAs substrate (screenshot from Bruker LEPTOS software), measured along (224) asymmetric Bragg plane.](image)

Figure 2.8 shows the results of the asymmetric RSM measurement of a GaMnAs thin film grown on a GaAs (001) substrate. The vertical and horizontal axes are shown using reciprocal space coordinates. The reciprocal map shows that the thin film layer is fully strained. The GaMnAs lattice is constrained to the GaAs substrate lattice so that the reciprocal lattice points of the film and the substrate are lined up in the vertical direction (the $Q_z$ axis in Fig. 2.8), and these lattices have the same dimensions in the horizontal
direction (i.e., the $Q_z$ axis). It is very useful to express the positions and shapes of reciprocal lattice points using Cartesian coordinates (i.e., $Q_x$, $Q_z$) instead of $2\theta$ and $\omega$ for calculating the $d$-spacings. This conversion can be done following the simple formula shown in Eq. (2.4).

\[
Q_x = \frac{2}{\lambda} \sin \frac{2\theta}{2} \sin \left( \frac{2\theta}{2} - \omega \right) = \frac{1}{\lambda} \{ \cos \omega - \cos(2\theta - \omega) \},
\]
\[
Q_z = \frac{2}{\lambda} \sin \frac{2\theta}{2} \cos \left( \frac{2\theta}{2} - \omega \right) = \frac{1}{\lambda} \{ \sin \omega - \sin(2\theta - \omega) \}.
\]

In some cases, Eq. (2.4) is calculated with an additional multiplier $2\pi$. Both $Q_x$ and $Q_z$ are the inverse of lattice spacing, and can also be expressed as $Q_y$ and $Q_z$, because of the position relationships of the sample surface normal. For example, in our case $Q_z$ is parallel to crystal axis [001] of the sample, and $Q_x$ is parallel to [hk0], as shown in Fig. 2.9. In this instance, $d_{hk0}$ and $d_{001}$ are calculated from the central coordinates of the reciprocal lattice point distribution $(Q_x, Q_z)$, and from that the lattice constants can be calculated. Figure 2.9 shows the concept of a reciprocal space map and $Q$ coordinates.

![Fig. 2.9: Concept of reciprocal space map and $Q$ coordinates [10].](image)
The relative positions of reciprocal lattice points of an epitaxial film and its substrate, depending on lattice matching and on the presence or the absence of lattice relaxation. Figure 2.10 schematically illustrates the reciprocal space maps for relaxed, strained and misoriented films. The term lattice relaxation refers to the state of an epitaxial film having the same cubic crystal structure as the bulk of the material composing the film, as shown in Fig. 2.10(a). In this case, the reciprocal lattice point of the film with the indices \((hkl)\) (shown in yellow) is positioned on the line connecting the reciprocal lattice point \((hkl)\) of the substrate (shown in red) and the origin of the reciprocal lattice—along the line of the \(2\theta-\omega\) scan for both symmetric and asymmetric diffractions.

Fig. 2.10: Reciprocal space maps of hetero-epitaxial layer [10].

If the lattice of the film is strained at the interface between the epitaxial film and the substrate in a manner such that the in-plane lattice constants of the epitaxial film and the substrate exactly match, the reciprocal lattice point of the film with indices \((hkl)\) is
positioned directly below the reciprocal lattice point \((hkl)\) of the substrate for both symmetric and asymmetric diffractions (see Fig. 2.10(b)). In the case for asymmetric diffraction, the reciprocal lattice points of the substrate and the film are not positioned on the same line of a \(2\theta-\omega\) scan. If crystal orientation direction of thin film is tilted with respect to the substrate, the reciprocal lattice points of thin film will also be tilted, as shown in Fig. 2.10(c).

![Instrumental resolution functions in reciprocal space maps](Image)

**Fig. 2.11:** Instrumental resolution functions in reciprocal space maps [13].

When performing RSM measurements, we should also be careful about the resolution of the receiving optical system. If the resolution of the incident or receiving optics decreases, the scattering in a region in reciprocal space increases accordingly. When this happens, even if the true reciprocal lattice point is extremely small, the
reciprocal lattice point is observed with a spread corresponding to the resolution. The region of the reciprocal space in which the scattering is observed is called the resolution function. There are three major instrumental resolution functions, as presented in Fig. 2.11. The vertical green line represents the wavelength streak coming from the dispersion in wavelength of incident or receiving wave. The upward slanted blue line is called the monochromator streak, resulting from the divergence of incident angle, which can be greatly reduced by installing a monochromator in the incident optic path. And the downward slanted red line is the analyzer streak due to a finite resolution of the detector, normal to the exit beam. This streak is an instrumental artifact that generally cannot be completely eliminated, and is therefore present in most reciprocal space maps obtained on our samples (e.g., in Fig. 2.8).

2.5 Magnetic Characterization

The magnetic characterizations and measurements are of central importance to this thesis, as the thesis focuses on ferromagnetic semiconductors. We will be using the superconducting quantum interference device (SQUID) to determine the magnetization, the magnetic anisotropy, the Curie temperature, the coercive field, the \textit{ac} magnetic susceptibility, and other magnetic properties. Additionally, ferromagnetic resonance (FMR) will be used to investigate angular dependence and temperature dependence of magnetic anisotropy of III-Mn-V thin films and nanostructures.
2.5.1 DC Josephson Effect

The SQUID magnetometer we use is based on the *dc* Josephson effect [14], which is based on the fact that the tunneling of electron pairs across a superconductor-insulator-superconductor junction (a supercurrent of pairs) will flow across the junction in the absence of any applied electric field. In this process the tunneling current is observed with no voltage applied across the junction, and is given by

\[ I = I_{\text{max}} \sin(\varphi_2 - \varphi_1), \]

where \( I_{\text{max}} \) is the maximum current, which depends on the thickness of the tunnel barrier, \( \varphi_1 \) is the phase of the wave function for the Cooper pairs in one of the superconductors, and \( \varphi_2 \) is the phase of the corresponding wave function in the second superconductor.

When a dc magnetic field is applied through a superconducting ring containing two Josephson junctions in parallel (Fig. 2.12), the wavelength of the Cooper pairs taking one path around the area is increased, while the wavelength of those taking the other path is decreased. When the two currents rejoin, they will generally have different phases. The total current flowing through the system shown in the figure can be shown to be

![Fig. 2.12: A superconducting ring containing two Josephson junctions.](image-url)
\[ I = 2I_{\text{max}} \sin \varphi_0 \cos(\pi \Phi / \Phi_0), \]  

(2.6)

where \( \varphi_0 \) is the phase difference between the junctions in the absence of an external field, \( \Phi = \oint A \cdot dl \) is the total magnetic flux through the superconducting ring, and \( \Phi_0 = \frac{\hbar}{2q} \) is the magnetic flux quantum. An interference phenomenon takes place that is very similar to the double-slit interference experiments in optics. Constructive and destructive interference occurs sequentially if the intensity of the magnetic field is increasing steadily. The change of the total magnetic flux can be captured by a flux transformer made of coupled induction coils, and then read out by an electronic amplifying system. This makes the dc Josephson effect suitable for measuring even extremely weak magnetic fields (i.e., \( 10^{-14} \) Tesla). A detailed description of ac magnetic susceptibility will be presented in Chapter 3.

2.5.2 The SQUID Magnetometer

The SQUID system used in this study is a commercial system named Magnetic Properties Measurement System (MPMS) Model XL, manufactured by Quantum Design, Inc. This system is sufficiently sensitive to measure the sample magnetic moment as low as \( 10^{-9} \) emu over a broad range of temperatures. The whole system has two major hardware components: (i) the MPMS dewar and probe assembly, and (ii) the associated control system in the MPMS control console, both shown in Fig. 2.13. The operation of the whole system is fully automated, as are the gas control and other ancillary functions in the system. Control and data collection are provided by a computer and two independent subsystem controllers, the Models 1802 and 1822. Inside the cryogenic dewar, a superconducting magnet integrated with a SQUID detection system is employed to probe the magnetic moment of the sample placed inside the chamber. The system...
provides rapid and precise measurements of the magnetic moment of the sample over a temperature range of 1.9 K to 400 K. The superconducting magnet cooled by liquid helium is capable of providing fields from $-7.0$ to $+7.0$ Tesla with a stable 0.1 Gauss resolution.

The SQUID detector system used in this study has been configured to a highly balanced second-derivative coil with a total length of approximately 3 cm. The basic detection works as follows. As the sample is moved through the center of the superconducting coils, it induces an electric current in the detection coils. Since the detection coils, the connecting wires, and the SQUID input coils form a closed superconducting loop, any produced change in current is then detected. This change is proportional to the change in magnetic flux. Using a highly linear current-to-voltage converter, the variations in SQUID voltage output thus provide a measure proportional to the magnetic moment of the sample. The coils are designed to reject the uniform field from the superconducting magnet to a precision of approximately 0.1 percent.

The SQUID system can detect a change of 0.001 of a flux quantum (one flux quantum is $2.07 \times 10^{-7} \text{ G} \cdot \text{cm}^2$), thus providing a sensitivity that is more than three orders of magnitude higher than that of conventional magnetic sensors. With such precision, the SQUID system is especially suitable for studying magnetic properties of small specimens over a broad range of magnetic fields.
Fig. 2.13: Quantum Design MPMS XL system and probe components [15].
2.5.3 Introduction to Ferromagnetic Resonance (FMR)

Ferromagnetic resonance (FMR) is a spectroscopic technique that can be used for probing a number of magnetic properties of ferromagnetic materials, including spin waves (magnons) and spin dynamics. It was accidentally discovered by V. K. Arkad'yev when he observed the absorption of UHF radiation by ferromagnetic materials in 1911. Specifically, FMR arises from the precessional motion of coupled spins in a ferromagnetic material placed in an external magnetic field. The magnetic field puts a torque on the magnetization, which causes the magnetic moment of the ensemble to precess. The precession frequency depends on the orientation of the material and the strength of the magnetic field.

Ferromagnetic resonance is one of the most powerful experimental techniques for the study of ferromagnetic thin films, providing the opportunity for determining all their essential properties, including magnetic anisotropy, total magnetic moment, Curie temperature, magneto-elastic coupling coefficients, and parameters describing the relaxation of magnetization. High sensitivity, high resolution, and relatively easy set-up and sample exchange are among the advantages of the FMR experiment.

In a system such as GaMnAs or GaMnAsP of interest in this thesis, FMR involves the total magnetic moment of the Mn-ion/hole complex comprising the ferromagnetism of the GaMnAs system, which precesses at the Larmor frequency $\omega_L$ around the resultant of all static magnetic fields present in the system (i.e., applied external field, anisotropy fields, and demagnetization field). Since the experimental microwave frequency is fixed at 9.47 GHz by the resonance frequency of the cavity, a dc magnetic field is swept as the independent variable. When the Larmor precession frequency $\omega_L$ coincides with the
rf-frequency, a resonance takes place between the motion of the Mn-ion/hole spin complex and the microwave signal. This resonance condition manifests itself as a peak in absorption of the incident microwaves, resulting in a decrease of the quality factor of the cavity.

2.5.4 FMR Spectrometer and Experimental Setup

Fig. 2.14: Block diagram of Bruker EPR/FMR spectrometer [16].

In this thesis the FMR measurements are carried out at 9.4 GHz (X-band) using a Bruker electron paramagnetic resonance (EPR) spectrometer. Figure 2.14 shows the general layout of the EPR spectrometer. The electromagnetic radiation source and the detector comprise the microwave bridge; and the sample is in a microwave cavity, which amplifies weak signals from the sample as an applied magnetic field is swept. In addition, we have a console which contains signal processing, control electronics, and a computer.
used for coordinating all the units acquiring the FMR spectrum as well as for analyzing the data.

Fig. 2.15: Schematic diagram of the EPR/FMR apparatus [16].

The arrangement used for FMR measurements is shown in Fig. 2.15. Note that the $dc$ magnetic field of the EPR spectrometer is confined to the horizontal plane, and the weak microwave (rf) magnetic field is vertical. The magnetic film is placed in a suprasil sample tube, and the entire-tube-plus-sample assembly is inserted into a liquid helium continuous flow cryostat, which is in turn inserted into the microwave cavity of the EPR spectrometer. The helium flow is driven by a small-diaphragm vacuum pump, which circulates the helium gas through the system. The under-pressure produced by the pump is sufficient to achieve temperatures down to 4 K. By changing the temperature, we can
observe the temperature dependence of FMR; and by rotating the sample tube, we can study its angular dependence.

2.6 Electrical Characterization

2.6.1 Introduction to Magnetotransport Measurement

In this thesis, the magnetotransport measurement system has been implemented to perform electrical characterization of the samples under study. The system is set up to measure various transport properties. These transport properties include estimates of carrier concentration and mobility, temperature dependence of resistivity of the samples, and of the carrier type revealed by the Hall effect. However, since the III-Mn-V samples of interest are expected to exhibit ferromagnetism, the anomalous Hall effect (AHE) is our major focus in transport measurements. In fact, AHE serves as an extremely useful tool for detecting ferromagnetism and for measuring its relative temperature dependence.

Briefly, the Hall resistivity $\rho_{\text{Hall}}$ in a ferromagnetic semiconductor (such as GaMnAs) can be written in form [17]

$$\rho_{\text{Hall}} = R_0 B + R_S M,$$  \hspace{1cm} (2.7)

where $R_0$ is the ordinary Hall coefficient, $B$ is the applied field, $M$ is the magnetization, and $R_S$ is the so-called anomalous Hall coefficient, which is itself proportional to the resistivity $\rho$ of the material. The term involving $M$ generally dominates Eq. (2.7), so that in this case the AHE is influenced strongly by the magnetization of the sample below the ferromagnetic transition temperature, and thus provides valuable information about that parameter. However, the domination of $R_S M$ in Hall resistivity also results in a relatively lower sensitivity to the hole concentration, making it difficult to measure this important
parameter precisely. One possible solution is to apply ultra-high magnetic fields, so that the first term in Eq. (2.7) becomes the leading term.

2.6.2 Closed-cycle Helium Flow Cryostat

Fig. 2.16: Janis closed-cycle helium flow cryostat (adapted from the Janis closed-cycle system operating manual) [18].

All III-Mn-V samples in this work exhibit ferromagnetism below room temperature (RT), and thus a closed-cycle helium flow cryostat was employed in all magnetotransport measurements. A schematic diagram of the closed-cycle cryostat system is shown in Fig. 2.16. To operate this system, room temperature helium gas is first
compressed by a compressor unit, and then is supplied to the cold-head refrigerator via flexible gas lines. The compressed helium is cooled by expansion, and provides cooling to stations on the refrigerator. After cooling the refrigerator, the gas is returned to the compressor to repeat the cycle. The minimum temperature reached by this system is 10 K. Four samples can be measured simultaneously using this closed-cycle cryostat setup. This system also has two temperature sensors with a temperature range between 7.5 K and 300 K. The magnetic field in this case is provided by an electromagnet capable of producing up to ±0.8 Tesla. The field is measured by a Hall sensor with a sensitivity of 98.0 mV/Tesla at 293 K mounted between the poles of the electromagnet.

2.6.3 Magnetotransport Measurement Setup

In actual experiments, the cryostat described in the preceding paragraphs is connected to the measurement and control units. A total of four sets of voltmeters and DC current sources are utilized in the measurements. In each set, a Keithley 220 programmable current source is used to provide low DC current (typically on the order of μA), and two Keithley 2001/2000 multimeters are used for measuring the Hall and longitudinal resistances, respectively. Additionally, there is one set using HP 3478A multimeters instead of Keithley. The Lakeshore Model 665 Bipolar High Power Supply capable of driving the current up to 85 A to the electromagnet is utilized to provide the desired magnetic field in the electromagnet. And the magnetic field measured by the Hall sensor placed between the electromagnet pair is read out by a Keithley 2001 voltmeter, when the Hall sensor is powered by a Lakeshore Model 120 Current Source with a current of 100 mA. Thus the magnetic field is measured in real time rather than using the value of the current supplied by the bipolar power supply, in order to avoid artificial
hysteresis loops near the zero-field region. To obtain a steady temperature environment, we use a Lakeshore Model 331 Temperature Controller. Using an automated feedback (proportional-integral-derivative PID) system connected to the two temperature sensors, the controller is able to maintain the temperature of the sample holder at the desired value by regulating a heater coil.

Since the entire measurement in each scanning loop of the magnetic field is rather time-consuming, a semi-automated measurement program using LabVIEW computer software was written for running the process. Basically, the devices are computer-controlled by using the general purpose interface bus (GPIB) card and digital 8-bit parallel (bi-directional) data transfer cables. The same personal computer (PC) is also used to carry out data acquisition and data analysis through the GPIB interfaces.

