INVESTIGATION OF III-V FERROMAGNETIC SEMICONDUCTORS

A Thesis in

Physics

by

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III-Mn-V ferromagnetic semiconductors (FMSC) are attractive and promising material candidates for semiconductor spin-electronics, in which the carrier spin and charge are exploited for potential applications. In this thesis, we presented collective studies of important materials in this class, and focused on understanding and improving the physical properties of (Ga,Mn)As, as well as the investigation of new compounds.

We explored the physical parameters required to induce ferromagnetism in extremely diluted Ga$_{1-x}$Mn$_x$As ($x \leq 0.015$), where previous studies have focused mostly on highly doped samples ($x > 0.02$). Our data confirmed that insulating and ferromagnetic behaviors can coexist in this low doping regime, as the samples span from paramagnetic insulating to ferromagnetic conducting at this low doping level. In contrast to previous understanding, we found that the hopping energy and localization of hole-carriers critically determine the onset of ferromagnetism in this insulating system, regardless of the carrier density or the Mn impurity concentration.

We fabricated nanometer-scale wires to rejuvenate the effectiveness of thermal annealing on GaAs/Ga$_{1-x}$Mn$_x$As ($x \approx 0.06$)/GaAs heterostructures, where lateral sidewalls of the wires serve as free surfaces to assist the removal of Mn interstitial ($\text{Mn}_I$) defects, so the Curie temperature and electrical conductivity can be enhanced by annealing. We also studied the efficiency of annealing as a function of the wire width, and compared the out-diffusion of Mn$_I$ defects between (Ga,Mn)As epilayers and these wires.

We reported preliminary studies on a novel quaternary FMSC alloy (In,Al,Mn)As grown on indium phosphide, as well as a series of closely lattice-matched (In,Al,Mn)As and (In,Ga,Mn)As superlattices (SLs), wherein the SL period is fixed and the thickness ratio of the constituents systematically varied. We found that the Curie temperature, effective ferromagnetic moment and magnetic anisotropy of the SLs are strongly correlated to the thickness ratio of (In,Al,Mn)As and (In,Ga,Mn)As.
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Chapter 1

Introduction

Since the discovery of the giant magneto-resistance (GMR) effect in multilayered ferromagnetic metals in 1988,[1][2] the huge success led by IBM and other research groups[3] in converting this pronounced effect into commercially available product has significantly impacted the entire electronics industry and revolutionized the way information is exchanged. The most important efforts were the development of high-sensitivity magnetic recording heads using the magneto-resistance effect based on ferromagnetic metal alloys, which induced the enormous breakthrough in the size and capacity of magnetic storage media for the past decade. The areal density (bits/inch$^2$) of data embedded in hard drive disks is highlighted in Figure 1-1 as an example of the high growth rate, which is often compared to the evolution of the semiconductor industry ever since integrated circuits were invented.[4] Today, another milestone in the magnetic storage industry is set by the mass production of 1-terabyte hard drive since the gigabyte barrier was overcome 16 years ago.[5] The process of identifying key technologies inside the research laboratories and realizing them into marketable consumer products in such a short time period is truly remarkable, and it has inevitably triggered the anticipation of a “next-generation” technology revolution beyond the success of the GMR discovery.

One immediate and attractive proposal has been to combine the strength of the technologically mature semiconductor electronics with the permanent information storage
capability of ferromagnetic metals, and to integrate both features on a single device chip. An example is the recently marketed magnetic (or magneto-resistive) random-access memory (MRAM),[6] where the magnetic moments were used to determine the on-off state of a memory bit cell as opposed to the use of electric charges in conventional semiconductor memory. The apparent advantage of MRAM is that data are preserved during unintentional removal of electric power.

Figure 1-1: The areal density of hard drive disks since the first shipment from IBM in 1956 (reproduced from the Hitachi Global Storage Technologies website).[7]

The term “spintronics” (short for spin-based electronics) or alternatively known as magneto-electronics is built upon these foundations. It is also believed that quantum bits (or qubits) based on an electron’s spin state are a possible solution to constructing large-scale quantum computers.[8] It is a challenge to find cost-effective solutions to integrate ferromagnetic metals and conventional semiconductors to mass produce multifunctional
spin-logistic chips and convert advanced spintronics chip-making into an industry comparable to the current electronics market. To simplify the fabrication process of future spintronic devices, it is physically appealing to manipulate the dual properties of an electron charge and its magnetic spin in one material system. In the contents of this thesis, we will focus on a fundamental approach, which is to make semiconductor materials ferromagnetic by adding extrinsic magnetic dopants (e.g., Mn) and enrich the material selection for semiconductor spintronics. This new class of materials are called “ferromagnetic semiconductors”, in which the characteristics of ferromagnetism and conventional semiconductor are integrated.

Figure 1-2: Schematic showing the potential of combining the complementary properties of electron charge and magnetic spin to create functional spintronic devices.

The following two sections will serve as a brief review of the fundamentals of semiconductor physics and magnetism assuming the readers have a basic knowledge on solid state physics.
1.1 Basics of semiconductors

The distinction between metals, semiconductors and insulators is best described by the concept of energy band gap and their band structure, which originated from allowed and forbidden states that electrons can occupy in a crystalline solid. The term “band gap” is defined as the energy difference between two consecutive allowed bands. An important assumption is that when an allowed band is completely filled with electrons, the electrons inside this band cannot conduct any current; in other words, the electrons being fermions can have no net motion since an electron can only move from a filled state to an empty state, which does not exist in a filled band. A material in which an energy band is completely filled and the next allowed band is completely empty is called an “insulator” and in principle has infinite resistivity at zero temperature. When the material has an allowed band which is only half-full of electrons, it has a very low resistivity and is called a “metal”. The main difference between semiconductors and insulators is that the band gap for a semiconductor is typically $\leq 3.0$ eV, and at finite temperatures some of the electrons in a lower filled band of the semiconductor are transferred to an upper unfilled band which leads to an increase in electric conductivity. A critical difference between metals and semiconductors is that metals have a very high conductivity because of the large number of electrons that can participate in the transport. Therefore, it is very difficult to alter its conductivity in a simple manner. On the other hand, semiconductors have zero conductivity at $T = 0$ K and low conductivity at finite temperatures, but it is possible to increase their conductivity by orders of magnitude when extrinsic dopants are incorporated into the material.[9]
The valence band in a semiconductor is defined as the highest occupied band with electrons at \( T = 0 \) K, while the upper empty band is called the conduction band. In semiconductors, the material characteristics of interest are most sensitive to the features near the top of the valence band and at the bottom of the conduction band. For gallium arsenide (GaAs), these states originate from the outermost atomic levels of the valence shells of Ga: \([\text{Ar}] 3d^{10} 4s^2 4p^1\) and As: \([\text{Ar}] 3d^{10} 4s^2 4p^3\) (\([\text{Ar}]\): 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)), which are either \( s \)-type or \( p \)-type. The schematic of the valence band, direct band gap, and indirect band gap conduction bands of both direct (e.g., GaAs) and indirect (e.g., silicon) band gap semiconductors are shown in Figure 1-3.

Figure 1-3: Schematic of the valence band, direct band gap, and indirect band gap conduction bands.
When the conduction band edge is at $k = 0$, where $k$ is the wave vector of the reciprocal lattice, it is possible to approximate the band structure by the simple parabolic form of

$$E(k) = E_c + \frac{\hbar^2 k^2}{2m^*} \quad (1.1)$$

where $E_c$ is the conduction band edge and $\hbar$ is the Planck’s constant divided by $2\pi$. The $m^*$ here is called the “effective mass” and defined as

$$m^* = \left( \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \right)^{-1} \quad (1.2)$$

which depends on the $E(k)$. It is also different from the free electron mass $m_0$ in free space.

The concept of a “hole” in semiconductors is a representation of a missing electron in the valence band. When all the states in the valence band are occupied, the sum of all wave vector states is zero:

$$\sum k_i = 0 = \sum_{k_i \neq k_e} k_i + k_e \quad (1.3)$$

which indicates that all positive and negative $k$ states are equally occupied. In the case when an electron in the valence at wave vector $k_e$ is missing as illustrated in Figure 1-4, the new sum of the wave vector state is then

$$\sum_{k_i \neq k_e} k_i = -\sum k_e \quad (1.4)$$

This missing state is defined as a “hole” which can be interpreted as a virtual carrier with a positive electron charge in the semiconductor. The hole wave vector $k_i$ is $-k_e$. 


Similar to Eq. (1.1) that describes the conduction band structure, the energy-momentum relation for the light and heavy hole bands as shown in Figure 1-3 are expressed in Eq. (1.5) and Eq. (1.6), where $m_{lh}^*$ and $m_{hh}^*$ represent the effective mass of light and heavy holes respectively.

Light hole band: \[ E(k) = E_v - \frac{\hbar^2 k^2}{2m_{lh}^*} \quad (1.5) \]
The Fermi energy \( (E_F) \) in semiconductors is determined as the energy level in the midst of the conduction and valence band, which is different than the case in metals where \( E_F \) falls within an allowed band. To alter the electron or hole carrier density in a semiconductor, impurities which are called “dopants” can be incorporated into the crystalline structure of the semiconductor. The two types of dopants are called donors and acceptors, where each of them donates an electron to the conduction band or accepts an electron from the valence band (thus creating a hole) respectively. The carrier and transport dynamics depend on these parameters.

\[
E(k) = E_F - \frac{\hbar^2 k^2}{2m_{hh}^*}
\]

(1.6)

Heavy hole band:

\[
\text{Figure 1-5: Zinc blende crystal structure. Colored and transparent spheres represent two different atoms.}
\]
Essentially, all semiconductors that are of interest for electronics and optoelectronics have an underlying face center cubic (fcc) lattice structure. For example, gallium arsenide (GaAs) has a zinc-blende crystal structure which is constructed by Ga and As fcc lattices that inter-penetrates each other. The displacement between the origin of these two fcc lattices is 1/4 of their lattice parameter “a” as indicated in Figure 1-5.

1.2 Basics of magnetism

The fundamental origin of magnetism is a magnetic dipole moment, which is induced by a loop motion of charged particles. For an atom in free space, there are three main sources of magnetic moments: (i) the intrinsic spin of electrons (ii) the orbital angular momentum of electrons that surrounds the nucleus and (iii) a response of this orbital moment to an external magnetic field. The magnetic moments of the nuclei are usually $10^{-3}$ times smaller than those of the electrons.

Some of the terms in magnetism include the magnetization (M), which is defined as the magnetic moment per unit volume, and the magnetic susceptibility per unit volume ($\chi$) is defined by

$$\chi = \frac{\partial M}{\partial H}$$

where H is the applied magnetic field.

Materials with a negative susceptibility are called “diamagnetic”, the origin of which is associated with the tendency of the outer shell electrons that counteracts an applied magnetic field. It can be viewed as an atomic version of the Lenz’s law where
the configuration of the electrons will increase the internal moment in such a direction to oppose the change in the magnetic flux (i.e., opposite of the applied field). This is a form of magnetism that exists only in the presence of an external magnetic field. The susceptibility of diamagnetic materials is often in the range of $10^{-5}$ to $10^{-4}$.

Paramagnetism is another form of magnetism that requires the existence of an applied field, which is found in systems such as metals, transition elements or atoms, molecules, and lattice defects that possesses an odd number of electrons so the net spin of the systems cannot be zero. In paramagnetic materials, permanent dipole moments do exist and align with an external magnetic field, but are prevented from becoming perfectly aligned at non-zero temperatures due to thermal fluctuation, so the susceptibilities are also rather small (e.g., in the range of $10^{-5}$ to $10^{-3}$).

Ferromagnetism and antiferromagnetism are two other important types of magnetism. In these cases, the spins in a material system align parallel or anti-parallel with their neighbors respectively through exchange coupling. The term exchange coupling refers to the quantum mechanical interactions between localized spins that result in the lowest energy state (discussed more in section 1.5). All of these alignment effects occur only at temperatures below a critical temperature, which are termed the Curie temperature ($T_C$) for ferromagnets or the Neel temperature ($T_N$) for antiferromagnets. At temperatures above $T_C$ or $T_N$, thermal fluctuations overcome the exchange energy required to maintain their magnetic ordering and paramagnetism is observed. The characteristics of a ferromagnet include the spontaneous magnetization and magneto-hysteresis at $T < T_C$. Typical ferromagnets have very high susceptibility (> 1000) and are made of atoms with permanent dipole moments.
One can describe the exchange interactions of these two systems by assuming their spin Hamiltonian has the simple form

$$H^{\text{spin}} = -\sum_{i \neq j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

(1.8)

which sums the interaction energy of all pairs of ions (or atoms) \(i, j\) with the electron spins \(\vec{S}_i, \vec{S}_j\). The term \(J_{ij}\) is the exchange integral and Eq. (1.8) is called the Heisenberg model. Note that for the model to be valid, it is necessary that the moments \(\vec{S}_i, \vec{S}_j\) are far apart so their electronic wavefunction overlap is very small. Since the angular momentum as well as the spin part of each magnetic ion are included in the calculation, the coupling in the spin Hamiltonian will be dependent on the relative spin orientations. The exchange integral is positive for ferromagnets and negative for antiferromagnets.

### 1.3 Semiconductor spintronics

The motivation to exploit the potential of semiconductor spintronics is to provide an advantageous option in addition to metal-based spintronics. For instance, the spin coherence length inside semiconductors is much larger compared to metals, and we will show below that ideal ferromagnetic semiconductors have a broad range of magnetic properties that can be manipulated by tuning the density of carriers inside the semiconductor host. It was also mentioned earlier that important hierarchies of conventional semiconductor electronics such as the random-access memory (RAM) can be “upgraded” to spin-based MRAM. Similarly, for the metal-oxide-semiconductor field effect transistor (MOSFET), a proof-of-concept design of a spin-transistor as well as
electric gating[10][11] demonstrated that conventional electronic switching and logic components through the application of a gate voltage can be reproduced in the spin configuration based on magnetic semiconductors. Other proposals or demonstrated devices making use of spin-current over charge current include the magnetic-field dependent spin-valve[12] and magnetic tunnel junction (MTJ)[13] devices which can act as sensors, switches and modulators. These serve as potentially useful building blocks for semiconductor spintronics. Therefore, from the materials aspect, finding the right ferromagnetic semiconductor is the most important step towards fabricating semiconductor spintronic devices.

Here we have listed a few selection criteria that could help evaluate which of the existing ferromagnetic semiconductor material candidates has the potential to be used to fabricate functional devices:[14][15] (i) The ferromagnetic transition temperature (Curie temperature, T_C) should at least exceed room temperature (preferably tunable above 500 K) so that the potential devices are functional in a wide and practical temperature range. (ii) The magnetic properties of the material such as T_C, magnetic moment and stiffness (coercivity) should be sensitive to the density of the charge carriers in the host semiconductor. (iii) The ferromagnetic material should maintain the fundamental characteristics of a conventional semiconductor, where the carrier and electric properties are tunable by extrinsic doping, photon injection and localized electric field induced by gate voltages. In short, an ideal ferromagnetic semiconductor should inherit the highly-tunable nature of the electronic states in conventional semiconductors and exhibit a strong correlation between the magnetic and charge carrier characteristics. Therefore, it is intuitive that the material search and synthesis started out by trying to incorporate
magnetic elements such as Mn, Cr, Co, Fe into II-VI or III-V based semiconductor compounds and miscellaneous materials. In general, such materials are called diluted magnetic semiconductors (DMS) since the magnetic impurity level incorporated into the semiconductor host is typically below 10 atomic % (e.g., x is usually smaller than 0.10 in Ga$_{1-x}$Mn$_x$As). We will discuss some of the most important ferromagnetic semiconductor candidates reported in the literature:

(i) III-Mn-As compounds, especially (Ga,Mn)As. This is the most extensively studied ferromagnetic semiconductor because of the following attractive characteristics: (a) The ferromagnetism is mediated by the interaction between the carriers inside the semiconductor host and the doped Mn atoms, therefore the magnetic properties (such as the Curie temperature, coercivity) of the material can be fine-tuned by changing its electronic states through control of the incorporated Mn dopant concentration. (b) GaAs is a technologically mature material so high quality and low cost wafer substrates are readily available for synthesizing (Ga,Mn)As. The same advantage is also reflected in the available knowledge required to lithographically process devices based on (Ga,Mn)As, since it is highly-compatible with the well-developed recipes for GaAs.