We now turn to specific measurement quantities obtained in the transport setup. A schematic of the basic control and measurement unit is depicted in Fig. 2.17. In this schematic, six contacts have been made to the sample under study, denoted by numbers 1 to 6. The purpose of the setup is to measure simultaneously the longitudinal voltage $V_{24}$ (or $V_{35}$) and also the Hall voltage $V_{23}$ (or $V_{45}$) when a current $I_{16}$ passes through the sample (from contact 1 to contact 6 in Fig. 2.17) under an applied transverse magnetic field $B$ (oriented out of the page in the schematic). If the longitudinal voltage $V_{24}$ is measured between the contacts (2, 4) separated by a distance $l$, then the longitudinal resistivity $\rho_{xx}$ of the sample can be obtained as

$$\rho_{xx} = \frac{wt}{l I_{16}},$$

(2.8)

where $w$ and $t$ are the width and the thickness of the sample (III-Mn-V layer), respectively.
Fig. 2.17: Basic transport measurement unit for Hall effect measurements, involving a Hall bar sample of thickness $t$ and width $w$. The switch box allows us to select between various combinations of voltage probes. The sample and Hall sensor are mounted on the sample holder at a stable temperature regulated by the temperature controller. The magnetic field $B$ is controlled by the current supplied to the magnet coils by a bipolar magnet power supply [18].

The Hall voltage obtained from the measurements can be used to calculate the carrier concentration if the ferromagnetic sample becomes saturated at high field and/or at very low temperature. In this work, most of the samples measured by magnetotransport are (Ga,Mn)AsP, in which the magnetic easy axis is pointing perpendicular to the film surface due to the presence of phosphorus, as will be shown later. In this case the total magnetization can be saturated under a relative small field, well within the capability of our electromagnet (0.8 Tesla). However, in the case of (Ga,Mn)As samples, carrier concentrations obtained in this way must be regarded only as estimates, since the total
saturation condition could be well beyond our maximum magnet field limit. When the saturation condition is assumed, the carrier concentration can be obtained by calculating the slope of the linear part of the Hall voltage versus applied field, as follows:

\[
\left. \frac{dV_{23}}{dB} \right|_{B>B_{sat}} = \frac{I_{16}}{pqt} = R_H \frac{I_{16}}{t},
\]

(2.9)

where \( p \) is the carrier concentration (assumed to be holes), \( q \) is the charge of one carrier, and \( R_H \) is the Hall coefficient \( R_H \equiv 1/pq \). In the literature, the Hall coefficient \( R_H \) is usually a quantity needed to calculate the carrier mobility \( \mu_H \), using the relation

\[
\mu_H = \frac{|R_H|}{\rho_{xx}},
\]

(2.10)

where \( \rho_{xx} \) is the resistivity of the sample.

In most of the samples used for material characterization in this work, a macroscopic rectangular sample with dimensions of about 1×5 mm is used for the transport measurements. A small ratio of width versus length, typically smaller than 1:4, is desirable in order to avoid voltage shortages between the voltage probes and the current contacts at the two sample ends [19]. The voltage probe contacts (2 to 5 in Fig. 2.17) are prepared manually by directly soldering gold wires (0.5 mm diameter, using 99.9% pure gold) with indium onto the surface of the sample using a micro-soldering iron (coated with silver). The soldering was done by briefly heating the contact point to a temperature of around 240°C under a microscope, and by repeating this until a good bond is formed between the sample surface, the indium contact material, and the gold wire. Making the current contacts (1 and 6) should follow the same steps as the voltage probe contacts, but requires a pre-step that consists of spreading indium at the two ends of the sample with a clean straight edge, in order to make the current travel through the sample.
in parallel from 1 to 6. Each contact is then checked for ohmic behavior by measuring the $I$-$V$ curve of the contact. Since most samples are quite metallic, the ohmic contacts in our work were usually satisfactory.
2.7 References


CHAPTER 3:

ANISOTROPIC AC MAGNETIC SUSCEPTIBILITY IN (Ga,Mn)As FILMS

3.1 Synopsis

In this chapter we perform a systematic investigation of ac magnetic susceptibility in (Ga,Mn)As films as a function of temperature and magnetic field, carried out in parallel with dc magnetization measurements. The temperature dependence of ac susceptibility $\chi_{ac}$ shows anisotropic behavior: 1) a single peak in $\chi_{ac}$ is observed close to the Curie temperature $T_C$ for the $[1\bar{1}0]$ orientation of the driving ac field; 2) a single peak is also seen close to 22 K for the field along $[1\bar{1}0]$; and 3) peaks at both these temperatures are observed when the field is applied along [100]. A detailed analysis of the ac and dc data unambiguously indicates that the peak near $T_C$ is related to the paramagnetic-to-ferromagnetic phase transition, the ferromagnetic domains nucleating with their easy axes aligned with the $[1\bar{1}0]$ direction, providing a clear picture of uniaxial domain behavior of (Ga,Mn)As near $T_C$. The peak near 22 K, on the other hand, is related to the onset of biaxial domain structure in (Ga,Mn)As induced by competition between uniaxial and cubic anisotropy. More specifically, the ac susceptibility peak near $T_C$ involves 180° magnetization flips along the $[1\bar{1}0]$ easy axis of the domains, while the peak near 22 K originates from magnetization wobbling between two easy axes on either side of $[1\bar{1}0]$ separated by a small angle.
3.2 Introduction to ac Magnetic Susceptibility

*ac* magnetic measurements are an important tool for characterizing magnetic materials. Because the induced sample moment is time-dependent, *ac* measurements yield information about magnetization dynamics which is not obtained in *dc* measurements, where the sample moment is constant during the measurement time. In need for *ac* susceptibility measurements, the Quantum Design MPMS XL SQUID intended to drive a small *ac* magnetic field superimposed on the *dc* field, generating a time-dependent magnetic moment in the sample. The field of the time-dependent moment induces a current in the pickup coils, allowing measurement without sample motion.

Consider very low frequencies first, where the measurement is most similar to *dc* magnetometry. In this case, the magnetic moment of the sample follows the $M(H)$ curve that would be measured in a *dc* experiment. As long as the *ac* field is small, the induced *ac* moment is

$$M_{ac} = \left(\frac{dM}{dH}\right) \cdot H_{ac} \sin(\omega t), \quad (3.1)$$

where $H_{ac}$ is the amplitude of the driving field, $\omega$ is the driving frequency, and $\chi = dM/dH$ is the slope of the $M(H)$ curve, i.e. the susceptibility of the sample, which is the quantity of interest in *ac* magnetometry. One significant advantage of the *ac* measurement is that the measurement is very sensitive to small changes in $M(H)$.

At higher frequencies than those considered above, the *ac* moment of the sample can no longer follow along the *dc* magnetization curve due to dynamic effects in the sample. For this reason, the *ac* susceptibility is often known as the dynamic susceptibility.
In this higher frequency case, the magnetization of the sample may lag behind the driving field, an effect that is detected by the magnetometer circuitry. Thus, the \textit{ac} magnetic susceptibility measurement yields two quantities: the magnitude of the susceptibility, \( \chi \), and its phase shift \( \phi \) relative to the driving signal. Alternately, one can think of the susceptibility as having an in-phase, or real, component \( \chi' \), and an out-of-phase, or imaginary, component \( \chi'' \). The two representations are related by

\[
\begin{align*}
\chi' &= \chi \cos \phi \\
\chi'' &= \chi \sin \phi.
\end{align*}
\] (3.2)

In the limit of low frequency, where the \textit{ac} measurement is most similar to a \textit{dc} measurement, the real component \( \chi' \) is just the slope of the \( M(H) \) curve discussed above. The imaginary component, \( \chi'' \), indicates dissipative processes in the sample. In ferromagnets, a nonzero imaginary susceptibility can indicate irreversible domain wall movement or energy absorption due to a permanent moment. Also, both \( \chi' \) and \( \chi'' \) are very sensitive to thermodynamic phase changes, and are often used to measure transition temperatures.

3.3 Motivation

\((\text{Ga,Mn})\text{As}\) has emerged as the most fully studied ferromagnetic semiconductor [1], showing excellent magnetic properties. Many of the attractive properties of \((\text{Ga,Mn})\text{As}\) arise from the magnetic anisotropy and the dynamics of magnetic moment switching in this material [2][5]. The understanding of magnetization switching process in \((\text{Ga,Mn})\text{As}\) will therefore be essential in developing new devices, for which the control of magnetization is required [6][8]. Measurements of \textit{ac} magnetic susceptibility \( \chi_{\text{ac}} \) in \((\text{Ga,Mn})\text{As}\) have been shown as a highly promising tool for obtaining dynamic
information on magnetization switching phenomena [9][11]. The interpretation of the experimental $\chi_{ac}$ results are, however, still under debate. In particular, the issue is whether or not a single-domain spin-reorientation transition alone can describe the observed $ac$ susceptibility [11]. This has prompted us to carry out systematic parallel studies of $ac$ and $dc$ magnetic measurements on (Ga,Mn)As films, in the hope of obtaining further insight into the nature of $ac$ magnetic susceptibility of this material. Furthermore, these results may provide valuable insights into the dynamics of magnetic domain motion in (Ga,Mn)As films.

3.4 Sample Preparation

The (Ga,Mn)As samples for this study were grown on (001) semi-insulating GaAs substrates in a Riber 32 R&D molecular beam epitaxy (MBE) machine under As-rich growth conditions. As-grown 90-nm (Ga,Mn)As epilayers with a nominal Mn concentration of 6% were investigated in order to compare with the already published results in Refs. [9] and [10]. The growth of the samples was monitored by in-situ reflection high-energy electron diffraction (RHEED). Throughout the growth, no spotty patterns were observed in the RHEED pattern, indicating excellent two-dimensional deposition.

3.5 Results and Discussions

The magnetic $ac$ and $dc$ properties of the (Ga,Mn)As film were measured using a Quantum Design MPMS XL SQUID magnetometer on a 4.2 mm × 3.2 mm specimen cut from the as-grown epilayer. The $ac$ and $dc$ measurements were performed with the magnetic field applied in the plane of the (Ga,Mn)As film [i.e., in the (001)
crystallographic plane] as a function of temperature and magnetic field. Special attention was given to the temperature region near the Curie point, and to the temperature at which the dominant anisotropy switches from biaxial to purely uniaxial behavior.

Figure 3.1 shows the real and imaginary parts of the \(ac\) susceptibility, \(\chi'\) and \(\chi''\), with the \(ac\) magnetic field along the [110], [1\(\bar{1}\)0] and [100] crystal axes. The \(ac\) driving field was applied at three frequencies, 1 Hz, 10 Hz and 100 Hz, at an amplitude of 3.77 Oe. As reported in earlier studies [9], [10], a single peak at around 22 K is observed for the [110] field orientation, while another single peak is seen at ~53 K for the field along [1\(\bar{1}\)0]. Peaks with half-intensity can be seen for the field applied along the [100] direction at both these temperatures, representing projections of the behavior seen in the [110] and [1\(\bar{1}\)0] orthogonal axes. The presence of a strong \(\chi''\) contribution seen in Fig. 3.1 indicates a significant phase lag between the \(ac\) magnetization and the driving field.
Fig. 3.1: (a-c) Real and (d-f) imaginary components of the \( \chi \) magnetic susceptibility measured at frequencies of 1, 10, and 100 Hz in a driving magnetic field of 3.77 Oe applied along [110] (a, d), [1\bar{1}0] (b, e), and [100] (c, f) crystal axes.

The results illustrated by Fig. 3.1 clearly indicate the highly anisotropic properties of the \( \chi \) magnetic susceptibility in (Ga,Mn)As samples. One should also note that the peak occurring near \( T_C \) shows a clear dependence on the frequency of the \( \chi \) driving field, while the low-temperature peak appears to be only weakly-sensitive to frequency. As discussed below, this suggests that the mechanisms responsible for the two peaks in \( \chi_{ac} \) are different.
In order to gain insight into the origin of the ac susceptibility peaks seen in Fig. 3.1, we carried out dc measurements of the magnetization as a function of temperature, as well as a set of dc hysteresis loops at several key temperatures. As shown in Fig. 3.2(a), the Curie temperature $T_C$ of the (Ga,Mn)As sample is around 57 K. For $T < 17$ K remnant magnetization along [100] has the highest value, indicating that the magnetic easy axis of the film lies close to the [100] direction at low temperatures. Importantly, a prominent “kink” in $M$ versus $T$ curves is observed near 27 K for magnetizations along [100] and [110], indicating a change in the properties of magnetic anisotropy near that temperature [12], as discussed below.

Fig. 3.2: (a) Temperature dependence of remnant magnetization measured in a dc field of 10 Oe applied along [110], [110], and [100] axes, respectively. (b) Calculated ratio of anisotropy constants $K_C/K_U$ as a function of temperature.
It is well known that the in-plane magnetic free energy of (Ga,Mn)As can be described by a single-domain model [13], given by

\[ E = K_U \sin^2 \theta + \left( \frac{K_C}{4} \right) \cos^2 2\theta - MH \cos(\theta - \theta_H), \]

where \( K_U \) and \( K_C \) are the lowest order uniaxial and cubic anisotropy constants, \( M \) is the magnetization, \( H \) is the external magnetic field, and \( \theta \) and \( \theta_H \) represent, respectively, the orientation of magnetization and of applied magnetic field measured from the [\( \overline{1}10 \)] axis.

We thus apply the single domain model to fit the remnant magnetizations. The fitting results (solid lines in Fig. 3.2(a)) indicate that the system behaves as a single, uniform domain except around 27 K, so that Eq. (3.3) can be used to extract the ratio of anisotropy constants \( K_C/K_U \), which is plotted in Fig. 3.2(b). The temperature dependence of the \( K_C/K_U \) ratio clearly shows power-law dependence [10]:

\[ \frac{K_C}{K_U} = \frac{1}{\cos^2 \theta} = 10.56 \cdot T^{-0.719}, \]

with \( K_C/K_U = 1 \) at \( T = 27 \) K.

From Fig. 3.3(a) one can clearly see that at \( T = 5 \) K the in-plane magnetization is biaxial, but strongly dominated by cubic anisotropy. The departure from perfect cubic symmetry even at this low temperature is evidenced by the small intermediate step, which occurs as \( M_{[100]} \) switches sign during the reversal process. The admixture of uniaxial anisotropy increases with temperature, leading to a crossover of highest remnant magnetizations from [100] to [\( \overline{1}10 \)] orientations, as already reported in earlier studies [10][14][15].
Fig. 3.3: (a)–(c) Hysteresis loops measured at 5, 22, and 53 K in [110], [110̅], and [100] in-plane field orientations. Note the differences in scale in successive panels.

The dc hysteresis loops for $T = 22$ K and $T = 53$ K along different in-plane directions (i.e., near the temperatures at which the ac susceptibility exhibits peaks) are also shown in Fig. 3.3. In Fig. 3.3(b), for magnetic field applied along [110], the $M$-$H$ loop shows a coercivity which is smaller than the amplitude of the driving field (3.77 Oe)
used in the *ac* measurements. This means that the *ac* magnetic field applied along [110] is sufficient to switch the sign of the magnetization component along that direction, causing the total magnetization to “wobble” between two easy axes that lie very close, but no longer coincide, with the [1\(\overline{1}0\)] orientation because of the onset of biaxial symmetry [14].

To obtain a more detailed picture of the mechanism relevant to the *ac* susceptibility peaks, we carried out detailed measurements of *dc* hysteresis loops near \(T = 22\) K and \(T = 53\) K, i.e., where peaks are observed. The temperature mapping at the higher temperature (i.e., near the Curie point of the sample used in this study) is shown in Fig. 3.4. As can be seen, no hysteresis loops are observed when \(T = 57\) K, consistent with \(T_C\) of the samples being around 57 K. Upon lowering the temperature, the sample becomes ferromagnetic and is dominated by uniaxial anisotropy, with easy axis along [1\(\overline{1}0\)] and hard axis along [110]. Consistent with this anisotropy, a clear hysteresis is seen to emerge for the [1\(\overline{1}0\)] orientation (Fig. 3.4(b)), with Fig. 3.4(c) representing a projection of M on the [100] axis. (Note that the coercive field in Fig. 3.4(c) is larger by \(\sqrt{2}\) because the projection of the field on the [100] direction is smaller by that factor.)
Fig. 3.4: (a)–(c) Hysteresis loops at 49, 51, 53, 55, and 57 K, measured with the *dc* field applied along [110], [1T0], and [100] axes, respectively.

As the ferromagnetic domains begin to form below 57 K with their easy axes along [1T0], their coercive fields are sufficiently small to be “flipped” by the driving *ac* field, thus contributing to the resulting *ac* magnetization. However, as the temperature decreases, the coercivity increases, eventually exceeding the amplitude of the driving *ac*
field of 3.77 Oe. When this occurs, the spins can no longer be flipped by the ac field, and \( \chi_{ac} \) disappears (in our case near 49 K), thus explaining the peak in the susceptibility.

**Fig. 3.5:** Isothermal frequency-dependent ac magnetic susceptibility curves taken with the temperature steps of 0.5 K.