The current drawback of (Ga,Mn)As is its Curie temperature which limits its practical applications. On the other hand, the $T_C$ of the bulk (Ga,Mn)As has improved over the years (as shown in Figure 1-6) from below liquid nitrogen temperature (77 K) to above 150 K,[16][17] and even 250 K has been reported using delta-doping techniques.[18] Moreover, a recent theoretical study using ab-initio (first principle) calculations indicated that $T_C > 350$ K may be achievable by arranging the configuration of (GaAs)$_m$(MnAs)$_n$ digital superlattices on higher index GaAs substrates,[19] which has
strongly motivated ongoing material synthesis efforts using molecular beam epitaxy (MBE). For other III-Mn-As materials such as (In,Mn)As,[20][21] $T_C$ is well below liquid nitrogen temperature. Even though demonstrations have shown that magnetic properties can be controlled by photo-illumination[22] and electric fields,[23] the improvement in $T_C$ is not significant. Manipulation of the $T_C$ by an external electric field were also reported in (Ga,Mn)As[24] and GaSb/Mn digital alloys.[25]

(ii) III-Mn-Sb compounds: similar to the III-Mn-As series of diluted magnetic semiconductors, (Ga,Mn)Sb[26][27] and (In,Mn)Sb[28] were two of the materials sought for carrier-mediated ferromagnetism. Interesting features such as pressure-induced changes in the Curie temperature was observed in (In,Mn)Sb;[29] however, the
applicability still suffers from its extremely low Curie temperature (below 10 K) in addition to the low availability of InSb and GaSb substrates.

(iii) III-Nitride and III-Phosphide based compounds: (Ga,Mn)N, which is perhaps the most well-studied wide bandgap semiconductor material that exhibits ferromagnetism above room temperature.[30][31] It also has the highest predicted $T_C$ in zinc blende magnetic semiconductors by the Zener model,[32] and the wide bandgap characteristics are ideal for laser-optical related applications such as blue light emitting diode lasers.[9] On the drawback side, the ferromagnetism in (Ga,Mn)N is not carrier-mediated and cannot be controlled by impurity doping. The material synthesis is also relatively difficult, even by MBE growth. In fact, ferromagnetism has not been consistently demonstrated due to the sensitivity to the growth conditions (crystal quality, stoichiometry, and activated Mn concentration), and the mechanism for ferromagnetism is also unclear.[33] Sapphire (single crystal form of Al$_2$O$_3$) and other substrate materials used for GaN thin film growth are relatively expensive and also harder to obtain than GaAs and InP substrates.

Other magnetically doped nitride materials such as (Ga,Cr)N[34] and (Al,Cr)N[34][35] can also show very high Curie temperature ($> 900$ K); however, due to the lack of consistency in reported ferromagnetism and the possibility of other sources for ferromagnetic moments, further examination is still needed. (Ga,Mn)P, on the other hand, does not have a high $T_C$ ($T_C = 60$ K)[36] or a high $T_C$ in prediction,[32] yet it is extremely attractive because it is closely lattice-matched to silicon.[31]

Quaternary alloys based on material groups (i) – (iii) would also be of high interest because of the closeness to their relatives: for example, Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ could be
promising because of its closeness to GaAs which is yet to be explored,[14] while (In,Ga,Mn)As was already known to highly resemble (Ga,Mn)As in terms of the electric and magnetic properties, but can be grown lattice-matched on InP substrates which is attractive for potential optical applications.[37]

(iv) Miscellaneous ferromagnetic semiconductors with reported above room-temperature ferromagnetism include Cr-doped In₂O₃,[38] (Zn,Cr)Te,[39] (Co,Ti)O₂,[40] (Zn,Mn)O,[41] (Sn,Fe)O₂,[42] (Sn,Co)O₂,[43] (Zn,Co)O,[44] MeGe,[45], (Cd,Mn)GeP₂,[46] (Zn,Mn)GeP₂,[47][48] ZnSnAs₂.[49] Many other candidates have also been suggested based on theoretical predictions.[50] We note that while some of the wide bandgap oxide semiconductors do have interesting optical properties, the main obstacle is the lack of detailed understanding of the host material, as well as uncertainty about ferromagnetism and its sources.

Therefore, despite the fact that the current Curie temperature of the diluted magnetic semiconductor (Ga,Mn)As has not exceeded room temperature, it still appears to be the leading material candidate that meets the selection criteria for semiconductor spintronics. In addition, (Ga,Mn)As is also an ideal model system for fundamental research, and a deeper understanding of its material characteristics can provide insight and guidelines to the ongoing synthesis of new ferromagnetic semiconductors. The main scope of the thesis will be focused on understanding and improving the ferromagnetic properties of III-Mn-As diluted magnetic semiconductors, in particularly (Ga,Mn)As. Table 1-1 summarizes the discussion above.
Table 1-1: A summary of ferromagnetic semiconductor material candidates.

<table>
<thead>
<tr>
<th>Materials Group</th>
<th>Examples</th>
<th>Strength</th>
<th>Weakness</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-Mn-As</td>
<td>(Ga,Mn)As, (In,Mn)As</td>
<td>1. Ferromagnetism (FM) is carrier-mediated and can be electrically fine-tuned</td>
<td>$T_C$ did not exceed 300 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. GaAs and InP are well known and technologically mature</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Substrates are readily available and relatively inexpensive</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. Lithographic processing compatible with well-developed recipes</td>
<td></td>
</tr>
<tr>
<td>III-Mn-Sb</td>
<td>(In,Mn)Sb, (Ga,Mn)Sb</td>
<td>1. Pressure-induced change of $T_C$</td>
<td>1. Low $T_C$ ($In,Mn)Sb T_C &lt; 10 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Similar characteristics as III-Mn-As</td>
<td>2. Substrate materials not largely available as GaAs or InP</td>
</tr>
<tr>
<td>III-Nitride</td>
<td>(Ga,Mn)N</td>
<td>1. $T_C$ above room temperature (also the highest $T_C$ predicted)</td>
<td>1. FM not carrier-mediated</td>
</tr>
<tr>
<td>III-Phosphide</td>
<td></td>
<td>2. Wide-bandgap material, ideal for laser optical applications</td>
<td>2. Material synthesis difficult and gives inconsistent results</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3. FM is very sensitive to material synthesis processes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4. Mechanism of FM still unclear due to material uncertainty</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5. Substrate (sapphire and others) expensive and harder to obtain</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>(Ga,Cr)N, (Al,Cr)N</td>
<td>$T_C &gt; 900$ K reported</td>
<td>1. Inconsistent reports of FM and questions on the FM sources</td>
</tr>
<tr>
<td>Materials</td>
<td>Cr:In$_2$O$_3$, Zn,CrTeX,</td>
<td>2. Substrate issues similar to GaN</td>
<td>2. Substrate issues similar to GaN</td>
</tr>
<tr>
<td></td>
<td>(Co,Ti,O)$_5$, (Cd,Mn)GeP$_2$, ZnSnAs$_2$, (Zn,Co)O, (Zn,Mn)O</td>
<td>Above room temperature FM</td>
<td>3. FM and its sources unclear</td>
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<td></td>
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</tbody>
</table>
1.4 Ferromagnetic semiconductor (Ga,Mn)As

Diluted magnetic semiconductors have a long attractive history in the field of condensed matter because they combine the two important fields of magnetism and semiconductor physics. In the 1980s, II-VI magnetic semiconductors, in particular Mn incorporated alloys (e.g., (Zn,Mn)Se, (Cd,Mn)Se) were extensively studied since transition metals such as Mn$^{2+}$ can easily be incorporated into the II-VI host materials and high carrier concentration samples can be synthesized for electric measurements.[51] On the other hand, group III-V compounds suffer from a low equilibrium solubility of these transition metals and the material synthesis of III-V DMS was not successful until non-equilibrium growth conditions were achieved by low-temperature molecular beam epitaxy (LT-MBE). In 1989, (In,Mn)As was first synthesized with up to 18 atomic % of Mn incorporated which exhibited an n-type paramagnetic behavior;[52] three years later, the first p-type ferromagnetic (In,Mn)As was reported with $T_C = 7.5$ K, which is the first III-Mn-V ferromagnetic semiconductor.[53] (Ga,Mn)Sb with improved $T_C$ of 25 K was then added to the list in 1994.[54]
The major breakthrough for III-Mn-V diluted magnetic semiconductors was the introduction of the ferromagnetic (Ga,Mn)As in 1996,[55] where the meta-stable phase (Ga,Mn)As was successfully synthesized in non-equilibrium low-temperature conditions without the formation of 3-dimensional MnAs clusters on semi-insulating GaAs (001) substrates. Figure 1-7 shows the ideal zinc blende structure (Ga,Mn)As, in which the Mn atom replaces only the Ga site (termed “substitutional Mn”) in the stable form of Mn$^{2+}$ cation. Since the Mn$^{2+}$ contributes only two electrons to the GaAs host instead of three by the original Ga$^{3+}$, the substitutional Mn also acts as an acceptor and contributes an extra hole-carrier to the semiconductor host. The current picture for ferromagnetism in III-Mn-As and III-Mn-Sb compounds indicates that the long-range ferromagnetic ordering is mediated by the anti-ferromagnetic interaction between the hole-carriers and the Mn$^{2+}$ ($3d^5$) cations with $5/2$ electron spins (for details see Section 1.5). For instance, when a hole-carrier aligns anti-parallel with two Mn$^{2+}$ cations through anti-ferromagnetic
(AFM) coupling as shown in Figure 1-8, it will cause the two Mn$^{2+}$ cations to align in parallel state, which is equivalent to spontaneous ferromagnetic (FM) coupling between the two spin 5/2 magnetic moments. Macroscopic magnetic ordering is then induced by the propagation of spin-polarized “itinerant” hole-carriers in the bulk semiconductor according to the Zener model,[32] which assumed that (Ga,Mn)As is metallic and has a high carrier density. The Curie temperature of Ga$_{1-x}$Mn$_x$As was further predicted to be proportional to $x^*p^{1/3}$ (x: Mn concentration, p: carrier density), which suggested that a strategy to synthesize high-T$_C$ materials would be to increase the hole-carrier density and the Mn dopant concentration. However, during the material synthesis, it is extremely difficult to avoid the formation of undesired defects. In (Ga,Mn)As, there are two main types of defects that will compensate the hole-carriers: the Mn interstitial (Mn$_I$) and As anti-site (As$_{Ga}$) defects. When excess Mn$^{2+}$ dopants occupy the vacancy between the perfect GaAs lattice sites, they are called Mn interstitials and contribute as a double donor to the GaAs host. A similar contribution comes from the As antisite defects (denoted As$_{Ga}$), where the As atom occupies the Ga site and gives off two additional electrons than Ga (As: [Ar]3d$^{10}$4s$^2$4p$^3$). Other possible defects in (Ga,Mn)As includes As vacancies, Ga vacancies and As interstitials, which are relatively low in density compared to the two thermodynamically favorable Mn$_I$ and As$_{Ga}$. 
As we have mentioned above, the material synthesis of the meta-stable phase (Ga,Mn)As typically relies on the molecular beam epitaxy (MBE) growth technique, since it is advantageous to employ the relatively low (1 angstrom/sec) growth rate to obtain the best crystal quality and to minimize the undesired defects. The schematic of the MBE growth chamber is shown in Figure 1-9, where the (solid) source materials such as Ga, Al, In, As, Mn and Be are pre-installed in the effusion (Knudsen) cells and heated for material out-diffusion. The deposition rate of these high-purity elements (usually above 6N) on the substrate wafer are controlled by the temperatures of the effusion cells and the substrate, as well as the relative position of the cells and the substrate wafer. During the material growth, the substrate wafer is continuously rotated for material uniformity and the growth rate is monitored *in situ* by reflection high-energy electron
diffraction (RHEED) oscillations. The growth parameters must be fine-tuned so that an ideal stoichiometry of Ga:As with adequately doped Mn can be obtained during the thin film growth.

In reality, the material synthesis of the non-equilibrium phase of (Ga,Mn)As cannot be completely defect-free. Post-growth thermal annealing studies aiming to improve the Curie temperature of (Ga,Mn)As have shown that these defects can greatly affect the electric and magnetic properties of the material. Hayashi et al.[56] first reported that annealing can improve the crystalline structure of as-grown (Ga,Mn)As and increase its Curie temperature to above 100 K. Research efforts conducted in parallel by
numerous research groups, such as Potashnik et al.,[57][58] showed that the conductivity and ferromagnetism of the material can be significantly improved under prescribed annealing protocols (optimized time and temperature), where the effect of annealing leads to a complicated interplay between the primary defects that has been demonstrated in GaAs and the evolution of the defects involves at least two different processes. Sørensen et al.[59] had also reported a clear correspondence between the change in the Curie temperature and the carrier concentrations of thin (5 nm to 20 nm) (Ga,Mn)As samples upon similar thermal conditions, as well as its dependence on the film thickness.[60] Edmonds et al. had studied the effects of annealing by monitoring the resistance of the material in situ during the annealing process,[61] and identified that the out-diffusion of the Mn interstitials towards free surfaces is the key mechanism of low temperature annealing.[62] Other important and related work includes studies on the effect of capping materials (e.g., GaAs[63] and arsenic[64]) on top of (Ga,Mn)As epilayers and the application of oxygen atmosphere upon annealing.[65] Material characterization studies include the use of particle-induced x-ray emission (PIXE), Rutherford backscattering (RBS) and x-ray absorption spectroscopy (XAS) to track the distribution of Mn atoms on various lattice sites[66] and x-ray diffractometry (XRD) to measure the effects of defects on the lattice parameter of (Ga,Mn)As.[67] All of these have contributed to our understanding of the electrical, magnetic, and structural properties of (Ga,Mn)As. We would like to add a note here that in addition to the widely adapted MBE growth technique, synthesis of ferromagnetic (Ga,Mn)As has also been demonstrated by implanting Mn ions into GaAs followed by pulsed-laser melting.[68]
Overall, all of these material synthesis efforts were aimed at a very clear goal, which is to improve the ferromagnetic transition temperature ($T_C$) of (Ga,Mn)As. The quest for a solution unavoidably requires an answer to one of the most important questions in (Ga,Mn)As: the origin of ferromagnetism. For (Ga,Mn)As, the carrier-mediated ferromagnetism is known to be highly-sensitive to the complicated interplay between the charge carriers, localized magnetic spins and the underlying defects, which all have a strong dependence on the initial and post-growth material processing. Therefore it is extremely challenging to present a clear-cut mechanism of the exchange interactions between these elements, without mentioning that the spatial details (atomic scale) of the material are not available even with the most advanced techniques (e.g., high resolution transmission electron microscope, HRTEM).[69] As a result, simplified models and Hamiltonians that partially agree with the existing empirical data must be adapted to describe the magnetic-ordering in this system.

In the following section, we will go through the qualitative picture of ferromagnetism in (Ga,Mn)As and the main theoretical approaches taken to understand the ferromagnetism in III-Mn-V semiconductor compounds.

1.5 Theory of III-Mn-V magnetic semiconductors

In the previous section, we have presented a very brief carrier-mediated picture for ferromagnetism in III-Mn-V magnetic semiconductors, in particular (Ga,Mn)As and III-Mn-As based compounds, which are magnetic systems in which ferromagnetism is due primarily to coupling between magnetic elements that is mediated by conduction-
band electrons or valence-band holes. The ferromagnetism originates from localized Mn moments, and the dependence of the energy of the system that relies on the relative orientation of the Mn spins is referred to as the “exchange interaction”. Before we go into more details, we would like to introduce a few types of magnetic interactions, which are identified in other magnetic systems as well as the III-Mn-V semiconductors.

(i) direct exchange, which is the Heisenberg model that we have introduced in section 1.2. It describes an interaction that arise from direct Coulomb interactions among the electrons of any two magnetic ions that are isolated (i.e., overlap of the electron wave functions is small), and the energy of the interaction between any pair of atoms $i, j$ with electron spins $S_i, S_j$ follows the representation of the Heisenberg’s Hamiltonian [Eq.(1.8)] which depends on the magnitude and the relative orientation of the spins.

(ii) superexchange, this is a type of magnetic interaction similarly driven by the Coulomb interactions, except that in this case two magnetic ions are separated by a non-magnetic ion which has all of its electronic shells closed, and the magnetic interaction is mediated by the electrons of their shared non-magnetic ion neighbor. The process can be initiated with an electron transfer from the non-magnetic ion to an empty shell of the magnetic ion(s), which couples through direct exchange with the electrons that forms the magnetic moments of the magnetic ion(s). Polarization of the non-magnetic ion occurs when it couples with its two magnetic neighbors. Here the result of the superexchange can be ferromagnetic or antiferromagnetic depending on the sign of those two direct-exchange interactions. Also the interaction strength is usually much larger than the direct exchange interaction between the two magnetic ions. A typical example is MnO as illustrated in Figure 1-10. For III-Mn-V compounds, it is known that superexchange will
result in antiferromagnetic interactions between Mn ions that were positioned on nearby cation sites (e.g., Mn$_{Ga}$).

(iii) **double-exchange**, the mechanism was proposed by Zener in 1951[70] which also involve the role of an intermediate non-magnetic atom between two magnetic ions. The interaction occurs when the two magnetic ions have different number of electrons in their outer-orbitals (i.e., different valence charges), and those electrons hop from one of the magnetic states through the non-magnetic atom to the other magnetic ion. Since the process of electron transfer favors parallel spin alignment (increases the hopping probability) and Hund’s rule has to be obeyed, the spin-state of the transferred electron that arrive at the same outer-orbital from one magnetic state to the other remains the same and promotes ferromagnetic ordering of the inner shell electron spins. An illustration where the electron in the $eg$ state moves from Mn$^{3+}$ through the oxygen 2$p$ orbital to the Mn$^{4+}$ in a 180 degree Mn$^{3+}$(d$^4$)-O-Mn$^{4+}$(d$^3$) configuration and promotes ferromagnetic

![Figure 1-10: Illustration of MnO as an example for superexchange interaction.](image-url)
coupling between the two $t_{2g}$ states was shown in Figure 1-11. For the III-Mn-V magnetic compounds, a modified version of the double-exchange mechanism was proposed in which the Mn acceptor states form an impurity band with a mix $spd$ characteristic. The electron hopping conduction and Mn-Mn exchange coupling were realized within this impurity band. This model is often believed to be applicable in the case of low-Mn doped (Ga,Mn)As and wider band-gap III-Mn-V materials.[15] We would like to make remark here that there are experimental evidence that even in highly-doped metallic (Ga,Mn)As the conduction can be in the impurity band,[71] therefore a modified double-exchange model may be important for the origin of ferromagnetism in (Ga,Mn)As.

Figure 1-11: Illustration of an example Mn$^{3+}(d^4)$-O-Mn$^{4+}(d^3)$ that shows how the double-exchange mechanism promotes ferromagnetism.

(iv) kinetic-exchange or indirect-exchange interaction usually occurs in systems with partially-filled $d$-shell or $f$-shell localized moments, where the coupling is mediated
by s-band or p-band itinerant carriers.[72] Two scenarios were proposed according to Bhattacharjee et al.[73] and Dietl[74], where these local magnetic moments can either perform ferromagnetic coupling with the band electrons from the same lattice site through direct-exchange, and/or go through antiferromagnetic interaction that is caused by hybridization between the band electrons on neighboring lattice sites and the localized moment. The spin of the band electrons are polarized at a single site and eventually propagate to other lattice sites which induces itinerant spin-polarized carriers. In the case of a weak kinetic-exchange (e.g., when the spin-polarization of the band carriers are weak such as at temperatures close to the Curie temperature), the RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction sets in, where the interaction range is relatively long and the strength oscillates between positive and negative along the length scale of the band’s Fermi wave vector as shown in Figure 1-12. Therefore the interaction can be either ferromagnetic or antiferromagnetic depending on the spatial separation of the localized moments.[15]
We would like to comment here that the kinetic-exchange model was originally proposed by Zener in 1951 for transition-metal ferromagnets, and the RKKY model of indirect coupling between $d$-shell Mn magnetic moments mediated by spin-polarized itinerant hole-carriers was revisited by Dietl et al. in 1997 to explain the ferromagnetism in diluted magnetic semiconductors.[75] The main difference between III-Mn-V diluted magnetic semiconductors such as (Ga,Mn)As and the initial assumptions of Dietl’s model for Mn-doped IV-VI and II-VI DMS is that the substitutional Mn ($\text{Mn}_{\text{Ga}}$) on Ga site is simultaneously an acceptor and a source of magnetic moments. Nevertheless, this mechanism is known to play a very important role in the ferromagnetism of (Ga,Mn)As and other III-Mn-As/Sb compounds.

Recall that in Figure 1-8, we have adopted a simple picture of carrier-mediated ferromagnetism where we stated that the hole-carriers will interact and align anti-parallel
with the spin 5/2 Mn moments (assuming Landé factor $g = 2$). The statement originated from the identified fact that the substitutional Mn (MnGa) acts as a moderately shallow acceptor in GaAs, where the band gap is 1.52 eV (which is confirmed by STM and EPR/IR spectroscopy measurements). Note that the elements in (Ga,Mn)As have the nominal atomic structures, Ga: $[Ar]3d^{10}4s^2p^1$, Mn: $[Ar]3d^54s^2$ and As: $[Ar]3d^{10}4s^2p^3$. Therefore, the top of the valence band in the GaAs host is dominated by the 4p orbitals that weighs more heavily on the As site than Ga. In a straightforward physics picture shown in Figure 1-13, we could assume that the filled Mn $d$-shell spin-down states are deep in the valence band and the empty Mn $d$-shell spin-up states is high above the Fermi level in the conduction band, hybridization (which is defined as level repulsion between like-spin states) induces a splitting of the spin-up and spin-down states of the valence band $p$-orbital. The separation lifted the spin-down $p$-orbital states above the spin-up states to lower the system energy, and therefore the “$p$-$d$ hybridization” induces antiferromagnetic coupling between the valence-band states and the localized Mn moments as illustrated in Figure 1-13. This same picture can be easily converted to the viewpoint of “hole-carriers” in diluted magnetic semiconductors which undergo antiferromagnetic coupling with localized Mn moments. In addition, we are able to rule out the direct exchange between the holes and the localized Mn $d$-orbital since the MnGa and As atoms are positioned on different sublattices and the interactions are relatively weak compared to the $p$-$d$ hybridization. The exchange energy of the carrier-carrier interactions is also negligible.[15]
For a complicated magnetic system such as (Ga,Mn)As, the strategy to develop a useful and predictive model of ferromagnetism relies on good fits of partial-phenomenological assumptions to model Hamiltonians, as well as taking the right theoretical approaches. We will not go into the detailed discussion of the strength and weaknesses of different calculations associated with various theoretical approaches, such as the *ab initio* (first-principle) calculations, microscopic tight-binding models, $\mathbf{k}\cdot\mathbf{p}$ effective Hamiltonian theories and impurity-band and polaronic models, but leave it to a more detailed review on the theory of III-Mn-V magnetic semiconductors that can be found in reference [15].
1.6 Thesis overview

In the content of this thesis, we will present our research work on the carrier-mediated ferromagnetic semiconductor (Ga,Mn)As and other III-Mn-As compounds. The objective is to understand and improve the material properties of (Ga,Mn)As, as well as to search for new materials in this class. We start out by identifying a few key issues of interest in the field that we can perhaps address as experimentalists. For example, one important question which has a direct impact on the criteria for selecting a valid model to describe the origin of ferromagnetism in (Ga,Mn)As is whether the valence-band electrons (holes) are itinerant or bounded. Another is how the system changes from metallic to insulating phase with doping. Since our current understanding of (Ga,Mn)As was built largely upon the metallic phase of (Ga,Mn)As with relatively high Mn-doping, it is extremely interesting to study the important and unexplored regime of insulating (Ga,Mn)As where the onset of ferromagnetism takes place.

In this chapter, we have explained the motivation of this thesis research and compared the strength and weakness of candidate materials for semiconductor spintronics using the selection criteria we have listed in section 1.3. A brief introduction on the ferromagnetic semiconductor (Ga,Mn)As was presented.

In the next chapter, we will give a brief overview of the general experimental techniques that have previously been applied to understand the electrical, magnetic and structural properties of (Ga,Mn)As, and then focus on the details of the important techniques that were utilized for our own research work, as well as the instrumentation that was built in the laboratory for our research.
In Chapter 3, we will present our work on how we have rejuvenated the effectiveness of thermal annealing, which can enhance the Curie temperature and electric conductivity of (Ga,Mn)As, by applying nanolithographic techniques to fabricate nanometer-scale wires. This was performed on GaAs/(Ga,Mn)As/GaAs heterostructures, which can be part of a design for potential spintronic devices. Systematic studies on the annealing efficiency as a function of the wire width and the lateral out-diffusion mechanism of Mn interstitial defects were presented.

In Chapter 4, we will report our recent work on how we probed the physical parameters required to induce ferromagnetism in the extremely diluted limit of Ga_{1-x}Mn_xAs (x \leq 0.015). Our electric and magnetic measurements will confirm the existence of an insulating ferromagnetic phase of (Ga,Mn)As, and reveal that the hopping energy and localization of hole-carriers critically determine the onset of ferromagnetism in this insulating system, regardless of the carrier density or the Mn impurity level.

In Chapter 5, we will discuss our preliminary study on the magnetic properties of a series of novel quaternary ferromagnetic (In,Al,Mn)As/(In,Ga,Mn)As superlattices (SLs) grown on semi-insulating (100) InP and its dependence on the thickness ratio of closely lattice-matched constituents, wherein the Mn impurity density (~ 11 atomic %) is fixed throughout the SL periods.
1.7 References


3. e.g., Toshiba (Japan) and Philips Research Laboratories (Netherland).

4. Moore had predicted in 1965 (and later proven to be true) that the number of transistors or data density on each square inch of integrated circuits typically doubles every 12 to 18 months. The same growth momentum applies to the magnetic storage industry discussed here.


6. Freescale Semiconductor (Motorola) marketed the first 4-megabit magnetic random-access memory (MRAM) in 2006.

7. Hitachi Global Storage Technologies (previously IBM Storage Technology Division) was formed through the combination of Hitachi’s and IBM’s hard disk drive businesses.


70. C. Zener, Phys. Rev. 82, 403 (1951).


Chapter 2

General Experimental Techniques

Over the past decade, the attractiveness of magnetism and semiconductor characteristics combined in the ferromagnetic semiconductor (Ga,Mn)As and other III-Mn-As compounds have led to extensive research efforts in many different aspects, which can be categorized into these important directions: that is, to understand its electrical, magnetic, optical and structural properties. In this chapter, we will start out with a brief introduction of a variety of experimental techniques that have been applied to probe the material properties of (Ga,Mn)As that belong to or branch out from these categories and discuss their capability. Then we will provide more details on a few important techniques that were applied in this thesis research.

From the semiconductor materials point of view, the tunable electrical properties are perhaps its most important characteristics. Physical parameters of semiconductors such as the resistivity and optical reflectivity are highly-sensitive to the density and mobility of charged carriers (holes and electrons), and therefore identifying the carrier density of a doped semiconductor is always an important step of characterization. Methods for measuring the hole-carriers density of (Ga,Mn)As that were reported in the literature include the Hall effect measurement,[1][2] electrochemical capacitance-voltage (ECV) method,[3] and Raman spectroscopy.[4] Among these techniques, the ECV technique is capable of performing depth profile of semiconductor thin films by using a conducting electrolyte that simultaneously etches away the surface material and serves as
an electric contact; however, it possesses a destructive nature and cannot be operated at cryogenic temperatures since the electrolyte will freeze and lose conductivity. The determination of the carrier density by Raman spectroscopy utilizes the inelastic scattering of incident photons, where the energy shift of the photon is related to the interactions with different phonon modes in the material, and it is possible to avoid the anomalous Hall effect dominance observed in transport measurements. On the down side, the data analysis is relatively complicated and laborious. Other techniques used to measure the carrier concentration of GaAs include the infrared spectroscopic ellipsometry,[5] which is also a non-destructive technique that measures the plasma-edge reflectivity, but a detailed knowledge of the effective mass and band structure is required. Compared to these other techniques, the electrical Hall effect measurements have the advantage of simplicity and are often applied to determine the carrier density of conventional semiconductors with accuracy. Although the scattering of electrons from magnetic impurities (i.e., the anomalous Hall effect) inside magnetic semiconductors is always present, high magnetic field (> 10 Tesla) can be applied to eliminate the effect to obtain a precise carrier density which we will describe in section 2.1.