In Fig. 3.5, we show frequency scans for the ac magnetic susceptibility carried out at several temperatures to explore the thermal dependence of the magnetic relaxation time. The least-squares fitting [solid lines in Fig. 3.5 upper panel] of the real susceptibility data \( \chi' \) versus frequency according to the Debye model produces the characteristic relaxation time (\( \tau \)) at different temperatures [as shown in Fig. 3.6] [16]. Fitting the six temperature points to a Vogel–Fulcher law [17],

\[
\tau = \tau_0 \exp \left[ \frac{E_a}{k_B(T - T_{VF})} \right], \tag{3.5}
\]

58
where \( \tau_0 \) is the relaxation time constant, \( E_a \) is the anisotropy energy, \( k_B \) is the Boltzmann constant, and \( T_{VF} \) is the Vogel–Fulcher characteristic temperature, yields values of \( E_a/k_B = 79.9 \text{ K}, T_{VF} = 46.5 \text{ K}, \) and \( \tau_0 = 5.0 \times 10^{-7} \text{ s} \) (see Fig. 3.6). More significantly, when used in a Cole–Cole plot (Fig. 3.7), these results represent a phase transition between two dynamic modes of domain wall movement [18]: 1) a semicircle-like curve at higher temperatures (just below \( T_C \)) suggests a switching mode (complete polarization reversal of the domain during field cycling) and 2) an arc-like curve at lower temperatures (i.e. 52 K) indicates a slide mode (viscous wall motion in an \( ac \) field), as noted in Fig. 3.6. These results thus shed interesting light on the dynamics of domain movement around the critical temperature.

Fig. 3.6: Logarithmic plot of \( \tau \) versus \( T \), and a fit to the Vogel–Fulcher law (solid line). The red bar represents the width of losses at half-height.
Fig. 3.7: Cole-Cole plots of the \( ac \) magnetic susceptibilities for \( H_{ac} \) applied along [100] axes at various temperatures close to \( T_C \), in which the highest frequency is the first point on the left-hand side of each curve, while the lowest frequency is the last point on the right-hand side.

The mechanism behind the \( ac \) susceptibility peak near 22 K is different, and is associated with the emergence of a finite \( M_{[110]} \) that signals a transition from a purely uniaxial domain to biaxial domains. Just as this begins to occur (at about 27 K in Fig. 3.8), the coercivity for the [110] direction is sufficiently small for the magnetization to be driven back and forth by the \( ac \) magnetic field, thus contributing to the \( ac \) susceptibility for that direction. As in the case near \( T_C \), however, the [110] coercive field increases with decreasing temperature, eventually exceeding the \( ac \) driving field (in our case below about 17 K), thus resulting in the low temperature peak seen in Fig. 3.1. The presence of
the low temperature peak in the [100] panels in Fig. 1 arises of course simply from a
projection of $M_{[110]}$ on the [100] direction.

![Graphs showing hysteresis loops at different temperatures.](image)

**Fig. 3.8:** (a)–(c) Hysteresis loops at 17, 19, 22, 27, and 31 K, measured with the dc field along [110], [1\bar{1}0], and [100] axes, respectively.
In Fig. 3.9, detailed frequency-dependences of the $ac$ susceptibilities $\chi'$ and $\chi''$ are plotted as function of temperature ranging from 18 K to 28 K. We note that, unlike the case of the $ac$ susceptibility peak observed just below $T_c$, the peak around 22 K appears to be weakly sensitive to the frequency of the applied $ac$ field. In particular, both $\chi'$ and $\chi''$ monotonically decrease as the frequency increases for temperatures below 22 K, while $\chi'$ is not frequency-sensitive above 23 K. We speculate that such frequency dependence is related to the dynamics of biaxial domain wall movements, as discussed below.

![Fig. 3.9: Temperature dependence of $ac$ susceptibility at different frequencies at zero $dc$ field around 22 K.](image-url)
Physically we can visualize the emergence of a $M_{[110]}$ component as a tilt of the easy axes by an angle $\theta$ away from the [110] direction, so that the $ac$ susceptibility is a measure of a “wobbling” of the magnetization vector between two easy axes positioned symmetrically on either side of [110]. In order to obtain the easy axes, we differentiate Eq. (3.3) with respect to $\theta$. The obtained equation can then be solved for minimum energy conditions at zero applied field. When $K_u > K_c$, $\theta = 0$ is the minimum energy solution, representing biaxial symmetry. In the latter case, two-step hysteresis loops are observed when the field is applied along [100], arising from a linear combination of two independent hysteresis loops associated with [110] and [110] directions. At this condition at $H = 0$ the magnetization points at angles $\pm \theta$, obtained from

$$\theta = \tan^{-1} \frac{M_{[110]}}{M_{[1\overline{1}0]}}.$$  (3.6)

We extracted the values of $M_{[110]}$ and $M_{[1\overline{1}0]}$ at zero field from the $M-H$ loops shown in Figs. 3.8(a) and 3.8(b), and calculated $\theta$ for each temperature. The results are plotted in Fig. 3.10. Below $T \sim 27$ K, $\theta$ is monotonically dropping from 36° to 0° as the temperature increases, thus suggesting a biaxial domain structure shown by the inset in Fig. 3.10 (in the bottom left panel). On the other hand, when $T > 27$ K, the minimum energy point is at $\theta = 0^\circ$, indicating uniaxial domain structure. Thus $\theta$ undergoes a transition at about 27 K, i.e., when $K_u/K_c = 1$. In Fig. 3.10, the solid curve below 27 K was produced based on the Eq. (3.4). This feature was previously investigated in Ref. [14]
using planar Hall effect measurements. In addition, our result is also consistent with some several other works [19][21].

![Figure 3.10: Orientation of the easy axis of magnetization $\theta$ as a function of temperature. At 5 K, the easy-axis direction is at 34° (i.e., near the [100] direction). It is clear from the data that the easy-axis direction monotonically approaches $\theta = 0$ (i.e., the [1\bar{1}0] direction) as $T$ increases, reaching $\theta = 0$ at 27 K. Insets: schematics of magnetic energy density at zero external field. Red arrows: magnetic easy-axis direction.]

As stated above, a phase transition from biaxial to uniaxial domain structure occurs at a discontinuity in $\theta$ around a critical temperature $\sim 27$ K, where a drastic increase in domain nucleation events is observed [20][21]. In (Ga,Mn)As films, uniaxial Néel-type domain walls oriented along the easy axis $[1\bar{1}0]$ dominate in the temperature range between $T_C$ and 27 K, while at temperatures below 27 K the magnetic reversal
along the [110] direction is governed by a biaxial domain wall mechanism. Since the \( ac \) susceptibility peak just below \( T_C \) involves the dynamics of uniaxial domain walls, which may require relatively large response times, a frequency-sensitive behavior is expected, as is indeed observed in Fig. 3.6. On the other hand, the “wobbling” magnetization vector between two biaxial easy axes separated by \( 2\theta \) might require small response times, so that the \( ac \) responding peak shows considerable frequency dependence below 22 K in our frequency window.

Note, finally, that along the [110] direction a small \( ac \) susceptibility signal appears at \( T_C \) and gradually increases with decreasing temperature (seen in Fig. 3.1(a)). This “tail” can be well explained as a field-induced rotation of magnetization proposed in [10]. Indeed, as we apply the single domain model, the expected susceptibility is proportional to \( 1/|K_C - K_U| \), suggesting a singular point in the condition of \( K_C = K_U \) (i.e., \( T = 27 \) K). However, the dramatic peaking of \( \chi_{ac} \) observed for [110] at \( T = 22 \) K suggest an alternative mechanism, which we attribute to the onset of biaxial domain structure, as discussed above.

3.6 Conclusion

In summary, we carried out systematic \( ac \) and \( dc \) measurements on a (Ga,Mn)As epilayer. The \( ac \) magnetic susceptibility is observed in the form of two peaks, one occurring just below \( T_C \), and the other just below the temperature of the “kink” in the \( M \) versus \( T \) curves, where uniaxial domains make a transition to biaxial domains. We
associate the high-temperature peak with 180-degree reversal of the magnetization of domains that form and gradually grown below $T_C$, and we interpret the low temperature peak as arising from the “wobbling” of total magnetization between two easy axes oriented symmetrically around the $[\overline{1}10]$ direction due to the competition between cubic and uniaxial anisotropies. The two $ac$ susceptibility peaks show a very different dependence on the frequency of the $ac$ driving field, suggesting that different domain wall movements are involved in these two cases. Further study of their frequency dependences is expected to provide important information on spin dynamics in (Ga,Mn)As films.
3.7 References


CHAPTER 4:
TEMPERATURE-DEPENDENT SHAPE ANISOTROPY IN PATTERNED FERROMAGNETIC (Ga,Mn)As FILMS WITH LOW Mn CONCENTRATION

4.1 Synopsis

In this chapter we discuss magnetic properties of lithographically patterned nanoscale stripes of dilute ferromagnetic semiconductor (Ga,Mn)As aligned with [110] crystallographic direction, i.e., perpendicular to the easy axis of uniaxial magnetocrystalline anisotropy of this material. We find that at temperatures where uniaxial anisotropy becomes dominant, shape-induced effects strongly compete with intrinsic anisotropy of (Ga,Mn)As, tending to align the total magnetization along the stripe direction. The present study revealed, however, that low-temperature annealing of the stripes markedly reduces such shape-induced behavior. The effect of annealing is not presently understood, and will require further detailed study. In comparison, nanoscale stripes aligned with [1-10] direction did not demonstrate such effects.

4.2 Motivation

Manipulating magnetic anisotropy in GaMnAs has drawn intensive research interests for many years, and is still actively pursued for the sake of potential application in
nonvolatile memory devices. New discoveries by approaches such as illumination by light [1] and doping with lithium [2] were recently reported in this connection. Also, anisotropy could be engineered by different lithographically-patterned shapes, especially at low temperatures [3]. Since previous work was carried out in metallic-like systems (more than 5% Mn) [4] and no systematic study on temperature-dependent shape effects has been performed in specimens containing lower Mn concentrations, in this chapter we investigate low-Mn (Ga,Mn)As films patterned laterally at nanometer scale, with special attention to how their physical dimensions affect magnetic anisotropy and the temperature variation of magnetic properties. Additionally, since magnetic anisotropy could also be affected by thermal annealing in (Ga,Mn)As films with a low Mn concentration [5], the effect of annealing in nanostructures is worth further investigation.

4.3 Sample Fabrication and Structural Characterization

Films used in this study were grown by Riber 32 R&D molecular beam epitaxy (MBE) on GaAs (001) substrates to thicknesses of 50 nm, with Mn concentration of ~2%. By following the process presented in Fig. 4.1, the (Ga,Mn)As films were then patterned by electron-beam lithography into stripes of different widths, down to 200 nm. The brief procedure of lithography is as follows (step-by-step detailed standard protocol can be found in Appendix B):
First we spin coated a thin layer of Poly(methyl methacrylate), or PMMA, which is a common e-beam resist (ER), on the top surface of (Ga,Mn)As specimens after cleaning and baking. We then exposed the specimens covered by a pre-designed e-beam mask to the Vistec EBPG 5200 electron beam lithography system, whose dose was selected to be 680 \( \mu \text{C/cm}^2 \), at a frequency of 44.1 MHz. After exposure, the pattern on the mask was transferred onto the ER and the exposed parts were removed by the developer. In order to protect the patterned GaMnAs layer, we deposited a 25-nm-thick Cr capping layer on top using the Oerlikon Leybold 8-pocket electron-beam dual thermal
evaporation system, and then removed the remaining ER by acetone. Finally, we used Argon plasma in the Oxford PlasmaPro 100 ICP-RIE system to physically etch the specimens to a depth greater than 100 nm, to make the stripes as shown in the 3D sketch in Fig. 4.2.

![Fig. 4.2: Sketch of the nanostripes. Blue represents GaAs substrate, dark yellow represents (Ga,Mn)As layer and gold represents thin Cr capping layer.](image)

The orientation of the (Ga,Mn)As stripes chosen for this study was [110], which (as will be shown) allowed us to clearly observe the competition between intrinsic uniaxial magnetic anisotropy of (Ga,Mn)As and the effects induced by shape. For comparison, one specimen with patterned stripes along [1-10] axes was also fabricated. Figure 4.3 shows scanning electron micrographs (SEM) of films with 400-nm and 200-nm stripe arrays, the stripes separated by 400 nm. Note in Fig. 4.2 that the etching process penetrates the entire thickness of the (Ga,Mn)As layer, so that all the nanostripes are separated from each other, with no connecting (Ga,Mn)As material. Considering the relatively large separation between the stripes in our nanopattern design, along with the
small magnetization characteristic of GaMnAs (~26 emu/cc in our samples),
magnetostatic coupling between neighboring stripes can be ignored in this array based on
quantitative estimates for our pattern geometry. Since after fabrication the stripes emerge
covered by a thin layer of Cr, to allow comparison between properties associated with
stripe geometry and intrinsic film properties, we have also prepared a control sample by
exposing the (Ga,Mn)As film to all steps used in lithography of the stripes, but without
etching. Like the stripes, the resulting film is thus capped by a thin coating of Cr, a
feature that will become important for the study of annealing of patterned (Ga,Mn)As
specimens.
Fig. 4.3: SEM images of (a) 400-nm stripe arrays along [110] axis. (b) 400-nm stripe arrays along [1-10] axis. (c) 200-nm stripe arrays along [110] axis. (d) Zoomed in 200-nm stripe array along [110], viewed at a 45° tilt angle from horizontal plane. Note that the power setup of SEM was 10 kV and 13 pA for all samples. (a), (b), (c) were taken under 25,000 times magnification, and (d) was taken under 100,000 times. Detailed information can be found at the bottom of each image.
Results of high-resolution X-ray diffraction measurements (Fig. 4.4) show almost identical spectra for the three stripe samples and the control sample, in which the intensity reduction in film peaks reflects the effective surface area reduction due to patterning. Without a clear evidence of significant (Ga,Mn)As film peak shifting, we could conclude that lattice relaxation in the patterned film is negligible in the geometry studied in this chapter. This is consistent with earlier experiments carried out by some of us, where no lattice relaxation of (Ga,Mn)As was observed up to thicknesses of several micrometers even in films with significantly higher Mn concentrations. [6]
Fig. 4.4: High resolution X-ray diffraction spectra in the vicinity of GaAs (400) substrate peak for stripes with different widths and unpatterned control sample.

4.4 Magnetic Characterization by SQUID

Magnetic characterization of (Ga,Mn)As specimens investigated in this study was carried out using a Quantum Design SQUID magnetometer. We note that at low temperatures (Ga,Mn)As films are dominated by robust cubic anisotropy, with easy axes lying along in-plane <100> axes, and only a weak admixture of uniaxial anisotropy along the [1-10] direction [7, 8]. When applying a magnetic field $\mathbf{H}$ along [110] or [1-10] directions, we thus measure projections of the total magnetic moment onto these
directions. To allow comparison of magnetic properties between different samples, we normalize the measured magnetic moments by the total magnetization $M_{Total} = \sqrt{M_{[110]}^2 + M_{[1\bar{1}0]}^2}$ obtained by extrapolating the SQUID data to 0 K for each sample.
Fig. 4.5: Left panels: Normalized hysteresis loops measured at 5 K with magnetic field applied along [1-10] (black line) and [110] (red line) measured (a) on control sample; (b) on array of 400 nm nanostripes elongated along [110]; and (c) on 200 nm nanostripes elongated along [110]. Right panels: corresponding hysteresis loops measured at 22 K.
The hystereses measured at 5 K on the (Ga,Mn)As [110] stripes and on the control sample for $\mathbf{H}$ along [110] and [1-10] are shown on the left of Fig. 4.5. The magnetization at zero field and the coercivity are slightly smaller for the [110] field sweep than for [1-10] due to the small but finite intrinsic uniaxial anisotropy along [1-10], that exists even at low temperatures. It is interesting that this property is not affected by the width of the nanostripes, as nearly identical behavior is observed in the stripe samples and in the control at low temperatures.

When the temperature is raised to 22 K, however, magnetic properties change very significantly in samples with different stripe widths. We note that in the control sample (top right panel in Fig. 4.5), as the cubic anisotropy contribution decreases with temperature, uniaxial anisotropy now becomes clearly dominant, resulting in a square-like hysteresis loop for the [1-10] field sweep, with a very weak loop and small coercivity for sweeps along [110], indicative of a hard axis along that direction.

However, in the case of 400 nm stripes (middle right-hand panel of Fig. 4.5), applying the field along the [110], i.e., along the stripes, results in a significantly larger ferromagnetic signal than in the control film, even though this is the hard-axis of intrinsic uniaxial anisotropy. This indicates that the shape-induced anisotropy in the stripes (which tends to align the magnetization along the stripes) begins to compete with the intrinsic uniaxial anisotropy that tends to align $\mathbf{M}$ along [1-10]. This shape-induced effect
increases further as the stripes become narrower, as seen in Fig. 4.5(f), where it completely compensates the intrinsic uniaxial anisotropy seen in the control film at this temperature.

In the case of stripes we also see a progressive rounding of the hysteresis loops as the stripes become narrower, as compared to the data observed on the control film. We ascribe this to the presence of imperfections in the side walls introduced by Ar$^+$ ion milling during dry etching [9] seen in Fig. 4.3(d), which can pin magnetic domains in the stripes. Differences in such domains can lead to small differences in magnetic hardness of individual domains, and thus in a rounding of the overall hysteresis. This effect is expected to increase as the stripes become narrower, i.e., as the ratio of the side-wall area to stripe volume increases, as seen in Fig. 4.5(f).