To study the magnetization of low magnetic signal materials such as (Ga,Mn)As, techniques that are frequently used include the magnetic circular dichroism (MCD) spectroscopy,[6] magneto-optical Kerr effect (MOKE) setup[12] and the superconducting quantum interference device (SQUID) magnetometer, which are all capable of performing sensitive temperature and magnetic field dependent magnetization measurements. The MCD spectroscopy employs the differential absorption of left and right circularly polarized light of magnetic materials upon the presence of an external
magnetic field, where the switching of the field alters the direction of local magnetic moments, which is related to the detected magnetic circular dichroism signals. Similar to the Faraday rotation, magneto-optical Kerr effect setup utilizes the change of the polarization of reflected light from surfaces of magnetic media to measure its magnetization, which results from the off-diagonal components of the dielectric tensor where those terms are associated with the localized electric and magnetic field. In general, these spectroscopic techniques probe the magnetization in the vicinity of the material surfaces and it is natural that the results obtained are very sensitive to the surface conditions such as undesired oxidized layers. Therefore, we have chosen the SQUID magnetometer as our primary technique to measure the magnetization of (Ga,Mn)As and other III-Mn-V magnetic thin films, which we will introduce in section 2.2. Miscellaneous techniques that have been reported to study the magnetization of (Ga,Mn)As include the AC susceptibility,[7] polarized neutron reflectometry,[8] hot-electron photoluminescence,[9] and ferromagnetic resonance.[10] In addition to the two magneto-optical techniques mentioned above, the far-infrared (FIR) ellipsometry is another important spectroscopic method that has been used to study the optical conductivity of (Ga,Mn)As, which gives important information on its band structure and effective mass when the carrier concentration is pre-determined.[11] Imaging and microscopy techniques that were reported to study (Ga,Mn)As include MOKE microscopy[12] which probes its magnetic domains, and scanning tunneling microscopy (STM) which reveals the spatial structure of the Mn-acceptor on GaAs.[13] Transmission electron microscopy (TEM) has also been used to determine the local concentrations of Mn interstitial and As antisite defects in (Ga,Mn)As.[14]
It is well-known in the literature that the Mn concentration, defect density and defect structure of (Ga,Mn)As and other III-Mn-As materials strongly influence the ferromagnetism of these systems. From the material synthesis point of view, it is often beneficial to have feedback on the detailed structural information of grown thin films so growth parameters could be adjusted accordingly. For example, X-ray diffractometry (XRD) is often used to measure the lattice parameters of (Ga,Mn)As,[15] and techniques such as secondary ion mass spectroscopy (SIMS), Rutherford backscattering (RBS), particle induced x-ray emission (PIXE) and electron probe micro-analysis (EPMA) have been used to determine the Mn dopant concentration in bulk (Ga,Mn)As. We will only discuss the principles of operation of XRD and SIMS in section 2.3 since they were applied in this thesis work.

2.1 Resistivity and Hall effect measurements

The electrical properties of doped semiconductors are their most fundamental and well studied characteristics, which have been exploited to design electrically functional devices in the modern electronics industry for many decades. The resistivity ($\rho$) and conductivity ($\sigma$) of a material was first introduced by Ohm’s law on an empirical basis as shown in Eq.(2.1), which describes how a current $I$ would flow through the material when an electric potential $V$ is applied to a sample with a resistance $R$.

$$I = \frac{V}{R} \quad \text{or} \quad R = \frac{V}{I} \quad (2.1)$$
If $A$ is the cross section area of a sample material through which the current flows, and $L$ is the longitudinal length, then Ohm’s law can be rewritten as

$$R = \rho \frac{L}{A} = \frac{1}{\sigma A} \quad (2.2)$$

Alternatively, the current density $J (= I/A)$ and an electric field $E$ that is applied to the sample can be derived into the form of

$$J = \sigma E \quad \text{or} \quad J = \frac{E}{\rho} \quad (2.3)$$

Therefore, the resistivity and conductivity are measures of how easily electrons propagate through a material under an external electric field.

The Hall effect, first discovered in 1879, is a consequence of the forces induced by an external magnetic field that act on moving charged particles driven by an electric field inside a conductor. In semiconductor materials, it is often used to determine the carrier density of the majority carriers and whether the materials are n-type or p-type. As we can see in the Hall effect measurement setup in Figure 2-1, force on a moving charge $q$ driven by an electric field $E$ in the presence of a magnetic field $B$ is given by

$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B}) \quad (2.4)$$

For a positively charged particle that travels along the +x direction with velocity $v$, there will be a net force that drives it towards the -y direction due to the magnetic field pointing in the +z direction, and similarly a negative charge traveling with the same speed in the –x direction will also move towards the –y direction.
As both positive and negative charges accumulate on the –y end of the sample and eventually reach equilibrium, the induced electric field $E_H$ along the +y and –y direction (termed the Hall field) for positive and negative charges respectively will balance the magnetic field term of the Lorentz force and yields

$$qE_y = qv_x B_z$$  \hspace{1cm} (2.5)

The Hall voltage ($V_H$) falling across the y-direction is by definition

$$V_H = E_H W$$  \hspace{1cm} (2.6)

Using simple algebra and the relations in Eq.(2.7) and Eq.(2.8), where $W$ and $d$ are the physical dimensions of the sample and $e$ is the magnitude of an electron charge, we can easily obtain the expression for $V_H$ in Eq.(2.9) by assuming the semiconductor is p-type.

$$V_H = v_x WB_z$$  \hspace{1cm} (2.7)
When performing these measurements, the carrier density is extracted from the slope of the Hall resistance as a function of the magnetic field, which can be expressed as

\[ V_H = \frac{I_z B_z}{e p d} \]  

(2.9)

However, in magnetic materials such as (Ga,Mn)As where the carrier scattering involves localized magnetic moments, the above mechanism alone cannot describe the measured Hall resistivity. Instead, the Hall resistivity is described by Eq. (2.11)

\[ \rho_{xy} = \rho_{xy}^o + \rho_{xy}^a = R_0 B + R_a (\rho_{xx}) M \]  

(2.11)

where the first normal Hall effect term \( \rho_{xy}^o \) is proportional to the applied magnetic field \( B \), and the Hall coefficient \( R_0 = 1 / p e \). The second anomalous Hall effect term \( \rho_{xy}^a \) is proportional to the macroscopic magnetization \( M \) of the sample.[1] The origin of \( R_a \) is still under debate and proposed mechanisms such as the “skew scattering” or “side-jump scattering” have predicted that \( R_a \propto \rho_{xx} \) or \( R_a \propto \rho_{xx}^2 \) respectively, where \( \rho_{xx} \) is the longitudinal resistivity.[16] In (Ga,Mn)As, \( R_a \) is found to be proportional to \( \rho_{xx} \) based on comparisons between the magnetization and magneto-transport results.[17] Therefore contributions of the anomalous Hall effect term can be neglected at high magnetic fields (> 10 Tesla) where the longitudinal resistivity approaches a constant value and the
multiple of \( R_a(\rho_s)M \) is a constant that no longer affects the slope of \( R_H(B) \), or at temperatures well above the Curie temperature (T\(_C\)) such that the net magnetization is zero. The hole-carrier density of (Ga,Mn)As can then be extracted from the slope of \( R_H(B) \) similar to the normal Hall effect measurements, except the data should be taken from the high magnetic field part or at temperatures well above T\(_C\).

To perform the temperature and magnetic field dependent transport measurements (resistivity and Hall effect), we have used commercial cryostats (Quantum Design PPMS) to control the temperature of the sample between \( T = 2 \text{ K} - 400 \text{K} \) and magnetic field up to 14 Tesla; the electronics of the PPMS were used to measure samples with longitudinal resistance smaller than 1 M\( \Omega \). For highly-resistive samples such as low Mn-doped GaAs where the resistance can reach above 1 G\( \Omega \), we have set up external electronics dedicated for this purpose as described in section 4.2. To study the transport properties of (Ga,Mn)As/GaAs and other magnetic semiconductor thin films, hall bars with precisely defined geometry (e.g., Figure 2-2) were patterned using conventional photolithography techniques; annealed indium was used to create Ohmic junctions between the sample and gold wire leads to the input and output of external I-V source-meters. Details of the sample preparation procedure were listed in Appendix B.
2.2 Magnetization and superconducting quantum interference device (SQUID)

Due to the diluted magnetic impurity level of the III-Mn-As semiconductor compounds, the magnetic moments in each unit volume of the material is significantly lower compared to ferromagnetic metals such as Fe, Co or Ni. Magnetization studies therefore rely on very sensitive magnetometers such as the superconducting quantum interference device (SQUID) magnetometer, which utilizes Josephson junction(s) that can in principle detect the magnetic flux quantum $h/2e$ ($h$: Planck’s constant, $e$: the magnitude of an electron charge).[18] The Josephson junction is a device where two pieces of superconductors are separated by a thin insulating layer. When an AC voltage is applied to the two superconductors, a DC current will flow through the insulator proportional to the sine of the phase difference between two sides of the insulator. The SQUID is composed of a ring of superconductor interrupted by one, two or more Josephson...
junctions as shown in Figure 2-3, and when a small magnetic dipole moves vertically through the center of ring, the change in the magnetic flux $\Phi = \oint B \cdot d\vec{a}$ induces a period of voltage variation ($V$) as described by Faraday’s law:

$$V = \oint E \cdot d\ell = -\frac{\partial \Phi}{\partial t}$$

(2.12)

The flux in the superconductor ring is quantized and the current density tunneling through the Josephson junctions is related to the phase difference between the current on its two sides, except that this phase difference is now dependent on the magnitude of the field induced by the magnetic dipole.

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Figure 2-3: Illustration of a superconducting quantum interference device (SQUID).
These voltage oscillations can then be used to detect the magnetic signal change in multiple units of the flux quantum $\hbar/2e$ which is approximately $2 \times 10^{-15}$ Tesla*m$^2$, though in reality the noise level limits the sensitivity. To study the magnetization of our diluted magnetic semiconductor samples, we have used commercial SQUID magnetometers (Quantum Design MPMS) which are capable of detecting magnetic signals as low as $1 \times 10^{-7}$ emu when operated in the DC (static) mode. The magnetization of our samples can be measured between $T = 1.8$ K – 400 K and at magnetic fields up to 7 Tesla. The DC mode indicates that the sample travels at a constant speed through the sensing coils of the SQUID magnetometer during the measurement, and the output (voltage) signal was fit to an idealized form for a magnetic dipole to determine the sample magnetization.

In the III-Mn-As carrier-mediated ferromagnetic systems such as (Ga,Mn)As, the Curie temperature ($T_C$) is most commonly determined by its temperature dependent magnetization $M(T)$, where $T_C$ is defined as the lowest temperature with zero magnetization or the temperature with the steepest descending slope. For high-$T_C$ metallic (Ga,Mn)As samples, the characteristic peak observed in the temperature-dependent resistivity is also a useful indication of $T_C$.[19][20] To determine ferromagnetism, a hysteresis loop has to be observed at temperatures below $T_C$ in the field-dependent magnetization data $M(H)$. The Hall effect measurements can also be used to effectively measure $M(H)$ at low magnetic fields when the normal term is negligible compared to the anomalous term [see Eq.(2.11)], which makes $R_H \propto M$.[21]
2.3 X-ray diffractometry (XRD) and secondary ion mass spectroscopy (SIMS)

In this section, we will introduce the basic principles of the X-ray diffractometry (XRD) and secondary ion mass spectroscopy (SIMS), which were applied in this thesis work to assist the synthesis of III-Mn-As thin films and to determine their Mn dopant concentration respectively. For materials synthesis using molecular beam epitaxy (MBE) growth, it is very important to find the ideal conditions (e.g., element flux ratio) so that the growth layer can have the right composition and lattice parameter. When the synthesized thin film is lattice-matched to the host substrate wafer, such as (Ga,Mn)As on GaAs, or (In,Ga,Mn)As and (In,Al,Mn)As on InP, these high crystalline quality samples will often have better controlled electric and magnetic properties. In Chapter 5, we have used XRD to calibrate the growth parameters of (In,Al,Mn)As and (In,Ga,Mn)As thin films so they can be grown lattice-matched on semi-insulating (001) InP substrates using MBE.

The X-ray diffractometry measurement in its simple 1-dimensional form is an application of the Bragg’s law. When a parallel array of X-ray beam with wavelength $\lambda$ bombards an evenly spaced crystal array with lattice spacing $d$ at an incident angle $\theta$, the phase difference between the diffracted x-ray beams from two adjacent layers of the surface (as shown in Figure 2-4) must meet the conditions of Eq.(2.13) to induce a constructive interference, which was described by Bragg in 1912.

$$n\lambda = 2d \sin \theta \ , \ n \in \mathbb{N}$$  \hspace{1cm} (2.13)
In a real 3-dimensional crystal structure, the lattice structure is much more complicated than Bragg’s ideal case, and will have to be represented in the vector form of the reciprocal space. We will not go into the detailed applications of the XRD such as diffractions from powders and amorphous materials, or consider the imperfections of crystals since those topics are beyond the scope of this thesis work, but limit our discussions to the concept of Ewald construction which is essentially Bragg’s law in 3-dimensional vector form. The Ewald sphere (presented as a circle) in the reciprocal space with a radius of \(2\pi / \lambda\) is illustrated in Figure 2-5, where the solid nodes represent the reciprocal lattice of a given crystal structure; vectors \(k\) and \(k^*\) denote the incident and diffracted beam respectively, and \(G = k^* - k\) is a reciprocal lattice vector. Calculations based on simple geometry in the reciprocal space indicate that \(G\) can be represented by \(k\)

\[
G = 2|k|\sin \theta = 2(2\pi / \lambda)\sin \theta
\]  

(2.14)
Assuming that node B is an arbitrary reciprocal lattice point “hkl” and \( d_{hkl} \) is its real space position vector, then by definition we get

\[
G = \frac{2\pi}{d_{hkl}}
\]  
(2.15)

Since Eq.(2.14) and Eq.(2.15) represent the same vector G, we can prove that Eq.(2.16) is equivalent to the Bragg’s law

\[
\lambda = 2d_{hkl} \sin \theta
\]  
(2.16)

In fact, for any reciprocal lattice that satisfies \( k^* = k + G \), that is, when the Ewald sphere overlaps with any one of these nodes, a diffraction beam is formed and accounts for the diffraction of X-rays from perfect crystals. More details on the applications of the X-ray diffraction can be found in reference [22].

Figure 2-5: Illustration of the Ewald sphere (presented as a circle).
In the following, we will introduce the secondary ion mass spectroscopy (SIMS), which is one of the most sensitive techniques that can perform compositional analysis of bulk materials with the detection limit of parts per billion (ppb).[23] In Chapter 4 of the thesis, we have used commercially available SIMS to determine the dopant concentration of very low Mn-doped GaAs as illustrated in Figure 2-6. The basic operating principle of SIMS is to bombard the sample species with highly energetic (up to 50 keV or even higher) ion beams which will eject or sputter atoms from the bulk material. A small portion of these atoms will leave the material surface with either positive or negative charges which are referred to as the “secondary ions”. These collected secondary ions are then analyzed by very sensitive mass spectrometers, which utilize the mass-to-charge ratio under the presence of a magnetic field to identify their atomic masses. Quantitative elemental and compositional information could then be obtained.

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**Figure 2-6:** Schematic of a secondary ion mass spectrometer (SIMS).
The main advantage of the SIMS analysis is its high sensitivity depth profiling capability and broad range of signal sensitivity (larger than six orders of magnitude). On the down side, sputtering of the specimen to create secondary ions is a destructive and irreversible process. In general, a proper selection of the ion sources is important to the sensitivity of SIMS. Broad beam sources such as Cs$^+$ and O$^-$ are commonly used for electronegative and electropositive elements respectively, while higher spatial resolution work requires liquid metal ion sources (e.g., Ga$^+$) since they can be focused to generate smaller beam diameters. For our low Mn-doped GaAs samples, Cs$^+$ ion beam sources were used to obtain the best results, which is in agreement with a recent literature report.[24]
2.4 References


Chapter 3

Nanoengineered Curie Temperature in Laterally Patterned Magnetic Semiconductor Heterostructures

The III-V ferromagnetic semiconductor (Ga,Mn)As is an extremely attractive material candidate for semiconductor spintronics[1][2] because of its carrier-mediated ferromagnetism and compatibility with the technologically mature III-V semiconductor technology. The magnetic properties of this material system can be manipulated through control of its electronic properties,[3][4][5] which suggests an advantageous approach to demonstrate new “proof-of-concept” devices.[6][7][8][9][10] Heterostructures derived from (Ga,Mn)As are therefore important bases for future large-scale spintronic circuits. In contrast to well-studied (Ga,Mn)As epilayers, where prescribed post-growth thermal annealing protocols[11][12] can effectively enhance the material $T_C$ to above 150 K,[13] the Curie temperature of (Ga,Mn)As with a thin GaAs capping layer (10 monolayers) added on top does not benefit from the effects of annealing.[14] This effect has now been understood through in-situ resistance monitoring of uncapped samples which show that the out-diffusion of Mn interstitial defects (Mn$_I$) toward free surfaces is the primary effect of annealing,[15] and the removal of Mn$_I$ from the bulk (Ga,Mn)As plays an important role in the enhancement of $T_C$ by reducing the compensation of hole-carriers as described earlier in section 1.4. As a result, the Mn$_I$ in heterostructures based on GaAs/(Ga,Mn)As/GaAs cannot be removed with efficiency since no free surface is present.
From the application point of view, it is essential that the effect of thermal annealing can be rejuvenated on these heterostructures so similar high $T_C$ characteristics can be acquired through annealing protocols. In this chapter, we will describe how we demonstrated the manipulation of the Curie temperature of GaAs-capped ferromagnetic semiconductor (Ga,Mn)As buried layers by patterning them into nanometer-scale wires using electron-beam lithography methods, where the sidewalls of the (Ga,Mn)As wires provide free surfaces for the out-diffusion of Mn$_I$.\[16\] In addition, these fabricated wires provide an alternative system to understand the rate-limiting factors of the Mn$_I$ removal in (Ga,Mn)As, and the results are compared to the vertical diffusion of Mn$_I$ observed in (Ga,Mn)As epilayers.\[15\] We also studied the time-dependence effect of annealing in a series of GaAs-capped (Ga,Mn)As wires fabricated with different widths, and the rate of defect diffusion along different crystalline directions.\[17\]

3.1 Fabrication of nanometer-scale wires on GaAs-capped (Ga,Mn)As

Our nanometer-scale wires were fabricated by electron beam lithography followed by liftoff and dry etching of a GaAs / (Ga,Mn)As (Mn content ~ 6%, thickness of 15 or 50 nm) / GaAs (10 nm) heterostructure grown by molecular beam epitaxy (MBE) on semi-insulating GaAs (001) wafers. The data shown in this thesis were taken from 50 nm thick magnetic layers, but the results are qualitatively the same for the 15 nm thick samples. Typical growth conditions were used for the ferromagnetic (Ga,Mn)As layer.\[13\] To lithographically pattern the wires, materials were first spin-coated with a bilayer of 400-nm-thick electron beam photoresist P(MMA-MAA) copolymer/PMMA
with molecular weight of 950. The desired patterns (and the width of the wires) were defined on the sample using direct-write electron-beam lithography at electron energy of 100 keV. After development of the resist in MIBK:IPA 1:1 solution, a metallic layer of either 45 nm Al or Al/Au was deposited on the sample using thermal evaporation. Using standard liftoff techniques, we then obtained metal wires that serve as a hard mask for the subsequent chlorine-based dry etching process. After dry etching, for samples with an Al mask, the metal layer is dissolved in CD-26 photoresist developer, leaving just the semiconductor nanowire; for samples with an Al/Au mask, the metal is retained on portions of the sample. We note that in the latter case the undoped GaAs capping layer serves as an insulator that prevents the shunting of current through the metal during the measurement.

Figure 3-1: FESEM images of (a) the layout of a four-probe resistance measurement for a 70 nm wide single wire patterned on GaAs / (Ga,Mn)As (50 nm) / GaAs (10 nm) and (b) 220 nm wide single wire under higher magnification.
Figure 3-1(a) shows a field emission scanning electron microscopy (FESEM) image of the designed layout for four-probe resistance measurement of a 70 nm wide wire. Figure 3-1(b) shows a more detailed feature of a 220 nm wide single wire under higher magnification. All the wires for our study were patterned on the same wafer along the [110] direction of the GaAs substrate for consistency, although no effect of crystalline anisotropy in resistivity is expected, as described below. Each set of wires (up to three wires) can be patterned on a 4 mm x 6 mm sample piece cleaved from the GaAs / (Ga,Mn)As (50 nm) / GaAs (10 nm) wafer.

3.2 Determining $T_C$ of fabricated single wires

We probe the ferromagnetic phase transition in patterned single wires using four-wire measurements of the temperature-dependent resistivity $\rho(T)$, where it has been well-established that $\rho(T)$ shows a well-defined peak close to $T_C$ in metallic (Ga,Mn)As, especially for those with $T_C < 100$ K. Though for higher $T_C$ samples, the peak can sometimes overestimate the ordering temperature ($\sim 10$ K), it still serves as a reasonable indication of $T_C$.[18][19] In our experiment, we relied on using the $\rho(T)$ peak to determine $T_C$ because it is difficult to separate the patterned wires of interest from the wider and larger (Ga,Mn)As contact leads to perform magnetization measurements; moreover, the magnetic moment of each nanowire is beyond the detection limit of our SQUID magnetometer. Note that with a four-wire measurement, we are only probing the resistance of the single wires, so the external (Ga,Mn)As contact leads do not contribute to the measured resistance as indicated in Figure 3-1(a). This layout is also the most
recent design used to fabricate the wires for our width dependent studies presented in section 3.5. An older version of the layout was previously used where part of the leads still contribute to the measured resistance value,\cite{16} so unintended contribution of the resistance was subtracted when converting to resistivity. The new layout resolved the complication.

To examine this method and to cross check the $T_C$ of as-grown and annealed GaAs-capped (Ga,Mn)As wafer substrates used to fabricate these wires, we have measured their temperature-dependent magnetization using commercial superconducting quantum interference device (SQUID) magnetometers (Quantum Design MPMS) and resistivity using commercial cryostats (Quantum Design PPMS). Sample magnetization was measured while warming in a 0.005 T in-plane field after precooling in 1 T magnetic field. The resistivity of the wires was measured at zero magnetic field using the van der Pauw technique. Figure 3-2(a) shows the magnetization as a function of temperature for both as-grown and annealed (~5 mm$^2$) pieces of a GaAs/(Ga,Mn)As(50nm)/GaAs heterostructure. As expected from earlier studies, the capping layer suppresses the effect of annealing, and in Figure 3-2(b), the temperature dependence of the sample resistivity shows no temperature shift in the peak of $\rho(T)$, confirming the result. In addition, there is no significant reduction in the resistivity of the sample with annealing, indicating that the electronic states were not altered. The annealing protocol used here was 190 °C in ultrahigh purity nitrogen gas (5N) for 5 hours.
3.3 Manipulation of $T_C$ using nanolithographic techniques

We first prepared two sets of 4 $\mu$m long wires with the width of 1 $\mu$m and 70 nm on GaAs/(Ga,Mn)As (Mn content ~ 6%, thickness of 50 nm)/GaAs (10 nm) substrates using electron-beam lithography process described in section 3.2. The resistivity of the
wires was measured using four-probe technique before and after 5 hours of thermal annealing at 190 °C in ultrahigh purity nitrogen gas (5N). In contrast to bulk pieces of GaAs-capped (Ga,Mn)As heterostructures and mesas patterned from it, these 70 nm and 1 μm wires patterned along the [110] GaAs crystalline direction have distinctive behavior after annealing.

Figure 3-3(a) shows the temperature-dependent resistivity of both as-grown and annealed 1 μm wires, where the temperature shift in the peak of ρ(T) for annealed wires indicates that annealing slightly increased the $T_C$ as well as the resistivity of the (Ga,Mn)As wires. These observations suggest that annealing has induced partial diffusion of the Mn interstitials from the bulk of GaAs/(Ga,Mn)As/GaAs wires to the lateral free surfaces on the sidewalls. Based on the diffusion coefficient ($D \sim 100 \text{ nm}^2/\text{hr}$ at $\sim 190$ °C) estimated for bulk (Ga,Mn)As thin films,[15] the 5 hour annealing time applied here is not enough to allow significant removal of Mn interstitials and a large increase in $T_C$. The small increase in the high temperature resistivity may be due to a change in the electronic states or the defect structures, for which we do not have an explanation at this point. However, a similar effect has been observed in previous studies of long term anneals at slightly higher annealing temperatures.[12] Figure 3-3(b) shows the prominent effect of annealing for the 70 nm wide wire, where an increase in $T_C$ of almost 50 K was accompanied by a significant decrease in the wire resistivity. These data strongly suggest an effective removal of Mn interstitials from the bulk of the (Ga,Mn)As nanowire through lateral diffusion. The time and length scales for Mn out-diffusion observed here ($\sim 35 \text{ nm in 5 hours}$) are consistent with the results of previous annealing studies using the same annealing temperature.[15]
To examine whether the diffusion of Mn$_I$ is dependent on the crystalline directions, four different nanowires of the same dimensions (70 nm wide) were patterned along the principal cubic directions ([110], [1-10], [100], and [010]) of (Ga,Mn)As. 

Figure 3-3: Temperature dependence of the (four-probe) resistivity of as-grown and annealed single wires which are (a) 1 μm and (b) 70 nm wide. Both sets of wires are patterned along the [110] direction. Note that the data for the annealed 70 nm wire in (b) are plotted using a different scale (axis on right hand side). Plot (c) shows the same measurements for four individual 70 nm wires patterned along different crystalline orientations. All wires are patterned from the same wafer used in Figure 3-2, and the annealing conditions are identical as well.
These nanowires were further annealed under the same condition as before (190 °C for consecutive 5 hrs). The temperature-dependent resistivity data are shown in Figure 3-3(c). We can conclude that, based on the processing and the low temperature annealing protocol (190 °C) used in this study, there is no noticeable variance in the Mn$_I$ diffusion along different crystalline directions.

3.4 Width dependence of annealing effects in (Ga,Mn)As nanowires

We have demonstrated that it is possible to manipulate the $T_C$ of (Ga,Mn)As buried layers by fabricating nanometer-scale wires in the previous section, and here we investigate the efficiency of defect removal for nanowires of different width, which can provide material processing guidelines for potential applications. The materials used to fabricate the wires with different width have the same structure as those used for the 1 μm and 70 nm wide wires, and were synthesized under the same conditions. For consistency, we have measured the remanent magnetization of as-grown and annealed (190°C, 5 hrs, N$_2$ gas flow ~ 1.5 scfh) pieces of these samples using SQUID magnetometers. The samples were precooled in 1 T magnetic field and measured while warming in a 0.005 T in-plane field. The results are shown in the inset of Figure 3-4(a), where the as-grown and annealed piece both show similar $T_C$ of ~ 66 K, identifying suppressed effect of annealing due to GaAs capping. The equivalence is confirmed in Figure 3-4(a) by the resistivity versus temperature data from 1 mm x 2 mm mesas patterned on the same as-grown and annealed pieces.
Figure 3-4: (a) Resistivity versus temperature (measured in van der Pauw geometry) of as-grown and annealed 1 mm x 2 mm mesa patterned on GaAs / (Ga,Mn)As (50 nm) / GaAs (10nm) heterostructures. The inset shows magnetization versus temperature for the same sample measured in a magnetic field of 50 Oe in-plane while warming after field cooling in 1 T field. The values of $T_C$ obtained from both measurements are consistent. (b) Temperature dependence of the resistivity of unannealed wires, patterned from the same sample. (c) The temperature dependence of the resistivity of the same wires after six one-hour annealing.
We then fabricated wires of widths 1 μm, 420 nm, 220 nm and 120 nm using the layout designed for four-probe resistivity measurements. We measured the temperature-dependent resistivity, ρ(T), of all the wires and then annealed for an hour at 190 °C in flowing N2, and then measured again, and then annealed again for another hour. This cycle was repeated for 6 hours of total annealing time, but the samples degraded during a longer anneal which was attempted after 6 hours, and became unmeasurable. Typical data are shown in Figure 3-4(b) and 3-4(c) for the wires as-grown and annealed for 6 hours total.[20] Compared to the results for the macroscopic pieces of sample [Figure 3-4(a)], there is a significant effect of annealing on the nanowires. The increase in $T_C$ after annealing is almost 45 K for the 120 nm wire, indicating that annealing has efficiently removed MnI towards the lateral free surfaces. Although we have no explanation for the slightly increased resistivity in our set of annealed wires compared to the unpatterned as-grown sample, similar effects have been observed in conditions such as higher annealing temperatures and longer annealing times.[11][12] The monotonically decreasing resistivity with the wire width of “as-grown” samples as observed in Figure 3-4(b) could be attributed to the dry-etching process to etch out designed features on the wafer surface, since accelerated particles that bombarded on the edge of the wires can cause localized annealing effects on wires of different width. When the heat cannot be dissipated with efficiency, and assuming the heat conduction path decreases with the wire width, thinner wires will suffer from more severe and unintended annealing.

In Figure 3-5(a) and (b), we show the annealing time dependence of $T_C$ and conductivity at 300 K. Note that after 6 hrs of annealing, the increase in $T_C$ for the 120 nm wire is three times of the 1 μm wire; at the same time, the resistivity at the ρ(T) peak
is reduced to half of the value of the 1 μm wire, confirming the strong correlation between the enhancement of $T_C$ and decrease of resistivity, which was observed in uncapped epilayers.[12]

Figure 3-5: (a) Curie temperature (b) conductivity at $T = 300$ K and (c) rate of change of conductivity (measured at $T = 300$ K) for the different wires as a function of total anneal time. Each of these wires was measured as-grown and after every additional hour of annealing at 190 °C for up to 6 hrs. The rate change of conductivity was calculated based on the neighboring conductivity values of the corresponding annealing time.
Figure 3-5(c) shows the rate change of conductivity versus annealing time, indicating the Mn\textsubscript{i} diffuse out faster in a thinner wire in the initial stages of annealing, and the rate of Mn\textsubscript{i} removal decreases with annealing time. This is somewhat different from the results of in situ resistance monitoring in uncapped epilayers, in which the thinner layers had a slower rate of change of resistivity.[15] Due to the limited time interval of our measurements, we cannot rigorously test our data against the 1-dimensional diffusion model used in that study. On the other hand, the higher rate of change of the conductivity in thinner wires suggests that a more complex model would be required, perhaps due to the more complex lateral surface geometry presented by the wires as opposed to the smooth surfaces of (Ga,Mn)As epilayers. In this scenario, the increased surface area can provide a larger reservoir for the accumulation of Mn\textsubscript{i} and better choice of diffusion pathways. Another possibility is that the mechanism of vertical diffusion (along the growth direction of the thinner epilayers) is different from the lateral diffusion of the nanowires, which is most likely due to the availability of energetically favorable pathways (although different lateral directions appear to be equivalent[16]). This can be further studied using ab initio methods[15] to calculate the energy barrier for different diffusion routes, which is governed by intrinsic distribution of the defect structures.