Keeping the width of the stripes constant at 400 nm, we compare the magnetic properties affected by the orientation of nanostripes. Seen in left panels of Fig. 4.6, hysteresis observed in the stripe sample elongated along [1-10] (Fig. 4.6(b)) is still nearly identical to the behavior of the control sample at low temperature ~ 5 K. However, as the temperature increases to 22 K, magnetic properties of the [1-10] stripe sample become significantly different from the control sample and the [110] stripe sample. Unlike the shape-induced enhancement of ferromagnetic signal along the intrinsic uniaxial hard-axis observed in Fig. 4.6(f), intrinsic magnetic anisotropy still dominates in the [1-10] stripe sample, similar to the control sample. As seen in the stripes patterned along the uniaxial
intrinsic easy-axis [1-10], defects in the side walls can pin the magnetic domains individually and increase their magnetic hardness, resulting in a greater coercivity and a rounding of the hysteresis loop, seen in Fig. 4.6(e).
Fig. 4.6: Left panels: Normalized hysteresis loops measured at 5 K with magnetic field applied along [1-10] (black line) and [110] (red line) measured (a) on control sample; (b) on array of 400 nm nanostripes elongated along [1-10]; and (c) on 400 nm nanostripes elongated along [110]. Right panels: corresponding hysteresis loops measured at 22 K.
The evolving competition between intrinsic and shape effects is clearly illustrated by magnetization measured over the entire temperature range shown on the left of Fig. 4.7. While at low temperatures magnetization components projected on the [110] and [1-10] directions remain nearly unaffected by the stripe width, at higher temperatures (i.e., above ~15 K, up to the Curie temperature) the anisotropy induced by sample shape gradually overcomes the intrinsic uniaxial anisotropy. This is seen especially prominently in the case of 200 nm arrays, in which the hard and easy axes clearly interchange above ~24 K. Note that the crossover point of the magnetization curves in panel (c) is consistent with the hysteresis loops observed at 22 K in Fig. 4.5(f), where the two types of anisotropy were seen to closely compensate.

For completeness, temperature-dependent magnetization curves of the 400 nm nanostripes elongated along [1-10] are also presented in Fig. 4.8(b). As expected, no shape-induced anisotropy is observed in accordance with the results in Fig. 4.6. Apart from the general similarity compared to the \( M-T \) curves of the control sample in Fig. 4.8(a), note the earlier drop (i.e. decrease at lower temperature) of magnetization along the hard axis in the stripes, suggesting the intrinsic magnetic anisotropy has been strengthened by lithographic patterning elongated along the uniaxial easy axis.
Fig. 4.7: Left panels: normalized magnetization as a function of temperature measured in 3 Oe magnetic field applied along [1-10] (black line) and [110] (red line), for control sample (a), 400 nm nanostripes (b) and 200nm nanostripes (c) elongated in [110]. Right panels (d) (e) (f): temperature dependence of normalized magnetization measured under the same condition on annealed samples.
Fig. 4.8: Normalized magnetization as a function of temperature measured in 3 Oe magnetic field applied along [1-10] (black line) and [110] (red line), for control sample (a), and 400 nm nanostripes elongated along [1-10] (b).

4.5 Annealed Samples

In addition to experiments carried out on stripes fabricated from as-grown GaMnAs film described above, we carried out a study on the same samples after they were annealed at 260 °C for 30 minutes. Such annealing of GaMnAs is known to dramatically change the magnetic properties of this material [10]. Annealing thus provides the opportunity to observe how changes in magnetic properties affect the shape-induced effects studied in this paper. Additionally, we note here that in the case of
GaMnAs films the effects of annealing depend on whether the surface of the film is or is not capped [11]. Since the GaMnAs stripes emerge from lithographic processing with a Cr capping layer, we have, as noted earlier, subjected the control GaMnAs film to identical processing, so as to allow comparison with the capped stripes.

Temperature dependence of magnetization measured after annealing is shown on the right of Fig. 4.7. First, we note that the low-temperature magnetization (below ~15 K) and the Curie temperature have not noticeably changed in any of our samples after annealing. Since changes caused by annealing of GaMnAs are known to arise due to drifting of Mn interstitials to uncapped film surfaces [12], there may be two reasons why this has not occurred in our control sample. First, as noted above, the film is capped by a thin layer of Cr, which is expected to inhibit such interstitial drift. And second, at the low Mn concentration used in this study (~2%) one expects very few interstitials. Both these reasons can underlie the absence of any significant changes between panels 4.7(a) and 4.7(d). On the other hand, the stripes do have the side-wall part of their surface uncapped, which could allow interstitials to accumulate at the side walls, allowing the Curie temperature of the stripe interior to increase. We thus ascribe the absence of any noticeable change in the Curie temperature of the stripes primarily to the fact that the interstitial concentration in our material is very low.
Fig. 4.9: (a) Temperature dependence of orientation of total magnetization vector measured from the [1-10] direction. Black filled points are for control sample, red filled points for 400nm [110] nanostripe array, and blue filled points for 200nm [110] array. (b) Similar measurements on annealed samples, shown as empty open points of the same color as in (a).

Annealing has, however, led to significant changes in the behavior of magnetic anisotropy at temperatures above ~15 K, i.e., where uniaxial anisotropy becomes important, as seen in Figs. 4.7(e) and 4.7(f). To further illustrate the consequences of annealing in patterned samples, we will compare the angular orientation $\theta$ of the total magnetization vector $\mathbf{M}$ calculated using equation $\theta = \tan^{-1}(M_{[110]}/M_{[1\bar{1}0]})$ (where $\theta$ is measured from the [1-10] direction) for as-grown and annealed samples, plotted as a function of temperature in Fig. 4.9.
At low temperatures (below ~15 K) the orientation of magnetization is seen to converge at $\theta \approx 40^\circ$ for all samples, both as-grown and annealed, attesting to the robustness of the cubic component of magnetocrystalline anisotropy. As the temperature increases, uniaxial anisotropy gradually begins to dominate the behavior of the control film, with magnetization increasingly aligning along the uniaxial [1-10] easy axis, with $\theta$ clearly approaching 0. For the control film this behavior is unchanged by annealing, for reasons already mentioned.

The situation observed in the nanostripes is, however, very different (compare Figs. 4.9(a) and 4.9(b)), suggesting that there are annealing effects specific for the stripe geometry. We see in Fig. 4.9(a) that, as the temperature increases (and thus the cubic anisotropy weakens), shape-induced effects gradually become sufficient to overcome the intrinsic uniaxial anisotropy of the film, re-orienting $\mathbf{M}$ toward the stripe direction, seen especially prominently in the case of 200 nm stripes.

Quite surprisingly, after annealing the effects induced by shape are greatly reduced, as seen in the right panel of Fig. 4.9, with the magnetization now tending to align with the intrinsic uniaxial easy axis of the material. Whatever the physical causes of this unexpected effect, it clearly becomes stronger in narrower GaMnAs stripes, thus suggesting that surfaces of the side-walls may play a role in this behavior. Given the number of parameters which characterize the stripes (defects in the side-walls and their role in pinning domains, possible aggregation of Mn interstitials at the side-walls due to
out-diffusion during annealing, changes in hole distribution across the cross-section of the stripe and their effect on the magnetization profile, to name only a few), it is clear that more systematic measurements are needed before undertaking a meaningful attempt at understanding the effects of annealing, particularly at temperatures where uniaxial anisotropy is dominant.

4.6 Conclusion

In summary, we have observed strong shape-induced changes in magnetic properties of narrow GaMnAs stripes at temperatures where the uniaxial magnetocrystalline anisotropy becomes dominant in this material. Specifically, the sample shape tends to align the total magnetization along the stripe direction. This study revealed, however, several unexpected consequences of low-temperature annealing that are not presently understood, and will require further detailed study. Since the shape-induced effects described in this study occur precisely under conditions where the intrinsic uniaxial anisotropy of GaMnAs is dominant, the competition of these effects described above may provide a useful tool for experiments aimed at understanding the mechanisms which govern the uniaxial magnetocrystalline anisotropy in this material.
4.7 References


5.1 Synopsis

In this chapter, we have performed systematically structural, magnetic and electrical characterizations on a series of GaMnAsP thin films and a reference GaMnAs sample with constant 6% Mn and various P concentrations up to 30%. Tensile strain is introduced into the film and enhanced with the increasing phosphorus mole fraction, then changes the magnetic anisotropy from in-plane to out-of-plane. As the P content rising, $T_C$ drops linearly and the sheet resistivity grows steadily. Anomalous Hall effect (AHE) and anisotropic magnetoresistance (AMR) were observed and we concludes that the AHE should be attributed to the side-jump mechanism based on Arrot plots analysis.

5.2 Motivation

Reliable approaches for manipulating magnetic anisotropy in diluted magnetic semiconductors (DMSs), especially Ga$_{1-x}$Mn$_x$As, are desirable for device applications. One such promising approach is to alloy Ga$_{1-x}$Mn$_x$As with phosphorous to form the quaternary alloy Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$. GaMnAs film grown epitaxially on GaAs (001)
substrate is under compressive strain [1], while GaMnAsP film is under tensile strain. Magnetic easy axis tends to lie perpendicular to the film surface in GaMnAsP, due to the strain condition [2]. The magnetic anisotropy of the thin films can be visualized by calculating the magnetic free-energy as a function of the crystalline orientation and then plotting the surfaces in three-dimensional view as shown in Fig. 5.1. The plots clearly show that the energy minimum lies in the plane of sample surface for a GaMnAs thin film while it lies out of the plane for a GaMnAsP thin film, and the axes of magnetization have the preference to stay at the lowest energy. The shape of energy barriers for magnetization reorientation is tailored by the changing strain condition. Also the bandgap of GaMnAsP can be enlarged by increasing P concentration, and the impurity band level will be tuned, leading to a transition from metallic conduction to thermally activated impurity band conduction [6]. Though previous studies [2][5] were carried out with various phosphorus concentrations, GaMnAsP films with P mole fraction higher than 20% hasn’t been investigated. In order to systematically investigate the effect of phosphorous on structural and magnetic properties in this alloy, with a relative lower Mn concentration, we performed detailed studies on a series of MBE-grown Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ thin films with different phosphorus mole fractions y up to 30%. The mechanism of the changes in magnetic anisotropy and magnetotransport properties in GaMnAsP layers also demands special attention in research.
Fig. 5.1: Three-dimensional plot of magnetic free-energy without external magnetic field at temperature below $T_C$ of (a) GaMnAs thin film and (b) GaMnAsP thin film. The cross-sections at plane of $z=0$ are projected below the 3D plots.

5.3 Sample Growth and Structural Characterizations

A series of thin $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y$ films were grown on GaAs (001) substrates by the molecular beam epitaxy (MBE) technique. Based on the variation of the source flux and the record of growth time, the thicknesses of the films were estimated to range between 50 and 75 nm. During the growing procedure, the flux of Mn source was well controlled and the Mn contents were kept constant at $x = 0.06$. The opening sizes of the P source valve were tuned with a steady progress from 0.8% with a step of 0.4% up to 2.4%, aiming for different phosphorous mole fractions $y$ lying between 0.1 and 0.3. A reference GaMnAs sample with no phosphorus was also fabricated with about 6% percent Mn under the same growth condition.
Transmission Electron Microscopy (TEM) provides an insight into the crystalline quality of the quaternary film. In Fig. 5.2(a) we could see the sharp and straight interface between the GaMnAsP thin film and the GaAs buffer layer, and in the TEM image (b) under higher magnification we couldn’t observe any mismatch between the lattices across the interface or any other forms of obvious defects, which suggest that high quality GaMnAsP thin film had been successfully grown on the GaAs (001) substrate epitaxially. In such case, the lateral lattice constants of GaAs and GaMnAsP film are identical, therefore the thin film is under tensile strain due to its smaller relaxed lattice constants compared to GaAs’s.

Fig. 5.2: TEM pictures taken from the cross-section view of GaMnAsP thin film. (a) and (b) are under different scales of magnification as (b) is a zoomed-in detail at the interface. Yellow dashed line is a guide of eye parallel to the interface between GaAs buffer layer and GaMnAsP film.
The quality of sample growth can also be confirmed by the X-ray diffraction (XRD) measurements. $2\theta$-$\omega$ coupled scans along the c-axis of lattices were performed on each thin film using the Bruker D8 Discover high-resolution X-ray diffractometer and the spectra are shown in Fig. 5.3. The sharpest peaks located around 66.06° represent the (004) Bragg’s peak of GaAs substrate, while the peak position of each sample where the Bragg’s condition met is marked by a pink arrow. Intensive film peaks and clear corresponding Pendellösung fringes indicate the films were well epitaxially-grown and the expected crystal structure was achieved without other phases. A significant progression of the film peak can be observed along with the increasing P concentration, moving from a lower Bragg’s angle to a higher one, suggesting a reduction in the lattice constant of c-axis, in line with the rising tensile strain on GaMnAsP thin films.
Fig. 5.3: XRD spectra for the $2\theta$-$\omega$ coupled scans on the series of as-grown GaMnAsP epilayers grown on (001) GaAs substrate and a reference GaMnAs thin film. The concentration of P for each sample in the legend was calculated based on the spectra.

Moreover, the accurate mole fractions of Mn and P in the GaMnAsP thin films can be calculated based on the XRD analysis. Detailed procedure was introduced by Zhang et al., and the simplified steps are described as follows [6]. Taking the XRD spectrum of the reference GaMnAs sample (sample number: 160830A) at the bottom of Fig. 5.3 as the example. The highest point of the film peak to the left of the substrate peak locates at $2\theta=65.654^\circ$, then the vertical lattice constant $c$ is 5.68378 Å, calculated by the Bragg’s law equation. In order to determine the relaxed lattice constant $a_0$ for the heteroepitaxial layer, one may use
where \(a\) is the lateral lattice constant of the GaMnAs epilayer which is identical with the lateral lattice constant of (001) GaAs substrate assuming that GaMnAs is coherently strained by the GaAs buffer layer, taking the value of 5.65353 Å. And \(\nu\) is the Poisson ratio of the heteroepitaxial layer, defined as the negative of the ratio between the lateral and the longitudinal strains under uniaxial longitudinal stress. The parameter \(\nu\) is related to the elastic stiffness constants \(C_{11}\) and \(C_{12}\) as

\[
\nu[001] = \frac{C_{12}}{C_{11} + C_{12}},
\]

for the [001] orientation.

By making another assumption that the elastic constants of GaMnAs are equal to those of GaAs (i.e., \(C_{11} = 11.88, C_{12} = 5.32, \) and \(C_{44} = 5.94 \) in \(10^{11} \text{ dyn/cm}^2\) \([7]\), \(\nu[001]\) could be obtained and then the relaxed bulk lattice constant of GaMnAs film \(a_0\) was calculated to be 5.66942 Å by Eq. 5.1. One could continue to figure out the out-of-plane state of strain \(\epsilon_{zz}\) of the heteroepitaxial layer by

\[
\epsilon_{zz} = \frac{c - a_0}{a_0},
\]

and the result was 0.00143, where a positive value represents compressive strain.

The Mn mole fraction \(x\) could be determined from the relaxed lattice constants \(a_0\) by using the common Vegard’s law equation for GaMnAs provided by Sadowski et al. \([8]\),
\[ a_0(Ga_{1-x}Mn_xAs) = 5.65469 + 0.24661 \cdot x. \] \hspace{1cm} (5.4)

The value of \( x \) was yield to be 0.05971, in good agreement with the estimation from the growth condition.

The precise thickness of a uniform thin epilayer can be calculated from the fringe period \( \delta \theta_p \) of the Pendellösung oscillations [9] via:

\[ t = \frac{\lambda \sin \theta_B}{\delta \theta_p \sin 2\theta_B}, \] \hspace{1cm} (5.5)

where \( \theta_B \) is the Bragg angle and \( \lambda \) is the wavelength of the X-ray. For our sample, the thickness of the GaMnAs thin layer was determined to be 63.3 nm, which was in accordance with the approximate value 62 nm estimated from the growth rate and growth time.

The major structural parameters of the reference sample 160830A without any phosphorus are listed in Tab. 5.1, as well as those of other GaMnAsP samples’ in the same fashion. Since all the samples in this series have the same Mn mole fraction \( x=0.06 \), the relaxed lattice constant of \( Ga_{0.94}Mn_{0.06}As \) can be treated as the reference point in the Vegard’s law for \( Ga_{0.94}Mn_{0.06}As_{1-y}P_y \) quaternary alloy:

\[ a_0(Ga_{0.94}Mn_{0.06}As_{1-y}P_y) = 5.66942 - 0.2028 \cdot y. \] \hspace{1cm} (5.6)

Assuming the effects on the variation of lattice constant of the GaAs epitaxial layer by doping Mn and P are independent, one can use Eq. 5.6 to determine the concentration of P in the epilayer.
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Vertical Lattice Const.</th>
<th>Out-of-plane Strain</th>
<th>Concentration of P</th>
<th>Thickness of Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>160830A</td>
<td>5.67059 Å</td>
<td>0.00143</td>
<td>0%</td>
<td>63.3 nm</td>
</tr>
<tr>
<td>160822C</td>
<td>5.63221 Å</td>
<td>-0.00179</td>
<td>10.3%</td>
<td>48.3 nm</td>
</tr>
<tr>
<td>160819B</td>
<td>5.61783 Å</td>
<td>-0.00301</td>
<td>14.9%</td>
<td>74.3 nm</td>
</tr>
<tr>
<td>160812B</td>
<td>5.58753 Å</td>
<td>-0.00558</td>
<td>21.2%</td>
<td>47.2 nm</td>
</tr>
<tr>
<td>160812A</td>
<td>5.58429 Å</td>
<td>-0.00585</td>
<td>23.6%</td>
<td>66.9 nm</td>
</tr>
<tr>
<td>160811C</td>
<td>5.56141 Å</td>
<td>-0.0078</td>
<td>30.3%</td>
<td>63.8 nm</td>
</tr>
</tbody>
</table>

Note as shown in Tab. 5.1, along with the increasing P concentration, the vertical lattice constant $c$ is getting smaller and the out-of-plane tensile strain $\varepsilon_{zz}$ (negative sign) is growing larger, due to the reduced valence radii and bond length when replacing an arsenic atom with a phosphorus one.
Fig. 5.4: XRD spectra for the $2\theta$-$\omega$ coupled scans on the series of annealed GaMnAsP epilayers grown on (001) GaAs substrate and a reference GaMnAs thin film.

For the purpose of enhancing the ferromagnetism in GaMnAsP thin films, we annealed the as-grown pieces in a furnace tube with protective nitrogen atmosphere at about $270^\circ$C for 1 hour. The $2\theta$-$\omega$ coupled XRD scans were also carried out on every annealed sample and the spectra are displayed in Fig. 5.4. Without significant change to the intensity of peaks or the period of fringes, one must note that the diffraction spectra from the epilayers are entirely shifted to the right by about $0.2^\circ$, suggesting an elimination of interstitial Mn atoms via annealing process on GaMnAsP samples. Therefore, it is not appropriate to determine the element mole fractions by annealed samples, which should be figured out based on the XRD analysis on as-grown samples.
It is known that the lattice of GaMnAs epilayer under compressive strain won’t get relaxed even with thickness up to several micrometers [10], so it’s natural to wonder if the lattice can still be held in GaMnAsP thin films under tensile strain, especially in highly strained condition with large concentration of phosphorus. To answer this question, reciprocal space mapping (RSM) measurements were carried out by the Bruker D8 Discover HRXRD equipment on the annealed GaMnAsP and GaMnAs specimen.

![Fig. 5.5: Reciprocal space maps in the vicinity of the (224) Bragg reflection of (a) Ga$_{0.94}$Mn$_{0.06}$As thin film and (b) Ga$_{0.94}$Mn$_{0.06}$As$_{0.851}$P$_{0.149}$ thin film. Elongated red stripes passing through the substrate lattice points are the analyzer streaks, which are originated from the finite resolution of the detector. Color bar corresponds to the logarithm of diffraction intensity.](image)

Presented in Fig. 5.5, the RSMs of annealed GaMnAs reference sample and the GaMnAsP sample with about 15% P were measured in the vicinity of the asymmetric (224) Bragg peaks. Negative h and k indices suggest that the grazing incident setup was
selected which was more surface-sensitive. Two figures are displayed in the Q coordinates and share the same size in reciprocal space for comparison convenience. Since $Q_z$ represents the inversed vertical lattice constant and $Q_x$ represents the inversed lateral lattice constant (assuming the lattice is in-plane isotropic) of the crystal, Fig. 5.5(a) confirms that the GaMnAs film lattice is fully constrained by the GaAs substrate and buffer layer as the reciprocal lattice point of the film locates directly below the substrate’s that they have the same $Q_x$. Observable Pendellösung fringes are still signs of high crystalline quality in the heteroepitaxial layer. When incorporating 14.9% of phosphorus into the epilayer to make it quaternary, the lattice is still fully strained laterally as shown in Fig. 5.5(b). The vertical lattice constant of GaMnAsP is smaller than GaAs due to its larger $Q_z$, in accordance with the results we obtained from the $2\theta$-$\omega$ coupled scans.
Fig. 5.6: Reciprocal space maps in the vicinity of the \((\overline{224})\) Bragg reflection of (a) \(\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}_{0.85}\text{P}_{0.149}\) thin film and (b) \(\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}_{0.697}\text{P}_{0.303}\) thin film. Dashed black line indicates the line connecting reciprocal lattice point of the substrate and the origin of the \(Q\) coordinates. Cross-section data are extracted along the dot dashed blue line and plotted as black empty circles in (c). The red curve is the best fit to the measured data composing of two Lorentz peaks in blue.
When the P mole fraction in the GaMnAsP thin film has increased to 30.3%, the film is no longer fully pseudomorphically strained in the lateral plane. From the RSM taken around the \((\bar{2}\bar{2}4)\) lattice point of the heavily P doped sample shown in Fig. 5.6(b), we can find the 2D peak of the film is distant from the substrate in the \(Q_z\) direction as expected but is surprisingly skewed to the left, i.e. to the larger absolute value of \(Q_x\), deviated from the symmetric profile observed in the specimen with lower P concentration in Fig. 5.6(a). In order to better characterize the distorted film lattice point, the cross-section data points on the line \(Q_z = 45.199\) which passing through the peak maximum were extracted and plotted in the 1D figure in Fig. 5.6(c). The scattered experimental points were best fitted by two Lorentz peaks. The sharper one locates on the fully strained line that has the same \(Q_x = -31.439\) as the GaAs substrate lattice point, while the \(Q_x\) coordinate of the lower peak is -31.450 and the FWHM is four times wider than the other one. Recall that larger \(|Q_x|\) corresponds to smaller lateral lattice constant, which means that part of the epilayer lattices lost match with the substrate or buffer layer and starts to get relaxed. The portion of relaxed lattices can be estimated from the integrated area under each peak, which is approximately 70%. But the degree of relaxation is quite marginal. Compared to the fully relaxed line connecting the \((\bar{2}\bar{2}4)\) GaAs substrate lattice point and the origin of the Q coordinates, the deviation of the lower peak in the \(Q_x\) direction from the fully strained line accounts for only 2.2% of total deviation toward completely relaxed status. The wider spread of the lower peak also
suggests a larger dispersion in orientations of the lattices that may bring mosaicity to the crystal plane, as a slight tilt of main axis of the lattice ellipse toward $Q_z$ observed in Fig. 5.6(b) [10]. A possible scenario to explain the phenomenon is that the $\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}_{0.697}\text{P}_{0.303}$ lattices close to the interface with GaAs buffer layer are still 100% strained but the farther ones beyond the coherent length (about 20 nm in this sample) of the buffer layer become partially relaxed due to the large discrepancy between the intrinsic lattice constants of the two layers, similar to the observations in wurzite $\text{InGaN/GaN}$ layers [12].

Therefore, we have found that by incorporating over 10% phosphorus into $\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}$ heteroepitaxial layer on top of GaAs (001) substrate, the compressive strain can be converted to tensile strain in the film, and the film lattice is fully constrained by the GaAs lattice in lateral. However, if the P mole fraction is larger than 30%, then the coherent length of the buffer layer lattice would be reduced to a comparable length with the thickness of the epilayer, and part of the lattices would get relaxed but the degree of relaxation is far from 100%.

5.4 Magnetic Characterizations by SQUID

Both the as-grown and annealed GaMnAsP thin films series were measured by the Quantum Design MPMS XL SQUID magnetometer, as well as the reference GaMnAs samples. Temperature-dependent measurements were performed with a 3 Oe small magnetic field applied both perpendicular to the film plane, and parallel to the film plane.
along the [100] axis, which is the easy axis of intrinsic cubic magnetic anisotropy in GaMnAs thin films. Since there is a small zero-point shift in our SQUID, the magnetization was actually scanned under a zero field. Corresponding hysteresis loops were measured at T=5K both in plane and out of plane.
Fig. 5.7: Temperature-dependent magnetization curves measured with 3 Oe magnetic field applied along [100] crystal axis in plane (blue line) and out of plane (red line) for as-grown GaMnAs control sample (a) and as-grown GaMnAsP samples with various P concentrations (b-f).
Fig. 5.8: Hysteresis loops measured at 5K with magnetic field applied along [100] crystal axis in plane (blue line) and out of plane (red line) for as-grown GaMnAs control sample (a) and as-grown GaMnAsP samples with various P concentrations (b-f).
The magnetic moments in GaMnAs thin film prefer staying in plane to out of plane as the blue line is always above the red line below the Curie temperature at 77K in Fig. 5.7(a). The in-plane preference is also evident by the hysteresis loops in Fig. 5.8(a) that the loop measured along [100] direction parallel to sample surface has the normal rectangular shape, while almost no loop can be observed along the norm direction of the film plane which is a sign of magnetic hard axis. There are two major effects of the rising phosphorus mole fraction in GaMnAsP samples: First, the $T_C$ has dropped monotonically from 77K with no P to 30K with about 30% of P in the epilayer, approximately 1.6K decline per 1 percentage point increase of the phosphorus concentration; Second, the projection of the total magnetization on the vertical axis is generally increasing with the rising P mole fraction, which can be told from the elevating red line and the submerging blue line in Fig. 5.7 and the developing out-of-plane hysteresis loop from hard-axis-like flat loop to easy-axis-like rectangular shapes in Fig. 5.8. But due to the existence of interstitial Mn atoms in the GaMnAsP layer, some experimental magnetization data are not in consistence with other samples and the total trend, such as panel (e) in both Fig. 5.7 and Fig. 5.8 displaying the opposite results to expectations. In brief, the in plane antiferromagnetic (AFM) coupling between the magnetic moments of substitutional Mn and the moments of interstitial Mn has reduced the in-plane component of total magnetization [13], while the out of plane interaction is still unknown that the perpendicular component of total $M$ is undecided. The interstitial Mn can be out-diffused
toward the surface so the short-range AFM interaction between two types of Mn will be mostly eliminated [14]. To enhance the saturation magnetization and the Curie temperature [14] and to accurately characterize the magnetic anisotropy in the GaMnAsP thin films, annealing process had been carried out as introduced before.
Fig. 5.9: Temperature-dependent magnetization curves measured with 3 Oe magnetic field applied along [100] crystal axis in plane (blue line) and out of plane (red line) for annealed GaMnAs control sample (a) and annealed GaMnAsP samples with various P concentrations (b-f).
Fig. 5.10: Relationship between $T_C$ and P concentration in both as-grown (blue) and annealed (red) GaMnAsP specimen and GaMnAs control samples. Experimental data are represented by filled spheres and the linear trends are displayed in dashed line.

After annealing, the magnetic moments of substitutional Mn couple in the ferromagnetic (FM) manner that they all lie in parallel, so the total magnetization measured by SQUID can be almost treated as the summation of all the moments in the thin film. The total $M$ density is around 40 emu/cc at low temperature $T = 5K$ and doesn’t change with the variation of P mole fraction. The $T_C$ of each sample is enhanced by about 40 K after annealing and still follows the linear declining trend for as-grown samples in general as shown in Fig. 5.10. There is an exception that the $T_C$ of 21.2% P annealed sample grows higher than the $T_C$ of 14.9% P annealed sample, which is contrary to the
overall trend. This anomaly results from the different thicknesses of these two samples that the 21.2% P sample is only 47.2nm-thick while the 14.9% sample has the thickest 74.3nm epilayer. Diffusion process is more effective on a thinner layer and the deeper interstitial Mn atoms are harder to drift out due to the longer distance, so these two post-annealing Curie temperatures deviate from the trend line upward and downward respectively, as shown in Fig. 5.10.
Fig. 5.11: Hysteresis loops measured at 5K with magnetic field applied along [100] crystal axis in plane (blue line) and out of plane (red line) for annealed GaMnAs control sample (a) and annealed GaMnAsP samples with various P concentrations (b-f).
Another effect of annealing is to strengthen the magnetic anisotropy by getting rid of the disturbance from interstitial Mn. Clear out-of-plane preference of the magnetization can be observed in all annealed GaMnAsP samples with P mole fraction above 10%, and this preferential $M$ orientation holds for all temperatures up to $T_C$. When measured under nearly zero field, fractional $M$ was projected onto the in-plane $[100]$ axis while almost all moments aligned automatically along the perpendicular direction to the film plane. The minimum positions of magnetic free energy don’t locate within the sample plane (Fig. 5.1(b)) so no loop is observed in plane in Fig. 5.11(b-f). (Small opening comes from the projection from out-of-plane magnetization as the orientation of the specimen during measurements was not perfect.) Rectangular-like hysteresis loops were obtained along the out-of-plane easy axis, and the positive monotonic correlation between the coercivity and the P concentration (Fig. 5.12) may suggest that stronger magnetic anisotropy could be achieved by incorporating more phosphorus into GaMnAsP heteroepitaxial thin film, as the energy barrier for the switching process between the two vertical easy axes has a considerable in-plane component. It is notable that there is a dramatic increase in coercivity around 22.5% of phosphorus and above that the increase rate drops steeply when the coercive field tends to saturate. This phase-transition-like abrupt change possibly arises from the onsite of strain relaxation in high P samples.
Fig. 5.12: Relationship between coercivity and P concentration for annealed GaMnAsP specimen and GaMnAs control sample. Red filled spheres represent the experimental data and the blue line is the guide of eye to indicate the trend.

The degree of magnetic anisotropy can be characterized by the saturation magnetic field along the hard axis, i.e. in plane along [100] axis for GaMnAsP thin films. Since 1000 Oe external field is not enough to force all the magnetic moments to align along the hard axis seen in Fig. 5.11, we scanned the field from 1 Tesla to -1 Tesla and saturated all the specimen along [100] direction in plane. The normalized MH curves are shown in Fig. 5.13.
Fig. 5.13: $M-H$ curves measured with large field loop of annealed GaMnAsP sample series. The vertical axis is the magnetization density normalized by the corresponding saturation magnetization.
Fig. 5.14: Relationship between the anisotropic field (subtracted from the saturation field in Fig. 5.13) and the P concentration as well as the state of strain for annealed GaMnAsP specimen and GaMnAs control sample. Boxes with 10% error bars represent the experimental data and the red curve is the best fit to data.

As the saturation fields are ordered from 2000 Oe to 6500 Oe by the mole fraction of phosphorus, together with the -4000 Oe anisotropic field for GaMnAs control sample, we can conclude that the out-of-plane magnetic anisotropy in GaMnAsP epilayer is enhanced by the increasing P concentration, and the marginal effect is diminishing therefore $H_{an}$ tends to saturate at a higher concentration (Fig. 5.14).
Since the strength of tensile strain in the thin film is positively related to the P mole fraction, the magnetic anisotropy of GaMnAsP can also be described as a strain-dependent property. Larger tensile strain leads to lower $T_C$ and bigger $H_c$ as well.

5.5 Magnetotransport Measurements

To further investigate the magnetic and electrical properties of the series of GaMnAsP specimens, magnetotransport measurements were performed on the annealed samples. The specimen was cut into Hall bar and connected by the 4-probe method with 5 terminals as introduced in Chapter 2, by which the sheet voltage and the Hall voltage could be collected simultaneously. During the measurement, the specimen was loaded into the Janis closed-cycle helium flow cryostat and the magnetic field was applied normal to the sample surface.
Fig. 5.15: Temperature-dependent sheet resistivity $\rho_{xx}$ under zero magnetic field for annealed GaMnAsP samples with various P mole fractions and annealed GaMnAs control sample.

Temperature-dependent zero-field sheet resistivity $\rho_{xx}$ for GaMnAsP and GaMnAs samples are presented in Fig. 5.15. All of the samples show a clear resistivity maximum point $T_\rho$ which can be regarded as estimation to $T_C$ (usually slightly higher than $T_C$) [15]. The Curie temperatures obtained from the $\rho$-$T$ curves are in accordance with those measured by SQUID, especially for the anomaly that 15% P specimen has a higher $T_C$ than the 21% P specimen. In addition to the enhancement of $T_C$, larger concentration of phosphorus also leads to higher sheet resistivity, because more defects and larger tensile strain are introduced by increasing P dopants then the mean free path of
the carriers are shortened by scattering. Moreover, when the P mole fraction is above 10%, $\rho_{xx}$ at low temperature becomes bigger than $\rho_{xx}$ at room temperature that the material has undergone the transition from the metallic type to the semiconductor-like type.

The longitudinal sheet resistivity can also vary with the changing magnetic field. In ferromagnetic materials, the spin-orbit interaction between the local magnetic moments and the carriers causes the strong dependence of electrical resistivity on the angle between the direction of the electric current and the direction of the magnetization, which is known as anisotropic magnetoresistance (AMR) [16][17]. The electrical resistivity is maximized when $M$ is in parallel with the current direction. AMR measurements for typical GaMnAsP Hall bar samples are shown in Fig. 5.16 and Fig. 5.17.
Fig. 5.16: Field dependence of sheet resistivity $\rho_{xx}$ on perpendicular applied field under various temperatures for annealed GaMnAsP specimen with 10.3% P. $\rho_{xx}(0)$ under zero field at each temperature has been subtracted from the data.
Fig. 5.17: Field dependence of sheet resistivity $\rho_{xx}$ on perpendicular applied field under various temperatures for annealed GaMnAsP specimen with 14.9% P. $\rho_{xx}(0)$ under zero field at each temperature has been subtracted from the data.