3.5 Conclusion

In summary, we have demonstrated that nanolithography techniques allow the engineering of defect diffusion pathways and manipulation of the Curie temperature of
ferromagnetic semiconductor heterostructures. This method can also be used to selectively control the ferromagnetism of potential heterostructure devices by varying the dimension of its features. For example, areas with different $T_C$ and resistivity can be made on the same wafer substrate by writing different feature sizes. Smaller features will have a higher Curie temperature and electrical conductivity due to the efficiency of defect out-diffusion. We further studied the time-dependence of annealing for a series of GaAs-capped (Ga,Mn)As nanowires of varying widths. For different annealing times, our measurements indicate that decreasing the fabricated wire width monotonically increases the Curie temperature enhancement associated with annealing, as well as drop in the resistivity. These results are consistent with the lateral diffusion of interstitial Mn as we have shown in the previous section. Furthermore, the thinner wires show a higher rate of change of conductivity with annealing time, suggesting a more efficient removal of Mn interstitials in thinner wires.
3.6 References


20. The monotonically decreasing resistivity with wire width in the as-grown samples is possibly due to local heating during the dry etching process resulting in some annealing of the wires.
Chapter 4

Ferromagnetic to Paramagnetic Transition in (Ga,Mn)As

As we have mentioned in the previous chapters, (Ga,Mn)As is the most extensively studied ferromagnetic semiconductor because of its potential as a material candidate for spintronic applications,[1][2] where the carrier-mediated ferromagnetism can be fine-tuned with a precise control of the carrier density of the host semiconductor gallium arsenide (GaAs) and the manganese (Mn) impurity dopant level. On the other hand, due to the nature of these semiconductor materials, the ferromagnetism is at the same time very sensitive to the underlying defects such as the As-antisites and Mn interstitials created during the material synthesis. These defects situated in the GaAs host serve as double donors which not only compensate the hole carrier density, but strongly alter the localized hole carrier wave function distributed in the vicinity of the substitutional Mn (denoted Mn_{Ga}, Mn atom incorporated on the Ga site). Ferromagnetism can thus be quenched due to insufficient density of hole carriers.[3]

Based on the combined Zener model with mean-field theory,[4][5] where the $T_C$ of (Ga,Mn)As was predicted to be proportional to $x^*p^{1/3}$ ($x$: Mn concentration, $p$: carrier density), it is clear that the strategy to fabricate high-$T_C$ (Ga,Mn)As is to increase the effective hole carrier density and the Mn impurity level with additional dopants, as well as to minimize the undesired defects during the material synthesis or through post-growth processes[6][7][8][9][10][11][12]. Therefore over the past decade, the motivated interest and obstacles in synthesizing (Ga,Mn)As with $T_C$ exceeding room-temperature expanded...
into inspiring experimental and theoretical efforts towards understanding the origin of ferromagnetism in this complicated system where the interplay of carriers, impurities and defects dominates the macroscopic magnetic and electric behavior. As a consequence of the research interest that weighs heavily on pushing the high-\(T_C\) characteristics of (Ga,Mn)As,[10] our understanding of (Ga,Mn)As has been built largely upon its metallic phase in which the Mn content is relatively high (~ 3 to 8 atomic %).

Figure 4-1: The Curie temperature of Ga\(_{1-x}\)Mn\(_x\)As plotted as a function of the Mn concentration (\(x\)) where the data is taken from recent literature reports.
Figure 4-1 shows the Curie temperature of (Ga,Mn)As plotted as a function of the Mn concentration using published data from various pioneering research groups. These data indicate that the amount of Mn needed for high-$T_C$ (Ga,Mn)As is typically above 5% and additional Mn can be incorporated in the meta-stable (Ga,Mn)As until it reaches the Mn solubility limit ($\sim 10\%$).\[13\] On the other hand, as the Mn concentration decreases below 5%, $T_C$ typically decreases with the electric conductivity and (Ga,Mn)As eventually approaches insulating behavior ($d\rho/dT < 0$) as the Mn impurity level is reduced. Interestingly, we find that ferromagnetism seems to disappear at $\sim 1\%$ Mn doping.

In reality, despite the fact that an insulating phase of ferromagnetic (Ga,Mn)As in a very diluted doping limit ($< 2$ atomic $\%$) has been observed,\[14\] almost all theoretical models that discussed ferromagnetism in this material system employ a low carrier density limit ($\sim 1x10^{19} \text{ cm}^{-3}$) that falls in the metallic regime or near but slightly above the metal-insulator transition. Although theoretical attempts have been made to predict the Curie temperature and possible origin of ferromagnetism in this low Mn regime,\[15\][16][17][18] empirical results are needed to confirm the validity of these models. Beyond the fundamental interest in studying the crossover from ferromagnetic to paramagnetic phases in (Ga,Mn)As, any further understanding about the origin of ferromagnetism may shed light on how we could improve the strategy to fabricate high-$T_C$ (Ga,Mn)As. Therefore, it is extremely important that this regime of (Ga,Mn)As is fully explored.
To verify that an insulating phase of ferromagnetic (Ga,Mn)As does exist with low Mn doping, we probed the electric and magnetic properties of a series of Ga$_{1-x}$Mn$_x$As with decreasing Mn concentration (x), where x = 0.03, 0.023, 0.015 and 0.01 respectively. These samples are grown by molecular beam epitaxy (MBE) using a conventional method [10] where the substrate wafer is continuously rotated at 10 rpm during the epitaxial growth for material uniformity. The optimized arsenic flux used here was pre-

Figure 4-2: Temperature dependence of the magnetization and resistivity of (Ga,Mn)As with different Mn concentration (x), where in (a) x = 0.03 (b) x = 0.023 and (c) x = 0.015. These samples are grown in molecular beam epitaxy using the conventional wafer rotating method. $\rho(T)$ and $M(T)$ data curves are represented by open and closed symbols respectively.
calibrated in other controlled growth efforts (at 2.3% Mn) such that the As-antisite defects were minimized to achieve the highest-$T_C$ at a fixed Mn level. Figure 4-2 shows the temperature dependence of the resistivity $\rho(T)$ and the magnetization $M(T)$ along the [100] crystalline direction of these Ga$_{1-x}$Mn$_x$As epilayers, where in (a) $x = 0.03$, (b) $x = 0.023$ and (c) $x = 0.015$ (the $x = 0.01$ sample does not show any sign of ferromagnetism). Typical metallic behavior of Ga$_{1-x}$Mn$_x$As is observed in (a) and (b) where a characteristic peak always occurs in $\rho(T)$ near $T_C$ due to spin-disorder scattering.[19][20] The decrease in the Mn doping level from $x = 0.03$ to 0.023 leads to an increase in the resistivity by almost a decade, which confirms that the electronic properties are indeed very sensitive to the impurity dopants. Interestingly, we find in (c) that as the Mn doping was further reduced to 1.5 atomic % ($x = 0.015$), the sample resistivity increases by five orders of magnitude compared to the 3.0 atomic % ($x = 0.03$) metallic sample; insulating behavior ($d\rho/dT < 0$) is observed throughout the measured temperature range between 300 K and 5 K. Even more unusual, the characteristic peak is no longer observed near $T_C$ or at temperatures as low as 5 K. Other approaches taken to probe the existence of a peak near $T_C$ such as plotting the $d\ln(\rho)/dT$ versus $T$ and $d\rho/dT$ or their higher order derivatives did not show convincing results.

We have further annealed a Mn = 1.5% (Ga,Mn)As sample ($x = 0.015$) for 24 hrs in ultrahigh purity forming gas at 190°C as a comparison to the as-grown piece. The results are shown in Figure 4-3 where the temperature-dependent resistivity data reveal that annealing effects are almost negligible in this low-Mn doping regime; similarly, the magnetization data show that the $T_C$ and the concavity of the $M(T)$ curves are not affected, which is in agreement with the resistivity data and indicate that the defect
density and its distribution in the bulk structure are not altered. One possibility suggests that these low-Mn doped samples have a significantly lower Mn$\text{I}$ defect density compared to the highly-doped ones, which can be explained by a weaker competition for the substitutional sites (i.e., the Ga site) during the epitaxial growth among Mn atoms due to a reduced Mn flux. In short, we have confirmed the existence of an insulating phase of ferromagnetic (Ga,Mn)As with low Mn doping. In the following section, we will describe how we applied a new synthesis method to fine-tune the electronic structures of Ga$_{1-x}$Mn$_x$As with fixed x and use them to study the onset of ferromagnetism.

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Figure 4-3: Features of as-grown and annealed Ga$_{1-x}$Mn$_x$As (x = 0.015) near T$_C$, where the resistivity $\rho$(T) and magnetization $M$(T) data are plotted as a function of the temperature. Higher temperature part of the as-grown and annealed $\rho$(T) and $M$(T)data curves (up to 300 K) still overlap (not shown).
4.1 Low Mn-doped (Ga,Mn)As synthesized by non-rotated sample growth

To systematically study Ga$_{1-x}$Mn$_x$As in the unexplored regime of low Mn-doping (x < 0.02), we first had to overcome the difficulty of sample synthesis since it is very difficult to utilize only a minimum amount of magnetic impurity Mn and combine good defect control to introduce ferromagnetism in (Ga,Mn)As. In this section, we will introduce a special growth method using molecular beam epitaxy (MBE), where the wafer substrate is not rotated during the epitaxial growth so that the inherent geometry of the effusion cells as shown in Figure 4-4 creates a continuous variation of the As:Ga flux along the y-axis of a 2” wafer for every fixed Mn concentration. With the arsenic cell temperature fixed, an arsenic flux which varies by +/-50% across a 2” wafer gives unprecedented control over the As:Ga stoichiometry, and it is much simpler to generate a stoichiometric region in which the As-antisite and Mn interstitial (Mn$_I$) defects are minimized than if the conventional rotation method was used. This growth technique was then applied to synthesize 100 nm thick Ga$_{1-x}$Mn$_x$As thin films on top of 300 nm GaAs buffer on semi-insulating (001) GaAs wafers for x = 0.015, 0.0125, 0.010 and 0.0075. Here, the quoted Mn concentration values were calibrated with the reflection high-energy electron diffraction (RHEED) intensity oscillation measurements and secondary ion mass spectroscopy (SIMS) was used in assistance.[21] Details of the sample growth technique were reported elsewhere.[22]

From each of the x = 0.015, 0.0125, 0.010 and 0.0075 wafer, we cleaved 2” long strips (~ 4 mm in width) side-by-side and parallel to the y-axis (As-gradient direction) from the center part of the wafer and used them for transport, magnetization and SIMS
measurements. Smaller sample pieces (~ 3 mm x 4 mm) were then divided from each wafer strip into approximately 15 samples with continuously varied As:Ga stoichiometry. We also performed control measurements to ensure that the carrier density and the Curie temperature are almost identical for samples cleaved from neighboring strips with the same y-position (i.e., material properties are independent of the position along the x-axis). Therefore, we can accurately correlate the transport and magnetization data taken from these cleaved pieces by their center positions along the y-axis.\cite{23} In addition, the $T_C$ of every ferromagnetic sample piece with Mn $\leq$ 1.0 % was measured before being used for transport measurements to ensure data accuracy.

Figure 4-4: Schematic of the MBE effusion cells and how the inherent geometry can be used to create a continuous variation of the As:Ga flux across a non-rotated 2” GaAs wafer.
Due to the low magnetic signal and the highly-resistive nature of these low Mn-doped GaAs samples, the sample magnetization was characterized using commercial superconducting quantum interference device (SQUID) magnetometers (Quantum Design MPMS) as we have described in Chapter 2, while resistivity and Hall effect measurements were performed in commercial cryostats (Quantum Design PPMS) using four-probe techniques with pre-calibrated external circuitry built in-house to measure resistances up to 1 GΩ and above. We will describe in the following section the design principle of the setup for high resistance measurements, and how to avoid common errors in these types of measurements. For all low Mn-doped (Ga,Mn)As discussed in this chapter, the magnetization versus temperature data presented were measured while warming in a 50 Oe field after initial cool down to 2 K in 1 Tesla magnetic field. Magnetization data as a function of the magnetic field were measured at T = 2 K and above to check the existence of ferromagnetism, especially for samples with Tc below 15 K. For transport measurements, annealed indium was used to create contacts on the lithographically patterned (Ga,Mn)As hall bars. These contacts were tested and shown to be ohmic between 1 μA and 10 nA source current and from 2 K - 300 K.

4.2 High resistance measurement technique

In this section, we discuss the technical details of how to accurately measure the high resistance of our low Mn-doped GaAs samples (up to 1 GΩ and above) with the four-point probe technique, and we describe the high resistance measurement setup (HRMS) that we have built in-house. The purpose of setting up a more complicated four-
point probe measurement is to perform Hall effect measurements to obtain the carrier concentration (cm$^3$) of our highly resistive samples, which is beyond the capability of high precision electrometers (two-probe) that are commercially available.

Figure 4-5: Realistic circuit diagram of a four-point probe resistivity measurement technique.

Figure 4-5 (reproduced from reference [24]) shows a realistic circuit diagram of a four-point probe (Kelvin) resistivity measurement which includes contact resistances at each probe ($r_1$ through $r_4$), finite resistances between the real earth ground and the LO of
the voltmeter \((R_V)\) and the current source \((R_C)\), and the input resistance of the voltmeter \((R_{IN})\). \(R_2\) is the measured sample resistance.

In the case of high sample resistance where \(R_2\) is very large \((> 10^8 \, \Omega)\), there are a few issues that can create a large error in the measured resistance:

(i) Insufficient output power from the source current: a large compliance voltage is needed for the current source to supply a minimum current required to perform a reliable measurement. In the case when the load is much larger than \(M\Omega\) resistance, insufficient compliance voltage will lead to unstable source current (typically < 500 pA) and makes the leakage current issue severe.

(ii) The voltmeter must have a much higher input resistance \((R_{IN})\) than the load: when the order of \(R_2\) is comparable or larger than \(R_{IN}\), a large portion of the current will flow through \(r_2\), \(R_{IN}\) and \(r_3\) instead of \(R_2\). For example, if the load is in the order of 1 G\(\Omega\) then the input resistance should be at least three orders of magnitude larger (e.g. > 1 T\(\Omega\)) to ensure precision. Note that typical voltmeters were designed to measure resistance up to 20 M\(\Omega\), so the input resistance is only in the order of 1 G\(\Omega\) (e.g., HP 34401A digital multimeter) and not applicable for G\(\Omega\) range resistance measurements.

(iii) When the isolation (resistance) between the input LO of the voltmeter and its chassis \((R_V,\) chassis usually connected to ground) is comparable to the sample resistance, an AC current will flow from the LO terminal of the source current through the mounted sample to the LO of the voltmeter and back to the ground (this is referred to as the common-mode current error) which can cause an enormous error since the voltmeter is expecting a voltage drop between \(R_2\) instead of \(r_3\).
To resolve these problems, the differential four-point probe measurement technique can be applied as shown in Figure 4-6 (reproduced from reference [24]) where the two unity-gain buffers with very high input impedance substantially reduces the common-mode current flowing through $r_3$. These buffers can be two electrometers with unity-gain outputs, or more cost effectively a pair of high input impedance electrometer op amplifiers. In our HRMS, we have employed two high-Z unity-gain buffers assembled in the lab using commercially available electrometer op amps (Texas Instruments OPA129U). However, whenever the input voltage at probe #2 exceeds the buffer working range (13.8 V), it was replaced by a Keithley 6514 electrometer that can
operate linearly up to 21 V of voltage input at probe #2 before the unity-gain response saturates. In short, the HRMS is pre-calibrated and capable of measuring up to 1 GΩ resistance (and above) outside in the atmosphere, as well as inside the PPMS sample chamber where potential leakage current issues coming from the humidity, electrostatic interference and photo-induced excess carriers in semiconductors can be avoided.

For the highly-resistive low Mn-doped GaAs thin films, a stable current below 5 nA could be sourced by Keithley 2400 through the patterned hall bar geometry to perform resistivity and Hall effect measurements, provided that the samples were carefully mounted on epoxy-filled dip sockets for good electrical insulation and thermal conduction. In addition, the electrical insulation between any of the two pins on the dip socket measured by the Keithley 6514 electrometer gives a resistance value greater than 35 GΩ. Details about the HRMS electronics are described in Appendix B.

4.3 Effect of the As:Ga flux variation

As we have mentioned in section 4.1, by employing the special sample growth technique, the inherent geometry of the MBE effusion cells generates a continuously varied As:Ga flux impinging on different parts of a non-rotated substrate wafer. Therefore, three distinctive region of Ga1-xMnxAs (As-rich, stoichiometric and Ga-rich) were created in sequence along the decreasing As flux gradient direction (y-axis) on 2” GaAs wafers for every fixed Mn level as shown previously in Figure 4-4. Here we have used the x = 0.015 series of samples to show the overall effect of the As-flux variation to the samples along the y-axis, where the electronic properties of the samples were found
to be extremely sensitive to the As:Ga stoichiometry. For example, within the 40 mm region along the y-axis of the non-rotated wafer, the As-flux variation, which is smaller than +/- 50 %, caused the hole carrier density to vary by more than two orders of magnitude between the stoichiometric region and two other parts of the wafer as shown in Figure 4-7. The carrier density at T = 300K and the Curie temperature are plotted as a function of the sample position along the y-axis, and non-ferromagnetic samples are labeled $T_C = 0$ as a guide to the eye. In the As-rich region, excess As-flux enforced the formation of As-antisites and compensated the hole carriers from the substitutional Mn; while in the Ga-rich region, the solubility of Mn may be suppressed by the roughened group-III rich surface.[22] As a result, the stoichiometric region had the highest carrier densities due to sufficient Mn incorporation and minimum compensation from the As-antisite defects. Ferromagnetic samples (a) – (d) as labeled in Figure 4-7 occur in this region. We note that similar trend was observed in other series of samples with different Mn doping level ($x = 0.0125, 0.010$ and $0.075$), and the carrier density data shown here extracted from Hall effect measurements at $T = 300$ K are consistent with the results obtained from van der Pauw measurements at room temperature.[25] More detailed discussions about the effect of the As-antisite defects on the carrier concentration and the Curie temperature were reported in reference.[22]
In the rest of this section, we will try to shed light on the magnetic anisotropy of these low Mn-doped samples and the effect of the As:Ga compositional ratio, which is interesting and important for application purposes (e.g. magnetic domain stiffness for designing magnetic storage devices) as well as for fundamental reasons since there is currently no complete model that can fully explain the reorientation of magnetic easy axis.[26]

For the ferromagnetic (Ga,Mn)As samples (a) – (d) from the stoichiometric region, we have measured the remanent magnetization as a function of temperature along the principle crystalline axes [110], [1-10], [100] and [001] to probe the temperature

Figure 4-7: Effect of the As-flux variation along the y-axis of the x = 0.015 non-rotated (Ga,Mn)As wafer. $T_C$ and the carrier density extracted from Hall effect measurements at $T = 300$ K are plotted as a function of the relative position along the y-axis. Samples (a) – (d) are ferromagnetic. Non-ferromagnetic samples are labeled $T_C = 0$ to guide the eye.
dependent magnetic anisotropy. Measurements were performed in the same protocol as previously described, i.e. while warming up the sample in 50 Oe field after precooling in 1 tesla. The results are plotted in Figure 4-8 where the subfigures (a) – (d) represent the samples (a) – (d) with increasing As:Ga flux ratio respectively.

Figure 4-8: The subfigures (a) – (d) correspond to the Ga$_{1-x}$Mn$_x$As samples (a) – (d) cleaved from the stoichiometric region of the x = 0.015 series. The remanent magnetization was measured as a function of the temperature along the principle crystalline axes [110], [1-10], [100] and [001] at 50 Oe field.
Notice that the magnetic easy axis rotates from the in-plane to the out-of-plane [001] direction with increasing arsenic flux ratio. This is consistent with the trend observed in other series of lower Mn-doped samples ($x = 0.0125, 0.010$ and $0.0075$, data shown in Appendix A). Interestingly, the temperature dependent reorientation of the magnetic easy axis seems to be independent of the Mn concentration in this low-doping regime and always happens at a critical As:Ga flux ratio where any small amount of excess arsenic diminishes ferromagnetism. Note that, although the quoted As:Ga flux ratios were precisely calibrated, it has been difficult to accurately convert the As:Ga flux ratio to the actual As:Ga stoichiometry in Ga$_{1-x}$Mn$_x$As even with high resolution x-ray diffraction measurements and simulations.[22].

Figure 4-8 does, however, demonstrate how excess arsenic alone can sensitively alter the magnetic properties of Ga$_{1-x}$Mn$_x$As, which appears to be a universal behavior in these low Mn-doped samples. The “borderline behavior” where the magnetic easy axis reorients to the out-of-plane direction hints that perhaps excess As-antisite defects in Ga$_{1-x}$Mn$_x$As not only quenched ferromagnetism by compensating the hole carriers, but can either induce strain (which is relatively small and less likely) or change the shape of localized carrier wave function and cause the switching in the magnetic easy axis. Recent calculations on the agglomeration of As-antisites in As-rich GaAs using density-functional based tight-binding methods suggested that atomic bonds are expected to rearrange in the most energetically favorable way for each additional As-antisite added to the GaAs host.[27] Our measurements may be the first on Ga$_{1-x}$Mn$_x$As with $x < 0.02$, such that the effect of As:Ga ratio on the magnetization anisotropy is pronounced. These
data can perhaps be used to test theoretical models of the magnetic anisotropy of III-V magnetic semiconductors.[28][29][30][31]

4.4 Variable-range hopping conduction and hopping energy

In this section, we will discuss in brief the mechanism of variable-range hopping (VRH) conduction model proposed by N. F. Mott in the 1970s which nicely describes the transport phenomena of doped semiconductors as well as other material systems at low temperatures.[32] The hopping energy derived from this model can be used to characterize the phase boundary between ferromagnetic and non-ferromagnetic (Ga,Mn)As with low Mn-doping. In the following context, we describe the VRH model in terms of conduction electrons, although holes are the majority carriers in III-V magnetic semiconductors.

If we consider a system where electron-electron interactions are not present and the states at the Fermi level are localized, and by assuming that the carrier wave functions are localized in which \( \langle \sigma(E) \rangle = 0 \) at low temperatures (\( \sigma \) is the electric conductivity), the conduction mechanism for such systems is now known to be dominated by thermally activated hopping.[32] The term “hopping” used here is defined as an inelastic tunneling transfer of an electron between two localized electronic states centered at different locations.[33] According to the original idea of hopping for impurity conduction,[34] every time when an electron “hops” from one localized state to another, an energy exchange between a phonon and the hopping electron must happen and the wave functions of the initial and final state must overlap. By assuming that the electron has to
overcome an energy difference $E_1$ to hop to the nearest site where $E_1 \sim [a^3 N(E)]^{-1}$ (a is the localization radius of the states near the Fermi level), the hopping probability has the form of Eq. (4.1):

$$v_{ph} \exp\left(-2\alpha R - \frac{E_1}{k_B T}\right)$$  \hspace{1cm} (4.1)

Here the $v_{ph}$ depends on the interaction strength of the hopping electron with phonons and the exponential factor $\alpha = \xi^{-1}$ describes the approximated decay of the wave function where $\xi$ is the radius of the localization state. In the extreme cases when $\alpha$ is large, it leads to the percolation theory to find the most-favorable path in resistor network problems[35] or even multiple hopping.[36] For small $\alpha$, the situation is similar to an $E = E_F$ system close to the Anderson transition and each localized state overlaps another. The mechanism described in Eq. (4.1) is usually termed nearest neighbor hopping (NNH), and since it is beyond the scope of our discussion, we will not elaborate the content.

Figure 4-9: Schematic of hopping conduction. The electron (red circle) hops from a state below the Fermi energy to (i) a nearby state or (ii) a distant state where the energy difference between the initial state is minimized.
Based on the concept of “hopping” and the circumstances where the density of states at the Fermi energy $N(E_F)$ is finite and the states near $E = E_F$ are localized, Mott has proposed a different hopping mechanism in which the electron hopping is not limited to its nearest neighbor; instead, the electron chooses the most energetically favorable state within a variable hopping distance. The idea is illustrated in Figure 4-9 and is known as the variable-range hopping conduction model. More explicitly, Mott expected the VRH mechanism to be important at a sufficiently low temperature for systems with non-interacting electrons, and the electric conductivity would follow the formula of Eq.(4.2):

$$\sigma = A \exp \left[ - \left( \frac{T_0}{T} \right)^{1/4} \right]$$ (4.2)

Here the constant $A$ depends on the assumptions used for electron-phonon interaction, and the relation between $T_0$, $\alpha$ and $N(E_F)$ is given in Eq.(4.3),[32] where the $\alpha$ denotes the decay rate of a localized wave function decay $\phi \sim \exp(-\alpha r)$.

$$k_B T_0 = 1.5 \alpha^3 / N(E_F)$$ (4.3)

The energy $W$ required for an electron to transfer from a localized state below the Fermi level to one above is minimized through this type of hopping process. Assuming the hopping distance to be $R$, then $W$ can be written as

$$W \sim \left[ \frac{4}{3} \pi R^3 N(E_F) \right]^{-1}$$ (4.4)

Therefore the electric conductivity has the form of
In fact, the analytical expressions Eq. (4.2) and Eq. (4.3) can be obtained by maximizing the conduction probability, i.e. the Eq. (4.5). We note that there can be a slight variation in the value of the coefficient “1.5” in Eq. (4.3) based on different theoretical models and calculations reported in the literature.\cite{32,37} In our work, we have used Eq. (4.3) to derive the formula to calculate the hopping energy. The derivation is shown in Appendix A. For further reading on the topic of variable-range hopping and metal-insulator transition, references \cite{32} and \cite{37} are suggested.

4.5 Criteria for ferromagnetic and non-ferromagnetic phase separation

We will now shift the focus back to our original interest of probing the onset of ferromagnetism in (Ga,Mn)As, where systematic series of low Mn-doped (Ga,Mn)As samples synthesized by the special non-rotated technique described earlier in section 4.1 were used for the study. For each of our Ga$_{1-x}$Mn$_x$As wafers ($x = 0.015$, 0.0125, 0.010 and 0.0075), we have cleaved $\sim 15$ samples from the center part of the wafer along the direction in which the electronic properties were sensitively altered by the continuously varied As:Ga flux during the sample growth. Therefore, we have a complete set of (Ga,Mn)As samples with a broad distribution of the electronic properties in this low Mn-doped regime. Recall that in the Figure 4-7, we have shown that for the $x = 0.015$ series of samples there is no clear dependence of the Curie temperature on the carrier density ($\rho$)
regardless of the As:Ga flux variation. Now in Figure 4-10 we have plotted $T_C$ as a function of $p$ at $T = 300$ K using the data from all low-Mn samples, where each data point represents an individually cleaved piece of sample from wafer strips with different $x$ values. In contrast to previous predictions,[38] the carrier concentration does not have a dominant effect on the $T_C$ or ferromagnetism of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ with relatively low Mn-doping ($x \leq 0.015$). Here the carrier density $p$ at $T = 300$ K is derived from the slope of Hall effect measurements between -2 T and 2 T magnetic field, although there can be a +/- 50 % difference in the extracted $p$ value from higher magnetic fields (12-14 T) due to the anomalous Hall effect (AHE). In addition, the huge longitudinal resistivity of these samples at low temperatures contributed significantly to the measured Hall resistance and caused enormous errors even when the lithography alignment errors of the hall bars are minimized at the micron scale. Therefore, we were unable to obtain the carrier density at these low temperatures, and data taken at $T = 300$ K were used instead. Though we are unable to completely rule out the possibility that $T_C$ depends very differently on the carrier concentration extracted at $T = 300$ K and at lower temperatures (e.g. $T = 25$ K), we have found the trend of $T_C$ versus conductivity is very similar at different temperatures (Appendix A, Figure A-4), so we have chosen $p(T = 300$K) as a suitable representative parameter.
Figure 4-11 shows the logarithm of the resistivity as a function of $T^{-1/4}$ between 80 K to 25 K for cleaved (Ga,Mn)As sample pieces from the $x = 0.015$ series of samples, where every open and closed symbol represents a set of raw data from each individually cleaved piece of sample described in section 4.1. The straight lines of the same color are the corresponding linear fits performed in this temperature range. The single dotted line in the center of the graph was drawn to guide the eye which separates the ferromagnetic (FM) and non-ferromagnetic (non-FM) samples (as determined from magnetization measurements). For temperatures lower than 25 K, the resistance of these low Mn-doped GaAs samples can rise to be larger than a few GΩs and become difficult to measure precisely. Similar trends of the phase separation and quality of fits were observed in the

Figure 4-10: Curie temperature of low Mn-doped Ga$_{1-x}$Mn$_x$As ($x \leq 0.015$) samples plotted as a function of the carrier concentration at $T = 300$ K.
transport data sets from the $x = 0.0125, 0.010$ and $0.0075$ series of samples (plots not shown).

![Graph showing logarithm of resistivity as a function of $T^{-1/4}$ plotted between $T = 80$ K and 25 K with the data taken from the $x = 0.015$ series of Ga$_{1-x}$Mn$_x$As.]

Figure 4-11: Logarithm of the resistivity as a function of $T^{-1/4}$ plotted between $T = 80$ K and 25 K with the data taken from the $x = 0.015$ series of Ga$_{1-x}$Mn$_x$As.

We fit the temperature-dependent resistivity data from every set of Ga$_{1-x}$Mn$_x$As samples with different Mn concentrations to the variable-range hopping conduction model expressed in the resistivity format:

$$\rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/4}$$  \hspace{1cm} (4.6)
or more explicitly in the form of Eq. (4.7) where the extracted slope fit from every logarithm of the resistivity versus $T^{-1/4}$ curve corresponds to a specific $T_0^{1/4}$ value.

$$\ln \rho - \ln \rho_0 = T_0^{1/4} \ast T^{-1/4}$$  \hspace{1cm} (4.7)

The hopping energy ($W$) at $T = 25$ K for each ferromagnetic and non-ferromagnetic sample was then calculated by the formula

$$W = 0.466k_B T_0^{1/4} T^{3/4}$$  \hspace{1cm} (4.8)

which was obtained based on the VRH model. The derivation is shown in Appendix A.

We further plot the Curie temperature of these low Mn-doped (Ga,Mn)As samples in Figure 4-12 as a function of the (a) hopping energy at $T = 25$ K ($W_{T = 25}$) and (b) electric conductivity at $T = 25$ K ($\sigma_{T = 25}$). Non-ferromagnetic samples are labeled with $T_C = 0$ K for the guide of eye. The rainbow color gradient is used to indicate the carrier concentration. Note that the electric conductivity and the hopping energy are both represented by their 25 K values, since that is the lowest temperature with reliable resistance reading for most samples. Every data point shown here represents an individual piece of sample cleaved from the $x = 0.015, 0.0125, 0.010$ and 0.0075 series of Ga$_{1-x}$Mn$_x$As. These pieces are exactly the same as those used in Figure 4-10. Although not explicitly shown, the two highly-resistive non-FM data points with $W_{T = 25K} > 21$ meV in Figure 4-12(a) are extracted from higher temperature VRH slope fits ($T = 85$ K to 160 K) as a reference. These two data points do not have a corresponding conductivity value in Figure 4-12(b) since their sample resistance at $T = 25$ K is too large to be measured with our apparatus.
From these data, we find that regardless of the Mn concentration and the carrier density, the ferromagnetic and non-ferromagnetic samples are well separated by a critical value of the hopping energy, which is \( \sim 15 \) meV at \( T = 25 \) K. Figure 4-13 shows a zoomed in version of Figure 4-12(a) where the data points crossing over from ferromagnetic to non-ferromagnetic phases are enlarged for a more clear view. Thus, for any (Ga,Mn)As sample with hopping energy greater than 15 meV at \( T = 25 \) K, ferromagnetism will be quenched. We also observed a similar cut-off dependence of the

Figure 4-12: Curie temperature of low Mn-doped \( \text{Ga}_{1-x}\text{Mn}_x\text{As} \) \( (x \leq 0.015) \) samples plotted as a function of the (a) hopping energy and (b) electric conductivity at \( T = 25 \) K. Non-ferromagnetic samples are labeled with \( T_C = 0 \) K for the guide of eye. Rainbow color gradient is used to indicate the carrier concentration.
ferromagnetism on the electric conductivity in Figure 4-12(a), which indicates that ferromagnetism is strongly correlated to the localization of the hole carriers. In addition, there seems to be a lowest $T_C \sim 10$ K for all of our low-Mn samples (regardless of the Mn content), which may have fundamental implications for the origin of ferromagnetism in low Mn-doped (Ga,Mn)As.