Magnetic field was swept in a closed loop between 0.6 T and -0.6 T at selected temperatures from 20K to room temperature. As the field is always perpendicular to the current, zero field would result in the smallest angle between $M$ and electric current so that the largest $\rho_{xx}$ is always observed at 0 T for every temperature in Fig. 5.16 and 5.17. Field with greater magnitude can collect more loose spins in film and rotate them normal to the current, leading to a downward slope for sheet resistivity versus field strength. Since the loose spin moments could be activated by thermal energy, the largest AMR effect should appear at a temperature close to $T_C$, which is the highest temperature for the
ferromagnetic phase. It is confirmed by experiments on GaMnAsP, i.e. 90 K in Fig. 5.16 and 80 K in Fig. 5.17, which are in the vicinity of corresponding Curie temperatures.

With the same setup that the field threading through the Hall bar sample perpendicularly, we measured Hall voltage across the width of the specimen at the same time. In a ferromagnetic material such as GaMnAs or GaMnAsP, the Hall resistivity should be expressed as [18]

$$\rho_{Hall} = \rho_{OHE} + \rho_{AHE} = R_O B + 4\pi R_A M,$$

(5.7)

where the first term represents the ordinary Hall effect (OHE) associate with the Lorentz force proportional to the applied magnetic field $B$, while the second term is called the anomalous Hall effect (AHE) resistivity which is determined by the magnetization $M$ in the sample. Because of the large value of $R_A$ compared to $R_O$ (e.g. 250 times stronger in Fe$_{80}$B$_{20}$ [19]), the second AHE term usually dominates the Hall resistivity in FM materials, especially at fields well below the saturation field. It is convenient to use $\rho_{Hall}$ to represent the magnetization of a specimen below $T_C$. Above $T_C$ when the $M$ drops to zero, AHE term vanishes in Eq. 5.7 and the ordinary Hall coefficient could be calculated from $\rho_{Hall}$.

No hysteresis loop was observed in the GaMnAs reference sample as the magnetic field was applied along the hard axes so the vertical $M$ component was nearly zero, as shown in Fig. 5.18. When incorporating around 10% of phosphorus element (Fig. 5.19), the easy axes of the magnetic moments reorient from an in-plane direction to a
normal direction to sample plane, and rectangular-like AHE hysteresis loops show up to suggest single magnetic domain feature in the GaMnAsP epilayer, which is in accordance with the experimental results collected by SQUID. The slope of the field-dependent Hall resistivity curve above $T_C$ is equivalent to the ordinary Hall coefficient $R_O$. Further calculation can lead to the carrier density $p$ and the carrier mobility $\mu_H$ of the material based on Eq. 2.9 and Eq. 2.10. Most of the specimens have p type hole carriers and the carrier concentrations at room temperature range among $1\sim3\times10^{20}$ cm$^{-3}$, corresponding $\mu_H$ are $4\sim6$ cm$^2/(V\cdot s)$. Adding more P into the quaternary material (such as 14.9% P in Fig. 5.20) results in larger coercivity and lower $T_C$ as expected, but also an increase in saturation $\rho_{Hall}$, though total magnetization $M$ is unchanged with the increasing phosphorus mole fraction. Ignore the OHE component, one can find out $\rho_{Hall}$ is not only proportional to $M$ but also proportional to the anomalous Hall coefficient $R_A$, which can vary with the P content.
Fig. 5.18: Hall resistivity $\rho_{xy}$ as a function of magnetic field applied perpendicular to the film surface at various temperatures observed on annealed GaMnAs specimen with 6% Mn.
Fig. 5.19: Hall resistivity $\rho_{xy}$ as a function of magnetic field applied perpendicular to the film surface at various temperatures observed on annealed GaMnAsP specimen with 10.3% P.
Fig. 5.20: Hall resistivity $\rho_{xy}$ as a function of magnetic field applied perpendicular to the film surface at various temperatures observed on annealed GaMnAsP specimen with 14.9% P.

In general, $\rho_{AHE}$ is a function of the resistivity $\rho$ and can be expressed as [20]

$$\rho_{AHE} = a\rho + b\rho^2,$$

where $a$ and $b$ are coefficients independent of $\rho$. The first term is called the “skew scattering” term associated with the average deflection of the trajectory of a carrier scattered by a local spin, after which the new trajectory is no longer parallel with the old one. The second term originates from the “side jump” mechanism as the carrier undergoes a finite lateral displacement $\Delta y$ from the scattering center and the Hall angle in this mechanism is inversely proportional to the mean free path $\lambda$ [21].
To simplify the discussion, we assume $R_A \gg R_O$ in Eq. 5.7 which is a common condition in FM materials, and then the resistivity dependence of the Hall coefficient $R_A$ can be determined by checking the following expression

$$R_A \propto \rho^\alpha,$$

(5.9)

where $\alpha$ is an index representing different microscopic mechanisms. Specifically, $\alpha = 1$ indicates that “skew scattering” is responsible for the AHE, thus $M$ is proportional to $\rho_{Hall}/\rho$ in this case. While $\alpha = 2$ is a signature for the “side jump” mechanism, so the magnitude of magnetization $M$ is proportional to $\rho_{Hall}/\rho^2$, respectively. If both mechanisms are present, $\alpha$ will be an intermediate value between 1 and 2.
Fig. 5.21: Arrot plots of \( (\rho_{xy}/\rho_{xx})^2 \) vs. \( H/(\rho_{xy}/\rho_{xx})^2 \) at each temperature, for (a) \( \alpha = 2 \) (side jump) and (c) \( \alpha = 1 \) (skew scattering) in the annealed Ga\(_{0.94}\)Mn\(_{0.06}\)As\(_{0.897}\)P\(_{0.103}\) sample. Square roots of the intercepts from the Arrot plots extrapolated to zero field at each temperature are marked by red spheres, and the blue line represents the normalized temperature-dependent magnetization measured by SQUID, present in (b) and (d) respectively.
The method to determine the mechanism inducing the AHE phenomenon by Hall resistivity and sheet resistivity measured in the magnetotransport experiments was developed by Arrot [22]. By plotting the Arrot plot with \( y = (\rho_{xy}/\rho_{xx})^2 \sim M^2 \) and 
\[ x = H/(\rho_{xy}/\rho_{xx}) \sim H/M \] 
at each temperature, we can extrapolate the quasi-linear high field regime to zero field and get the intercept. According to the Ginzburg-Laudau mean field picture for magnetism, the magnetization \( M(H) \) above saturation field satisfies the following equation
\[
M(H)^2 = \frac{1}{4b M(H)} - \frac{a}{2b} \frac{T - T_C}{T_C},
\]
where \( a \) and \( b \) are material constants, and the zero-field spontaneous magnetization \( M(0) \sim (T - T_C)^\beta \). \( \beta \) is the critical exponent that varies with materials but it takes the value 1/2 in the mean-field model where \( T \ll T_C \). Therefore, the intercepts at each temperature from Arrot plots are proportional to the square of spontaneous magnetizations, if the selected mechanism to explain AHE is correct.

Both the skew-scattering model and the side-jump model were tested by making Arrot plots assuming \( \alpha = 1 \) and \( \alpha = 2 \) for the annealed GaMnAsP samples. The control GaMnAs specimen measured in this setup can’t be analyzed by Arrot plots as it would take a huge field (up to 40 T) to get saturated which is far beyond our capability. Arrot analysis for 10.3% P GaMnAsP sample is shown in Fig. 5.2. Neither model could be well fitted by the normalized temperature-dependent magnetization curve, so the AHE in
this sample can’t be explained by a single mechanism. The discrepancy may also arise from the disobedience to the mean field assumption that $\beta$ is not 1/2.

When incorporating more phosphorus into the alloy, e.g. 14.9% presented in Fig. 5.22, the AHE can be attributed mainly to the side-jump mechanism, as the spontaneous magnetizations extracted from Arrot plots for $\alpha = 2$ are better fitted by the SQUID data. Since intercept at the origin in Arrot plot represents zero $M$, $T_C$ measured by SQUID is found to coincide with the critical point of the T-dependent intercepts shown in Fig. 5.22(b). In this way, Curie temperature could be determined by the magnetotransport results alone. In the Ising model, the idealized relation $M(0) \sim (T - T_C)^{1/2}$ is well held at low $T \ll T_C$, therefore larger deviations between the red spheres and blue line are observed as $T$ is approaching $T_C$. 
Fig. 5.22: Arrot plots of $(\rho_{xy}/\rho_{xx})^2$ vs. $H/(\rho_{xy}/\rho_{xx})$ at each temperature, for (a) $\alpha = 2$ (side jump) and (c) $\alpha = 1$ (skew scattering) in the annealed Ga$_{0.94}$Mn$_{0.06}$As$_{0.85}$P$_{0.149}$ sample. Square roots of the intercepts from the Arrot plots extrapolated to zero field at each temperature are marked by red spheres, and the blue line represents the normalized temperature-dependent magnetization measured by SQUID, present in (b) and (d) respectively.
Fig. 5.23: Arrot plots of $(\rho_{xy}/\rho_{xx}^\alpha)^2$ vs. $H/(\rho_{xy}/\rho_{xx}^\alpha)$ at each temperature, for (a) $\alpha = 2$ (side jump) and (c) $\alpha = 1$ (skew scattering) in the annealed $\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}_{0.788}\text{P}_{0.212}$ sample. Square roots of the intercepts from the Arrot plots extrapolated to zero field at each temperature are marked by red spheres, and the blue line represents the normalized temperature-dependent magnetization measured by SQUID, present in (b) and (d) respectively.
If P mole fraction in the GaMnAsP epilayer is increased to 21.2%, then the side-jump mechanism will almost dominate the AHE, evident from the good agreement between the square roots of extrapolated intercepts from Arrot plots and the $M-T$ curve by SQUID displayed in Fig. 5.23(b). It is reasonable that the AHE in GaMnAsP can’t be primarily attributed to the skew scattering model (Fig. 5.21-23(d)), as this mechanism usually plays a key role in low resistivity materials (such as in metallic samples at low temperature). The side jump mechanism was found to be favored even in low Mn concentration GaMnAs samples [23], when the GaMnAs control sample shows the lowest sheet resistivity among all the samples in this series (Fig. 5.15). Higher doping content may introduce more disorders into the crystal lattice (e.g. mosaicity induced by strain in Fig. 5.6), then the impeded mean free path of carriers makes the side-jump mechanism dominant.

5.6 Conclusion

In summary, we have systematically investigated a series of MBE-grown GaMnAsP thin films with constant 6% Mn and various P concentrations ranging from 10% to 30%, and a reference GaMnAs sample with the same Mn content. Every sample was then post-annealed at about 270°C for 1 hour.

High crystal growth quality was confirmed by structural characterizations. XRD analysis determined the accurate mole fractions of Mn and P in GaMnAsP as-grown samples, as well as the epilayer thickness and the strain status in each specimen: larger
tensile strain in the film is induced by higher P concentration. The strain can be partially relaxed when the P content has reached 30%, which was proved by the RSM measurements.

Annealing process could enhance $T_C$ in each specimen by 40°C, and the $T_C$ linearly decreases with the increasing P concentration, but the total $M$ doesn’t vary. Magnetic anisotropy is modified by incorporating phosphorus as the magnetic easy axes reorientate from the direction lying within the sample plane to the direction perpendicular to sample surface under tensile strain, observed in both $M$-$T$ curves and $M$-$H$ loops by SQUID. The degree of anisotropy is generally strengthened with rising tensile strain, but tends to saturate at high P fraction, seen from the out-of-plane coercivities and the in-plane saturation fields.

Magnetic properties above were reconfirmed by the magnetotransport experiments. In addition, we found the sheet resistivity of GaMnAsP and GaMnAs Hall bars grew with the rising tensile strain, and the specimen transited from metallic to semiconductor-like when the P concentration is above 10%, while the hole densities in GaMnAsP specimens are in the regular range. In order to explain the mechanism responsible for the anomalous Hall effect, Arrot plots were made from the sheet resistivity together with the Hall resistivity at each temperature, then the square roots of extrapolated intercepts were compared with the temperature-dependent magnetization curves measured by SQUID. It is evident that the AHE in high P GaMnAsP epilayers
should be primarily attributed to the side-jump mechanism but the skew-scattering doesn’t play an important role.

This study has filled the blank for the characterizations on GaMnAsP with P content higher than 20% and has laid a solid foundation for further investigations on structures associated with high P GaMnAsP material. The strain-induced out-of-plane magnetic anisotropy and its resulting magnetic and electrical properties may also provide application potentials in information storage devices.
5.7 References


CHAPTER 6:

PERPENDICULAR INTERFACIAL EXCHANGE COUPLING IN GaMnAsP/GaMnAs BILAYERS

6.1 Synopsis

In this chapter, we carried out a systematic study of magnetic order and magnetic interlayer coupling in (Ga,Mn)(As,P)/(Ga,Mn)As bilayers using superconducting quantum interference device (SQUID) magnetometry and ferromagnetic resonance (FMR). Our results show that the (Ga,Mn)(As,P)/(Ga,Mn)As bilayers are strongly exchange-coupled at the interface. In particular, we observe an abnormal interfacial exchange coupling between magnetic moments of (Ga,Mn)(As,P) and (Ga,Mn)As layers, that results in a horizontal shift of the hysteresis loops of the (Ga,Mn)As layer in nero-zero field-cooled condition.

6.2 Introduction

Ferromagnetic thin films with perpendicular magnetic anisotropy have been widely studied for perpendicular magnetic recording media applications [48][49]. In order to design a better perpendicular magnetic application with both high thermal stability [50] and good writeability [48], considerable research has been done on
multilayer magnetic films where exchange coupling between dissimilar layers can be used to tailor the magnetic response [51][52]. Ferromagnetic semiconductor (Ga,Mn)As have been widely used for research for spintronic application [53]. (Ga,Mn)As film grown on GaAs substrate by molecular beam epitaxy (MBE) exhibits the in-plane anisotropy due to the built-in compressive strain [54]. In addition, it is now well established that magnetic anisotropy in (Ga,Mn)As can be manipulated by alloying (Ga,Mn)As with phosphorous, which modifies strain conditions in epitaxially grown layer systems [55][56]. Interestingly, both MBE-grown (Ga,Mn)As and (Ga,Mn)(As,P) are totally strained by the GaAs lattice beneath without relaxation due to low-temperature non-equilibrium growth as discussed in Chapter 5. Therefore, by fabricating (Ga,Mn)(As,P)/(Ga,Mn)As bilayers on GaAs (100) substrates, we can thus obtain a ferromagnetic system consisting of two dissimilar magnetic domains with magnetizations at right angle to one another. This then provides a model system for investigating the behavior of perpendicular interfacial exchange coupling [49][57].

In this work, we grew Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$/Ga$_{1-x}$Mn$_x$As films on GaAs (100) substrates by low-temperature MBE technique. The structure of the samples was then studied by X-ray diffraction (XRD) and cross-sectional transmission electron microscopy (TEM). We carried out a systematic study of magnetic order and magnetic interlayer coupling in Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$/Ga$_{1-x}$Mn$_x$As bilayers using superconducting quantum interference device (SQUID) magnetometry. Our results show that the bilayers are
strongly exchange-coupled at the interface. In particular, we observe an unusual interfacial exchange coupling between magnetic moments of (Ga,Mn)(As,P) and (Ga,Mn)As layers, that results in horizontal shifts of the hysteresis loops of the (Ga,Mn)As layer in near-zero field-cooled condition. The anisotropy of the bilayers was also systematically studied by ferromagnetic resonance (FMR) at 9.48 GHz (X-band). The angular dependence of FMR allowed us to determine magnetic anisotropy parameters of the layers and the exchange coupling at interface.

6.3 Sample Preparation and Structural Characterizations

Three $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y/\text{Ga}_{1-x}\text{Mn}_x\text{As}$ bilayers on GaAs (100) substrates were grown with Mn content $x \approx 0.06$ and with P content $y \approx 0.20$. After the growth of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ films with thicknesses ranged from 10 nm to 18 nm, the valve of P cracker is open and then a ~20 nm thick $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y$ layer were deposited. We have selected the concentration of P so that the $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y$ and $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ layers present strong uniaxial magneto-crystalline anisotropies with orthogonal directions, out-of-plane in the case of $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y$ and in-plane for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, according to results in Chapter 5. Note that, due to the low magnetization, magneto-crystalline anisotropy controls the magnetic properties in both layers [54]. The growth is monitored by reflection high energy electron diffraction (RHEED), which shows streaky RHEED pattern (1×2) through both layers, suggesting that a high crystal quality sample is obtained. After growth all films were annealed at 270°C for 1 hour to optimize the magnetic properties.
Magnetization measurements on the annealed Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ quaternary films were carried out as a function of magnetic field and temperature using a Quantum Design SQUID magnetometer. X-ray diffraction measurements ($\omega$-2$\theta$) were taken using a Bruker Discover D8 diffractometer to calculate the corresponding c-axis lattice constants, and then determine the Mn and P concentrations for both layers respectively. The anisotropy of annealed (Ga,Mn)(As,P) films was then systematically studied by ferromagnetic resonance (FMR) at 9.48 GHz (X-band) using a Bruker electron paramagnetic resonance (EPR) spectrometer [58]. In FMR experiments the applied magnetic field $H$ was in the horizontal plane and the microwave magnetic field was vertical. The sample was placed in a suprasil tube inserted in a liquid helium continuous flow cryostat, which could achieve temperatures down to 4.0K. A detailed description of the apparatus, along with the coordinate system used in discussing our results, can be found in Ref. [58].
Figure 6.1 shows XRD data from a Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$(21nm)/Ga$_{1-x}$Mn$_x$As(12.5nm) bilayer sample on GaAs (100) substrates for the (004) reflection. As shown in figure, the lattice constant of Ga$_{1-x}$Mn$_x$As (Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$) is larger (smaller) than that of GaAs, respectively, revealing that LT-MBE-grown Ga$_{1-x}$Mn$_x$As film is under a compressive strain, while Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ film is under a tensile strain by the underlying buffer or substrate (GaAs in this case). The Mn and P concentrations can then be determined by calculated c-axis lattice constants by assuming that (Ga,Mn)(As,P) and (Ga,Mn)As films are totally strained throughout the thickness without relaxation. Cross-sectional TEM
were taken for same samples, which reveal the thicknesses of (Ga,Mn)As and (Ga,Mn)(As,P) layers, consist with the nominal thickness based on the growth rate and the growth time. From the TEM image, it is clear that the surface and interface of both magnetic layers are very abrupt apart from the existence of stacking faults along \{111\} planes in (Ga,Mn)(As,P) layer. Investigation in Chapter 5 suggests that such stacking faults do not make the (Ga,Mn)(As,P) film relax and it may be created by the nucleation of P adatoms on a As terminated surface.

6.4 Exchange Bias Effect Observed by SQUID

We begin to discuss the exchange bias effect, which usually results from the interfacial exchange interaction between a ferromagnetic and an antiferromagnetic material, manifested by a shift $H_{\text{EB}}$ of the ferromagnetic hysteresis loop along the magnetic field axis after field cooling through the Néel temperature of the antiferromagnet [59]. In our $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y/\text{Ga}_{1-x}\text{Mn}_x\text{As}$ bilayer system, two coupled ferromagnetic layers with orthogonal anisotropies, we have observed the similar effect with near-zero cooling field. All bilayer samples studied in this work shows exchange bias effect. Here, we use the data measured in $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y(21\text{nm})/\text{Ga}_{1-x}\text{Mn}_x\text{As}(12.5\text{nm})$ bilayer to illustrate the phenomena of interest in these coupled ferromagnetic layer systems with orthogonal perpendicular anisotropies.
Fig. 6.2: (a) Hysteresis loop at 5 K measured with the dc field along [001] axis for Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$(21nm)/Ga$_{1-x}$Mn$_x$As(12.5nm) bilayer sample. (b) Temperature dependence of remanent magnetization measured along [001] axis after a dc field of 1000 Oe is applied, the measurement starts at the point plotted in (a). (c) Hysteresis loops at 5 K measured with the dc field along [100] axis, observed after field cooling in +13 Oe (blue curve) and -12 Oe (green curve). Red curve presents a measurement after a dc field of 5000 Oe is applied to saturate the magnetization. (d) The temperature dependences of remanent magnetization at zero dc field, the measurements start at the colored points in (c).

Figure 6.2 shows hysteresis loops and temperature dependences of remanent magnetization measured at various conditions for Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$(21nm)/Ga$_{1-x}$Mn$_x$As(12.5nm) bilayer sample. As shown in Fig. 6.2(a), along the out-of-plane direction (i.e., [001] axis), as field sweeps down from 1000 Oe,
magnetization gradually decreases because the magnetization of (Ga,Mn)As starts to rotate from out-of-plane to in-plane in a reversible way until the external magnetic field reaches the “depinning field” (~390 Oe). Then, a sharp magnetization drop occurs which is associated with an avalanche-like growth of reverse domains in the film of (Ga,Mn)(As,P). Note that, the hysteresis loop of a single 21 nm Ga\textsubscript{1-x}Mn\textsubscript{x}As\textsubscript{1-y}P\textsubscript{y} is nearly-square and narrow (with coercive field ~100 Oe) seen in Chapter 5. The data showed in Fig. 6.2(a) demonstrate that the easy axes of two coupled ferromagnetic layers indeed are orthogonal, out-of-plane in the case of Ga\textsubscript{1-x}Mn\textsubscript{x}As\textsubscript{1-y}P\textsubscript{y} and in-plane for Ga\textsubscript{1-x}Mn\textsubscript{x}As. Temperature dependence of out-of-plane remanent magnetization shown in Fig. 6.2(b) indicates the Curie temperature of top (Ga,Mn)(As,P) is just above 80 K.

Figure 6.2(c) shows hysteresis loops at 5 K under various conditions along the in-plane direction. The sample was field cooled (FC) to 5 K with field of +13 Oe (-12 Oe), and hysteresis loops were measured with the magnetic field applied along the [100] direction of film. The in-plane hystereses observed at 5 K clearly show that the center of the hysteresis loop is shifted to the right (left) of the zero-field axis, indicating the presence of exchange bias. The position of the center of the loop gives an exchange bias field of about $H_{EB} = -52$ Oe (33 Oe) at 5 K. It is interesting that the shape of the hysteresis is slightly asymmetric at temperatures when exchange bias is observed. Note that, if we applied 5000 Oe to saturate magnetizations of both magnetic layers, the hysteresis loop becomes narrow and symmetric, without exchange bias. Accordingly,
temperature dependences of \textit{remanent magnetization} under these three conditions are plotted in Fig. 6.2(d). The abnormal deduction of magnetization below 85 K observed under FC -12 Oe is associated to the right shift of loop, indicating that the observed exchange bias survives up to the Curie temperature of top (Ga,Mn)(As,P) layer.

The observed exchange bias effect can be explained by the formation of a multidomain structure in thin (Ga,Mn)(As,P) films [51]. Due to out-of-plane anisotropy, under near-zero field cooling condition, domain structure in (Ga,Mn)(As,P) thin layers includes triangular domains with out-of-plane magnetization and trapezoidal domains with in-plane magnetization coupled to the (Ga,Mn)As layer, separated by 90° walls. Adjacent out-of-plane domains are separated by 180° walls. These arrangements provide partial flux closure while maintaining exchange coupling with the (Ga,Mn)As. Such model qualitatively explains the basic mechanism of the exchange bias effects experimentally observed for this bilayer system [60]. In specific, the unidirectional orientation of the in-plane (Ga,Mn)(As,P) domains thus produce the shift in the in-plane loops of the (Ga,Mn)As. The interfacial exchange coupling, which is proportional to the interface area, can be significant even at remanence state. As a 5000 Oe field is applied, top (Ga,Mn)(As,P) evolves into a single domain state, and the exchange bias effect thus disappears since two magnetizations are now orthogonal to each other at lower magnetic field.
6.5 Magnetic Anisotropy Observed by Angular-dependent FMR

To further investigate interface exchange coupling in the Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$/Ga$_{1-x}$Mn$_x$As bilayer system, we carried out angular FMR measurements in three geometries [58]. Specifically, mounting the specimen with the [-110] (or [110], [010]) axis vertical enables measurements with the dc field $H$ in any intermediate orientation between the normal to the layer plane, $H||[001]$, and the in-plane orientation, $H||[110]$ (or $H||[-110]$, $H||[100]$). Figure 6.3 shows FMR spectra at 4.0 K in four basic configurations: $H||[001]$, $H||[110]$, $H||[1-10]$, and $H||[100]$. Note that, two-peak FMR
spectra observed in the three in-plane geometries are conspicuous in the figure. By their strong dependence on crystal geometry, we have assigned the resonance positions in the FMR spectra to two magnetic layers respectively, as shown in Fig. 6.3.

To determine magnetic anisotropy parameters from the FMR data, we employ the Stoner-Wohlfarth model, where the ferromagnetic film is assumed to consist of a single homogeneous magnetic domain with four magnetic anisotropy fields: $H_{2\perp}$ and $H_{4\perp}$, representing the perpendicular uniaxial and perpendicular cubic anisotropy; and $H_{2\parallel}$ and $H_{4\parallel}$, representing in-plane uniaxial and in-plane cubic fields, respectively [61]. We analyze the FMR results in Fig. 6.4 using the formalism described in Ref. [58]. Specifically, the analysis yields five parameters: $H_{4\parallel}$, $H_{2\parallel}$, $4\pi M - H_{2\perp}$, $H_{4\perp}$, and the
$g$-factor. One can see the calculated results based on the FMR positions observed in three geometries at $\theta = 90^\circ$, as shown by the solid curves in Fig. 6.4, deviates from the experimental data at $\theta = 0^\circ$ ($\mathbf{H}||[001]$) for (Ga,Mn)As layer in an order of 1000 Oe. We attribute such deviation to the interface exchange coupling between two magnetic layers when they are parallel to each other as a resonance field is applied along [001] direction with magnitude over 4000 Oe field.

### 6.6 Conclusion

In summary, we have carried out a systematic study of magnetic order and magnetic interlayer coupling in (Ga,Mn)(As,P)/(Ga,Mn)As bilayers using SQUID magnetometry and FMR. The Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ and Ga$_{1-x}$Mn$_x$As layers show strong uniaxial magneto-crystalline anisotropies with orthogonal directions, out-of-plane in the case of Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ and in-plane for Ga$_{1-x}$Mn$_x$As. Our results also show that the (Ga,Mn)(As,P) and (Ga,Mn)As layers are strongly exchange-coupled at the interface. In particular, we observe an abnormal interfacial exchange coupling between magnetic moments of (Ga,Mn)(As,P) and (Ga,Mn)As layers, that results in a horizontal shift of the hysteresis loops of the (Ga,Mn)As layer in nero-zero field-cooled condition. Such shift can be explained by the specific multidomain structure in (Ga,Mn)(As,P) layer due to out-of-plane anisotropy. In addition, the analysis of angular FMR position suggests such interface coupling is in an order of 1000 Oe when both layer are parallel to each other.
6.7 References


CHAPTER 7: SHAPE ANISOTROPY IN PATTERNED FERROMAGNETIC GaMnAsP FILMS WITH PERPENDICULAR ANISOTROPY

7.1 Synopsis

In this chapter, we investigate the effects of physical dimensions on the behavior of magnetic anisotropy in lithographically-fabricated nanoscale squares of the ferromagnetic semiconductor GaMnAsP using SQUID magnetometry and ferromagnetic resonance (FMR). Both measurements show that perpendicular magnetic anisotropy is strongly affected by the size of the ferromagnetic nano-scale elements, while their Curie temperature and their in-plane anisotropy remain unchanged in the range studied. In addition to uniform-mode FMR, we observe a series of spin-wave resonances, whose analysis suggests that surface anisotropy plays an important role in determining the properties of nanoscale magnets.

7.2 Introduction

It is well established that thin films of ferromagnetic semiconductor Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ grown epitaxially on GaAs (001) substrates are subject to tensile strain in the film plane, which causes the easy axis of magnetization to lie along the growth
direction due to strain-induced perpendicular anisotropy [1]. In the following text I will present a study of the effects of dimensions on magnetic properties of this quaternary alloy when it is reduced to nanometer scale [2][4], with special attention on the behavior of magnetic anisotropy as determined by SQUID magnetometer and ferromagnetic resonance.

7.3 Sample Fabrication and Structural Characterizations

Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ films used in this study were grown by molecular beam epitaxy (MBE) to a nominal thickness of 25 nm, with Mn concentration of $x \sim 6\%$ and P concentration of $y \sim 9\%$, as determined by lattice constant obtained by X-ray diffraction (XRD) measurements. As expected, the XRD results also show that the films are under tensile strain, with no noticeable relaxation. After growth, the GaMnAsP film was then annealed at 260°C in N$_2$ flux, and patterned by electron-beam lithography into arrays of nanoscale squares with different dimensions: 1000nm, 700nm, 400nm and 200 nm, with square sides oriented along the $<110>$ directions. The total size of each nanofabricated array was 3mmx3mm, which was sufficiently large for magnetization and ferromagnetic resonance measurements. Additionally, a piece of the film without nanofabrication was used as a control sample. Figure 7.1 shows scanning electron micrographs (SEM) of the fabricated arrays. Note that the etching process has penetrated the entire thickness of the GaMnAsP layer, so that all the nano-squares are separated from each other, with no connecting GaMnAsP material.
7.4 Dependence of Magnetic Anisotropy on Nano-square Size

Ferromagnetic resonance (FMR) measurements were carried out at 9.48 GHz using a Bruker electron paramagnetic resonance spectrometer [5]. In FMR experiments the applied magnetic field $H$ was in the horizontal plane, and the microwave magnetic field was vertical. The sample was placed in a suprasil tube inserted in a liquid helium continuous flow cryostat, which could achieve temperatures down to 4.0 K. A detailed
description of the apparatus, along with the coordinate system used in discussing our results, can be found in Ref. [5]. Magnetization measurements on the GaMnAsP nano square arrays were carried out as a function of magnetic field and temperature using a Quantum Design SQUID magnetometer.

Fig. 7.2: Hysteresis loops measured at 5 K with magnetic field applied along the [001] direction. Black: control sample; red: 700nm squares; blue: 200nm squares. Inset: corresponding magnetization as a function of temperature measured in 8 Oe magnetic field applied along [001] for all samples. $M(H)$ and $M(T)$ measured on 1000nm and 400nm squares are similar to those obtained on 700nm squares.

Hysteresis loops at $T = 5$ K for the control sample and 700nm and 200 nm nano-square arrays measured with the magnetic field applied normal to the sample plane (i.e., along the [001] crystallographic direction) are shown in the Fig. 7.2. The hysteresis
loops for the 1000nm and 400nm nano-square arrays (not shown) are similar to that for the 700nm sample. The nearly square loop observed on the control sample indicates that the magnetic easy axis is oriented along the [001] direction, as expected for the built-in tensile strain in the GaMnAsP film. However, as the size of the nano-squares decreases, the hysteresis loop evolves into an elongated shape, suggesting that the easy axis direction is modified by the effects of reduced dimension. The temperature dependence of magnetization measured in an 8 Oe field applied along the [001] direction is shown in the inset in Fig. 7.2. Note that all specimens have the same Curie temperature of ~ 110 K, indicating that the overall quality of ferromagnetic order is not affected by the nanofabrication. However, the remnant magnetization seen in Fig. 7.2 is clearly reduced as the size of nano-square decreases, indicating that the size-induced anisotropy plays an important role in determining magnetic properties of the nano-sized squares.

In order to investigate anisotropy changes as a function of nano-square size, FMR measurements were carried out using two setups, which we will refer to as “vertical” and “horizontal” [5]. In the “vertical” setup, the [110] edge of the specimen was oriented vertically. This configuration allows measurements with the dc field in any arbitrary direction in the (1-10), from the [1-10] direction to [001]. In the “horizontal” setup, the sample was mounted with the layer plane horizontal (i.e., the [001] direction pointing up). In this configuration we could measure the angular dependence of FMR when the field
was confined to the layer plane, including the high-symmetry orientations $H \parallel [110]$, $H \parallel [1-10]$, and $H \parallel [100]$, as well as intermediate in-plane orientations.

![FMR spectra](image)

**Fig. 7.3:** FMR spectra observed at $T = 4$ K for control and all four nano-square arrays in high symmetry configurations of $H \parallel [001]$ and $H \parallel [100]$.

In Fig. 7.3 we show FMR spectra at 4.0 K for the control sample and all four nano-sized square arrays in two basic configurations: $H \parallel [001]$ and $H \parallel [100]$. Clear Lorentzian-shape FMR lines are observed for all samples (and persist up to the Curie
temperature $T_C$), indicating homogeneous strong long-range ferromagnetic order of Mn$^{2+}$ spins in these nanoscale squares. We find this to be remarkable, since each of 3mmx3mm GaMnAsP nano-square arrays contains between 25 and 625 million nanosquares. Observation of sharp and uniform FMR spectra in such arrays also suggests that the magnetization is nearly homogenous throughout the nano-square, and can thus be treated as a single magnetic moment precessing coherently around the dc magnetic field.

Through their dependence on the field orientation relative to the crystal lattice, the FMR spectra in Fig. 7.3 establish that magnetic anisotropy plays a major role in determining the field at which FMR occurs. Interestingly, the FMR positions at $H_{\parallel}[001]$ and $H_{\parallel}[100]$ cross as the nano-square size decreases. To determine magnetic anisotropy parameters of the nano-squares from the FMR data, we employ the Stoner-Wohlfarth model, where the ferromagnetic nano-square is assumed to consist of a single homogeneous magnetic domain with four magnetic anisotropy fields: $H_{2\perp}$ and $H_{4\perp}$, representing the perpendicular uniaxial and perpendicular cubic anisotropy; and $H_{2\parallel}$ and $H_{4\parallel}$, representing in-plane uniaxial and in-plane cubic fields, respectively. Note than the sign of $H_{2\perp}$ will be different for compressive and for tensile strains [6].
Fig. 7.4: Angular dependence of FMR fields for control and all four nano-sized square arrays at $T = 4K$. Top panels correspond to the $dc$ magnetic field $H$ and magnetization $M$ in the [110] plane; bottom panels correspond to the $dc$ magnetic field $H$ and magnetization $M$ in the [001] plane. The solid curves in the figure are theoretical fits to the FMR positions $H_R$.

In Fig. 7.4 we plot FMR fields $H_R$ as a function of applied field orientation for all samples, top panels corresponding to results obtained in the “vertical” setup, and bottom panels to results from the “horizontal” setup. Strikingly, two-fold symmetry dominates the angular dependence of $H_R$ fields observed in the vertical setup (top panels), and the in-plane angular dependence (bottom panels) is characterized by a four-fold symmetry. From the evolution of the angular dependence of $H_R$ with size, we note that, as the size of
nano-squares decreases, field orientations corresponding to the lowest resonance field (which indicates the orientation of the easy axis) shift from [001] direction seen in the top left panels to the [100] direction seen in the bottom panels. This indicates that the easy axis of the GaMnAsP sample, which lies along [001] for the control sample, gradually changes to the [100] direction as the square size decreases toward 200nm. The behavior of the bottom panels in Fig. 7.4, which show the angular dependence of $H_R$ for $H$ confined to the (001) plane, is particularly interesting for two reasons. First, it reveals that the magnetic in-plane anisotropy (which we attribute to the cubic anisotropy term $H_{4\parallel}$) is quite strong. And second, it is evident that this symmetry of FMR positions does not change as the nano-square size decreases, although the entire curve shifts downward with decreasing size due reduction of the dominance of perpendicular anisotropy.
Fig. 7.5: Magnetic anisotropy fields $4\pi M - (H_{2\perp} + H_{4\perp})$, $H_{4\parallel}$, and $H_{2\parallel}$ obtained from FMR data measured at $T = 4$ K as a function of square size.

To obtain the values of anisotropy fields quantitatively, we analyze the FMR results in Fig. 7.4 using the formalism described earlier [5]. Specifically, the analysis yields five parameters: $H_{4\parallel}$, $H_{2\parallel}$, $4\pi M - H_{2\perp}$, $H_{4\perp}$, and the $g$-factor. One can see the satisfactory fits which have been obtained in this manner for all data points, as shown by the solid curves in Fig. 7.4. The deviations between the fits and the results in the top panel for the smallest nano-square sizes can be ascribed to the presence of spin wave resonances. The resulting anisotropy fields for the control sample and for the four nano-square arrays are plotted in Fig. 7.5. Conspicuously, the in-plane cubic and uniaxial anisotropy fields are not size dependent. In sharp contrast, the overall perpendicular
anisotropy field [given by the parameter \(4\pi M - (H_{2\perp} + H_{4\perp})\)] is seen to strongly depend on size, illustrating the complex nature of shape anisotropy in a nano-patterned GaMnAsP system with built-in tensile strain. Importantly, one should note that the value of the overall perpendicular anisotropy parameter \(4\pi M - (H_{2\perp} + H_{4\perp})\) changes sign when the nanosquare size goes below 400nm. This indicates the condition at which the originally perpendicular anisotropy of GaMnAsP the larger squares transforms to in-plane anisotropy due to the effect of reducing size.

7.5 Spin-wave Resonances

In addition to the uniform-mode FMR, we also observed the presence of spin-wave resonances (SWRs) in the 400nm and 200nm nano-square arrays. This is illustrated in Fig. 7.6 by the spectra taken at \(T = 4K\) on the 400nm array at several field orientations. The spectrum clearly evolves as \(H\) is rotated from the out-of-plane (0°) to in-plane (90°) orientations. For the in-plane (\(H\|[1-10]\)) geometry, the resonance spectrum consists of five well resolved Portis-type SWR lines separated by equal magnetic field increments [7]. As one rotates the field away from the in-plane orientation, the SWR spectrum gradually evolves, generally consisting of three or four broad resonances. We tentatively identify the resonances on the high-field side of the uniform FMR mode as exchange-dominated non-propagating SW surface modes. If this identification is correct, it would suggest that surface spin excitations on edges are an important feature of nanoscale magnets. Further work is needed to explore this characteristic.
Fig. 7.6: Spin-wave resonance (SWR) spectra observed for the 400nm nano-sized square array at $T = 4$ K, with field $H$ applied at various orientations $\theta$ between out-of-plane and in-plane orientations, as indicated in the figure.

7.6 Conclusion

In summary, we observed strong size-induced changes in magnetic properties of nanoscale GaMnAsP square samples, including changes in the easy axis orientation from out-of-plane to in-plane as the nano-square size is reduced. We recall that perpendicular anisotropy in GaMnAsP originates from the built-in tensile strain in such layers. Thus a possible explanation of the effects observed in our patterned nanostructures could arise from relaxation of such strain. As shown in Fig. 7.5, the value perpendicular anisotropy parameter [represented by $4\pi M - (H_{2\perp} + H_{4\perp})$] is significantly reduced as the nano-square size approaches 200nm. This suggests that the strain in nano-squares must
be reduced by half if one attributes such change is solely due to the lattice relaxation. However, it is unexpected such large lattice relaxation can be realized in whole nanoscale magnet for the geometry studied in this paper (200nmx200nmx25nm). On the other hand, the observed spread of the spin-wave spectrum over 1000 Oe (see Fig. 7.6) suggests that surface anisotropy can be very different from the bulk anisotropy. This then could suggest an alternative explanation of the effects of size reduction, associated with the presence of surface anisotropy. The origin of such anisotropy is presently unknown, but could arise from surface depletion, strain relaxation, and/or from the presence of imperfections in the side walls introduced by Ar+ ion milling during the dry etching process. Such surface anisotropy could in turn lead to two major effects. First, as the size of nano-squares decreases, the surface-to-volume also ratio increases, so that the surface anisotropy will gradually become dominant, aligning the magnetization in the film plane. Secondly, for nano-square sizes around 200 to 400nm, such surface anisotropy can generate various spin-wave modes, which is similar to the previous reports, but in the case of nano-scale ferromagnetic structures Portis-type modes will appear primarily when $H$ is in nanostructure plane, where the confinement can occur.
7.7 References


APPENDIX A:

SPECIAL HANDLING REQUIRED FOR PHOSPHORUS IN THE MBE PROCESS

The MBE process requires the use of elements in gaseous phase, and the gaseous allotrope of P is diphosphorus (P$_2$), or atomic phosphorus (which is dissociated from P$_2$ molecule). P$_2$ can only be obtained under extreme conditions (e.g. high temperature over 1000 K) from tetrahedral P$_4$ molecules, which will preferentially condense into white phosphorus. However, white phosphorus is highly toxic and flammable, and can even self-ignite at room temperature. Compared to white phosphorus, red phosphorus has polymeric structure and does not ignite in air at temperatures below 240 °C; and it is also nontoxic. Therefore, red phosphorus is an appropriate form to transport and store P sources. The overall process to convert commercial red phosphorus source into the needed vaporous P$_2$ molecules is summarized by the following reaction:

$$P_{red} \xrightarrow{\text{Evaporation} \ (T=300 \sim 350 °C)} P_4\text{primary} \xrightarrow{\text{Condensation} \ (T<100 °C)} P_{white} \xrightarrow{\text{Evaporation}} P_4\text{secondary} \xrightarrow{\text{Cracking} \ (T>850 °C)} P_2.$$ 

In this process, red phosphorus is firstly evaporated at a temperature between 300 and 350 °C, transformed into primary P$_4$ molecules, and then condensed at a temperature lower than 100 °C into white phosphorus. The white phosphorus is re-evaporated into secondary P$_4$ at the previous condensing temperature, and subsequently cracked into P$_2$. 

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molecules at a temperature higher than 850 °C. All the different evaporation/condensation/evaporation stages occur simultaneously.

If the condensation and secondary evaporation steps are ignored (single chamber design), red phosphorus is sublimated at 300 °C and then directly cracked into \( \text{P}_2 \), so both white phosphorus vapor and red phosphorus vapor is produced before cracking. Some of the vaporous white phosphorus condenses on the walls of the source chamber. At an operating temperature of 300° C., the vapor pressure of white phosphorus is significantly higher than that of red phosphorus. As a result, when the valve between the source chamber and the MBE growth chamber is closed, a large pressure build-up occurs in the source chamber. When the valve is then opened to the cracker, pressure bursts may occur into the MBE chamber. Such excess release of phosphorus into the MBE chamber is harmful to the MBE growth system. In addition, the MBE chamber requires several hours after such a pressure burst to recover to a proper working pressure [1].
Based on this concern, we adopted a RIBER KPC 250 valved phosphorus cracker system to realize the process of converting red phosphorus into $P_2$ molecules. This is a two chamber effusion cell as shown in the design diagram Fig. A.1. It consists of the following parts [2]:

1. The phosphorus evaporator receives the charge of red phosphorus to be evaporated in order to produce the required quantity of white phosphorus. In working conditions the evaporator is heated at around 300 °C to sublimate the red phosphorus and to produce the primary $P_4$ vapor which will condense in the white phosphorus solid phase.

2. The condenser surrounds and receives the red phosphorus evaporator. It is connected to the flux valve and is placed in a self-limiting thermostatic enclosure, which enables one to heat the condenser around to 30 - 60 °C, and to adjust the flux required for growth. The primary $P_4$ vapor condenses on the condenser wall under the white phosphorus solid phase which is re-evaporated at a rate that depends on the condenser temperature. The flux stability is directly related to the stability of the condenser temperature.
(3) The all-metal flux adjustment and shutoff valve is situated between the white phosphorus generator and the transfer tube towards the cracker. The heater ensures that the valve is kept at above 80 °C. In working conditions, the valve is intended to precisely and rapidly adjust the flux.

(4) The cracking transfer zone ensures the transfer of the $P_4$ molecules to the cracking zone, which is maintained at a high temperature. The $P_4$ molecules entering the cracker are transformed into $P_2$ molecules inside the cracker, provided that the cracker is kept above the cracking threshold (800 °C).
A.1 References


APPENDIX B:

STANDARD PROTOCOL FOR LITHOGRAPHICAL PATTERNING PROCESS

In this Appendix I will describe the standard protocol for performing the patterning processes used in Chapter 4 and Chapter 7 (formats adopted from Ref. [1]):

1 Design a pattern layout for electron beam lithography (EBL).

   1.1 Using the L-edit software, design a 3 mm × 3 mm pattern with evenly spaced features, such as stripes or squares (see Fig. B.1). We can start from a unit pattern and use the repeating function in the software to extend the unit pattern periodically both in x and y directions.

![Fig. B.1: A zoomed-in pattern layout for a 400 nm nanocube lattice, exported from the L-edit software.](image)
1.2 Save the layout file as a .GDS file.

1.3 Log in to vistec-host02.ee.nd.edu with ssh, copy the layout GDS file to the AFS volume.

1.4 Launch LayoutBeamer, and convert layout into GPF format, in preparation for exposure on the Vistec EBL. Our system is a model 5200, 20 bit deflection, 100 kV, "HR" system.

1.5 Copy GPF layout file(s) from AFS directory to "patterns" folder.

1.6 Start Cjob, generate a .cjob file, and an EXPORTed.job file.

2 Clean and bake samples before EBL.

2.1 Cut a piece of GaMnAs or GaMnAsP thin film sample 1 cm × 1 cm in size, that will allow us to fabricate 4 patterns in one time.

2.2 Put the sample piece soak in acetone for 30 minutes with agitation by high-frequency sonication.

2.3 Put the sample piece soak in isopropanol or methanol for 10 minutes with agitation by high-frequency sonication.

2.4 Put the sample piece soak in DI water for 10 minutes with agitation by high-frequency sonication.

2.5 Using a nitrogen gun, blow-dry the sample piece.

2.6 Bake the sample piece at 150°C for 30 minutes, make sure of no water contamination.

2.7 Quickly cool down the sample piece by placing it on a steel plate.

3 Spin coat the electronresist (ER).

3.1 Attach a small chuck to a photoresist spinner. Ensure it is adequately fastened.

3.2 Using clean tweezers, place the sample on the spinner chuck. Ensure that the sample piece is centered on the chuck.

3.3 Using a plastic pipette, cover the entire sample piece in C2 type Polymethyl methacrylate (PMMA).
3.4 Spin the PMMA-coated sample at 3000~5000 RPM for 30~60 seconds. Usually faster RPM and longer time will result in thinner coating, depending on the desired thickness of Cr capping layer in later steps.

3.5 Bake the PMMA-coated sample at 170°C for 180 seconds.

4 Pattern the PMMA-coated sample piece by EBL.

4.1 Load the PMMA-coated sample piece into the Vistec EBPG 5200 electron beam lithography system, pump down.

4.2 Adjust the sample location and orientation in the chamber via Faraday rotation effect, and center the beam position at the center of the pattern, according to the system user manual.

4.3 Set the e-beam dose to be 680 µC/cm² and the corresponding frequency will be 44.1 MHz.

4.4 Execute the EBL system’s patterning program with the files generated in step (1.6) to expose the PMMA to the electron beam, according to the system’s user manual. Generally printing one pattern takes about 15 minutes, varying with pattern size and density.

4.5 Vent the EBL system and remove the post-exposure sample piece.

4.6 Develop the ER coated sample by immersing it in a PMMA-specific developer for 60 seconds at room temperature with mild and consistent agitation. The recipe of the developer is a mixture of methyl isobutyl ketone (MIBK), isopropanol and methyl ethyl ketone (MEK), by a volume ratio of 1: 3: 0.06. After developing, the exposed part of the ER is washed away.

4.7 Rinse the sample piece with isopropanol.

4.8 Using a nitrogen gun, blow-dry the sample piece.

5 Deposit chromium metal onto the ER mask-coated sample piece using an electron beam evaporator.

5.1 Vent the Oerlikon Leybold 8-pocket electron-beam, dual thermal evaporation system.

5.2 Tape the sample piece face down on the sample-holder wafer.

5.3 Open electron beam evaporator chamber door.
5.4 Place sample-holder wafer into substrate holder with sample piece facing down.

5.5 Check that Cr is among the deposition sources and has adequate amount.

5.6 Close the electron beam evaporator chamber door and pump the chamber to at least $1 \times 10^{-6}$ bar, this process usually takes 2 hours.

5.7 Deposit no more than 30 nm of Cr at 1 Å/s.

5.8 Following deposition, allow chamber to cool for about 7 minutes.

5.9 Vent electron beam evaporator chamber.

5.10 Remove sample-holder wafer and remove the sample piece from the plate.

5.11 Close the electron beam evaporator chamber door and pump the chamber.

6 Perform a metal liftoff.

6.1 Prepare a beaker of acetone sufficient to immerse the sample piece. Heating the acetone to 75°C is optional that may accelerate the liftoff process.

6.2 Immerse the sample in the acetone. High-frequency sonic agitation is optional but should be applied no more than 1 minute, because the metal is easy to get exfoliated.

6.3 Check the sample piece frequently under the Olympus optical microscope for the remains of ER.

6.4 Continue immersion in acetone until all the ER has been removed.

6.5 Rinse the sample piece with isopropanol.

6.6 Rinse the sample piece with DI water.

6.7 Using a nitrogen gun, blow-dry the sample piece.

7 Etch the sample piece into nanostructures using a reactive ion etching (RIE) system.

7.1 Vent the Oxford PlasmaPro 100 ICP-RIE system.

7.2 Load sample piece into the etching chamber.
7.3 This is an automatic system so the pumping process will be carried out by the system before executing the recipe.

7.4 For our specific GaMnAs or GaMnAsP samples, Argon plasma with a pressure of 8 mTorr and an ICP power of 2000 W is utilized. Applying 90 W radio frequency (RF), the etch rate is about 3 nm/s. The total etching time depends on the desired etching depth, usually is shorter than 1 minute.

7.5 Upon completion of the etching process, vent the etching chamber.

7.6 Unload sample and pump etching chamber.

8 Check the fabrication quality of the sample piece by a Magellan scanning electron microscope (SEM).

8.1 Clean the sample piece with an Argon/Oxygen plasma cleaner for 5 minutes, according to the system user manual.

8.2 Carefully adhere the sample piece onto the SEM sample-holder with carbon adhesive discs and the clamps on holder.

8.3 Vent the SEM chamber and install the sample-holder onto the rotation plate in the chamber, tight with a screwdriver.

8.4 Pump the system until the software has indicated ready status.

8.5 Turn on the electron beam with 10 kV voltage and 13 pA current.

8.6 Check the entire pattern first at a lower magnification, to see if there is any scratch on the surface or any missing part of the pattern. Save images.

8.7 Select a typical area and zoom in with a higher magnification (e.g. 100000 times) under immersion mode. View from both top view and a tilted angle (e.g. 45°) to check the shape of the nanostructures and if there is any defects on the surfaces or edges. Use the ruler tool in software to measure the dimension of the shape. Save images.

8.8 Turn off the electron beam and vent the chamber.

8.9 Remove the sample piece carefully and pump down the system.
B.1 References