![Figure 4-13: This is a zoomed in version of Figure 4-12(a) where the crossover from ferromagnetic to non-ferromagnetic phases is enlarged for a more clear view.](image)

Lastly, for all the ferromagnetic Ga$_{1-x}$Mn$_x$As samples, we have plotted $\ln(\rho)$ versus $T^{-1/4}$ in the full temperature range of our measurement ($T = 2$ K to 300 K) in
Figure 4-14. Interestingly, we observed a noticeable deflection in the slope of the curves at temperatures near $T_C$ in which the sign of the slope change can either be positive or negative. Although we do not have a clear explanation at this point, it seems quite probable that the deflection is a signature of the long-range magnetic ordering. Data for other lower Mn samples ($x = 0.0125$, $0.010$ and $0.0075$) are shown in Appendix A with the same deflection near $T_C$.

Figure 4-14: $\ln(\rho)$ versus $T^{-1/4}$ data shown between $T = 2$ K to 300 K for the ferromagnetic Ga$_{1-x}$Mn$_x$As samples in the $x = 0.015$ series. A deflection in the slope of the curves is observed at temperatures near the $T_C$ of each sample.
4.6 Conclusion and future work

We probe the onset of ferromagnetism in the low Mn doping regime of (Ga,Mn)As, which is a very interesting system where the crossover of ferromagnetic-paramagnetic and metal-insulator transition exist. Compared to other (Ga,Mn)As samples with similar Mn doping level, the resistivity of our ferromagnetic samples is several orders of magnitude lower,[39] which is attributed to an optimized control of the arsenic flux that reduces the As-antisites. Ferromagnetism is surprisingly preserved in samples with carrier density as low as \( \sim 1 \times 10^{17} \) cm\(^{-3}\). Our data indicate that neither the carrier concentration \( (p) \) nor its ratio versus the Mn impurity density as suggested[38] can be used as a standalone parameter to decide \( T_C \) or ferromagnetism. Instead, the strong correlation of the cutoff in ferromagnetism with critical values of the electrical conductivity and the hopping energy suggests that the localization of carrier wave functions dominate the exchange interaction strength for long-range ferromagnetic ordering. One possible scenario for ferromagnetism in this regime is that localization length of bounded carrier wave functions has to be large enough so each localized state overlaps with a large number of others, thus localized Mn-hole-Mn chains can form percolation paths and networks to create macroscopic magnetic homogeneity. We further suggest that the hopping energy is a more suitable parameter for determining ferromagnetism since it better describes the macroscopic effect of defects and disorder on the long-range interactions. Due to the difficulty in accurately estimating the density of states at the Fermi level, we are unable to calculate and compare the critical localization
length of the hole carriers in our low Mn-doped system with the average inter-spacing of Mn atoms inside (Ga,Mn)As.

Our finite temperature transport data show that this low Mn-doped system is well characterized by Mott’s variable-range hopping model, in which hopping energies are independent of the hole density. This model is also valid in Mn-rich systems with high compensation from As-antisite defects.[40] On these bases, our collaborators have developed a quantitatively predictive theory for impurity-band ferromagnetism in the low-doping regime of (Ga,Mn)As, which is not well described by the commonly-used mean-field theory focused on local carrier density. Calculations using microscopic double-exchange model found that the Curie temperature depends sensitively on the local fluctuations in the Mn-hole binding energy, which originate from the presence of disorder in the Mn distribution as well as As-antisite defects.

In summary, we have probed the criteria to induce ferromagnetism in (Ga,Mn)As within a very diluted doping limit ($\leq 1.5$ atomic %) by studying its magnetic and electronic properties. Our experimental data show conclusive evidence that the localization of hole-carriers plays an important role in the onset of ferromagnetism. In contrast to our previous understanding of highly-doped metallic $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ samples (where $x$ is typically above 0.02), neither the Mn concentration nor the carrier density had a dominant effect on the ferromagnetism. The strong “cut-off” of ferromagnetism at critical values of the hopping energy and electric conductivity clearly separates ferromagnetism and non-ferromagnetism, and suggests that overlapping of localized carrier wave function is essential for ferromagnetism to exist. We observed a minimum $T_C = 10$ K regardless of the dilution in all of these ferromagnetic low Mn-doped samples,
which may have fundamental implications in understanding the origin of ferromagnetism of the system. We also found that a deflection in the slope of \( \ln(\rho) \) versus \( T^{-1/4} \) curves always occurs at temperatures near \( T_C \), which is a signature of the magnetic ordering for insulating \( \text{Ga}_{1-x}\text{Mn}_x\text{As} \) with low Mn-doping (\( x \leq 0.015 \)). Our exploration confirmed the existence of insulating ferromagnetic \((\text{Ga,Mn})\text{As}\) and extended the understanding of the material to the insulating phase. These empirical results provide accurate parameters that can be used to examine the predictions of existing theories and serve as cornerstones for new models that describe the origin of ferromagnetism in diluted magnetic semiconductors. Directions for future work that may lead to important finding would include: (i) frequency-dependent capacitance measurements on similar low Mn-doped GaAs thin films synthesized on p-doped GaAs substrates, since this is one of the best techniques to study the characteristics of bounded hole-carriers (ii) optical spectroscopy measurements that could potentially give a better estimate of the density of state at the Fermi energy (iii) magnetic field dependence and the hopping conduction in anomalous Hall effect measurements. On the materials characterization part, it would be invaluable if the microscopic details of III-V magnetic semiconductors could be determined with precision (e.g., As:Ga stoichiometry and defect density in \((\text{Ga,Mn})\text{As}\)).
4.7 References

3. For a detailed review, please see the introduction chapter and the references wherein.
13. The solubility of Mn in the metastable (Ga,Mn)As is typically ~ 10 %, however, a recent report indicated that up to 20 % of Mn can be incorporated without the precipitation of MnAs clusters by lowering the growth temperature and reducing the film thickness to 10 nm. [e.g., S. Ohya, K. Ohno and M. Tanaka, Appl. Phys. Lett. 90, 112503 (2007)].
21. Due to the unavailability of an extremely low Mn-doped GaAs standard in the present industry, our SIMS data only reveal that our samples are less than 2.0 atomic % with +/-10 % uncertainty. However, we can accurately conclude (within 5%) that the nominal Mn = 1.5% sample has 40 % more Mn than the 1.25%, where their Mn content ratio = 1.42 +/-0.06.
23. Width of the transport samples on the y-axis can be 500 microns to 1 mm larger than the corresponding magnetic piece, so we want to ensure that the slight mismatch and the undetectable Mn content variation between the strips have negligible effect on $T_C$.
25. There can be a 50% difference between the carrier density extracted from van der Pauw and Hall effect measurements.


34. A. Miller and S. Abrahams, Phys. Rev. 120, 745 (1960).


Chapter 5

Quaternary Ferromagnetic Semiconductor Heterostructures grown on Indium Phosphide

In the previous two chapters, we have presented our work on improving and understanding the magnetic properties of (Ga,Mn)As, which has been the most attractive carrier-mediated ferromagnetic semiconductor for potential spintronic devices over the past decade. Based on the understanding of ferromagnetic (Ga,Mn)As and the material characteristics of other III-V compounds, such as indium phosphide (InP) in which the tunable bandgap is ideal for laser applications, there is substantial interest in introducing carrier-mediated ferromagnetism in these systems. One intuitive option is to incorporate Mn dopants into III-As semiconductor heterostructures such as InGaAs and InAlAs on closely lattice-matched substrates. These materials are physically appealing because of their technological maturity in optical applications, favorable wavelength for telecommunication, and potential for terahertz applications.[1] The flexibility in varying the composition and thickness ratio of InGaAs and InAlAs heterostructures creates a large degree of freedom for bandgap engineering,[2] which can be used to tailor the wavelength of InGaAs/InAlAs quantum cascade lasers,[3] as well as to control the electric properties of diodes based on InGaAs/InAlAs heterostructures that is applicable for high-speed FETs.[4]

In this chapter, we will report our preliminary studies of a novel ferromagnetic semiconductor (In,Al,Mn)As grown on semi-insulating (001) InP substrate by using molecular beam epitaxy (MBE).[5] Our primary interest focuses on the magnetic
properties of closely lattice-matched (In,Al,Mn)As and (In,Ga,Mn)As superlattices (SLs) grown on InP substrates, wherein the superlattice period is fixed and the thickness ratio of the constituents systematically varied. The effect of the SL thickness ratio on the Curie temperature, magnetization and magnetic anisotropy will be discussed.

5.1 Sample preparation

The quaternary (In,Al,Mn)As and (In,Al,Mn)As/ (In,Ga,Mn)As superlattices were grown on semi-insulating (001) InP substrates, where low-temperature non-equilibrium conditions were optimized for high crystal quality growth similar to the procedures used for ferromagnetic (Ga,Mn)As/GaAs. The element flux ratio (e.g., In, Al, Ga, As) of the MBE effusion cells were fine-tuned so that the lattice parameters of (In$_{1-y}$Al$_y$Mn$_x$)As and (In$_{1-z}$Ga$_z$Mn$_x$)As can match the InP substrate. This process was carried out by first growing InAlAs/InP and InGaAs/InP calibration samples and using X-ray diffractometry (XRD) to measure the offset between the (400) peak of the InP substrate and the InAlAs or InGaAs epilayers as indicated in Figure 5-1. When the peaks of the InAlAs or InGaAs were close enough to that of the InP substrate, the corresponding flux conditions were used to synthesize ferromagnetic (In,Al,Mn)As and (In,Al,Mn)As/(In,Ga,Mn)As superlattices which we will describe later. The synthesis details for these samples were reported in reference [5]. Similar to (Ga,Mn)As where post-growth thermal annealing increases its Curie temperature, we have found that annealing at 250 °C for 30 minutes in high purity forming gas (95% N$_2$ + 5% H$_2$, 1.5 scfh) is required to introduce ferromagnetism in our (In,Al,Mn)As samples.
For systematic study purposes, we have chosen two series of 30 nm thick samples (series A and series B), each with a total of five samples: (a) \((\text{In}_{1-y}\text{Al}_y\text{Mn}_x)\text{As}\) (b) \((\text{In}_{1-z}\text{Ga}_z\text{Mn}_x)\text{As}\) and (c) – (e) which represent three 10-period \((\text{In}_{1-y}\text{Al}_y\text{Mn}_x)\text{As}/(\text{In}_{1-z}\text{Ga}_z\text{Mn}_x)\text{As}\) SLs with different thickness ratio in each SL period, where in (c) \(\text{Al}/\text{Ga} = 21.6\text{Å}/7.2\text{Å}\) (d) \(\text{Al}/\text{Ga} = 14.4\text{Å}/14.4\text{Å}\) and (e) \(\text{Al}/\text{Ga} = 7.2\text{Å}/21.6\text{Å}\). Here the “Al/Ga” denotes the thickness of \((\text{In}_{1-y}\text{Al}_y\text{Mn}_x)\text{As}/(\text{In}_{1-z}\text{Ga}_z\text{Mn}_x)\text{As}\) in each SL period. The incorporated Mn \(x\) for all of the samples was calibrated by reflection high-energy electron diffraction (RHEED), where \(x \sim 0.11\). No noticeable differences were observed in the solubility of Mn between \((\text{In}_{1-y}\text{Al}_y\text{Mn}_x)\text{As}\) and \((\text{In}_{1-z}\text{Ga}_z\text{Mn}_x)\text{As}\) grown under the

Figure 5-1: The ω-2θ X-ray diffractometry scan of InAlMnAs / InAlAs / InGaAs / InP.
same growth conditions; nor were there any sign of MnAs clustering. Samples in both series were grown lattice-matched on a 100 nm InAlAs buffer on top of semi-insulating (001) InP substrates with an additional InGaAs (1 nm) layer capped on the surface to prevent the oxidization of the Al content. We further annealed these samples at 250 °C for 30 minutes in high purity forming gas to ensure they are ferromagnetic and to optimize the Curie temperature (T_C). This annealing protocol was also used in earlier studies of (In,Ga,Mn)As to increase T_C.[6] Note that the data shown in this thesis were taken primarily from series A which has better overall sample quality, with the series B grown later to confirm the principal results. Commercial superconducting quantum interference device (SQUID) magnetometers (Quantum Design MPMS) were used to measure the temperature (5 K - 300 K) and field (up to 1 T) dependence of the sample magnetization with the external magnetic field applied along the three in-plane principle crystalline axes [110], [1-10], [100] and the direction perpendicular to the magnetic thin film ([001]). The temperature and magnetic field dependent transport measurements were carried out in commercial cryostats (Quantum Design PPMS) and external electronics for highly-resistive samples as described in Chapter 4 and Appendix B.
To confirm the quality of the sample growth, high-angle annular dark-field transmission electron microscope (TEM) image of sample (e) was shown in Figure 5-2 with clear contrast of the 10-periods of (In,Al,Mn)As/(In,Ga,Mn)As superlattice. Thickness of (In,Al,Mn)As and (In,Ga,Mn)As in each period equals 7.2 Å and 21.6Å respectively.

5.2 Experimental results and discussion

We investigate the magnetic anisotropy of these quaternary heterostructures by measuring the field-dependent magnetization $M(H)$ along the principle axes of these
samples. Magneto-hysteresis data of 30 nm thick (In,Al,Mn)As and (In,Ga,Mn)As thin films at \( T = 5 \) K are shown in Figure 5-3(a) and (b) with the external magnetic field applied along the in-plane [110], [1-10], [100] and out-of-plane [001] crystalline directions. The magnetic easy axis (MEA) of the quaternary (In,Al,Mn)As and (In,Ga,Mn)As alloys are determined by their coercive field at \( T = 5 \) K, which is along the in-plane [110] and [1-10] direction respectively. The (In,Al,Mn)As epilayer also shows an apparent in-plane uniaxial anisotropy, which has been observed in (Ga,Mn)As,[8] though its origin remains unclear at this point.[9] The magnetization of both (In,Al,Mn)As and (In,Ga,Mn)As in the out-of-plane direction is relatively low, which is not unexpected because of the compressive strain effect from the buffer layer.

The same measurements are shown in Figure 5-3(c) – (e) for the other three 10-period (In,Al,Mn)As/(In,Ga,Mn)As superlattices with thickness ratio in each period of (c) Al/Ga=3/1 (d) Al/Ga=1/1 and (e) Al/Ga=1/3 [i.e., samples (c) – (e) as describe in section 5.1]. These three SLs exhibit superimposed magnetic characteristics inherited from the two constituents according to their volume ratio in each SL period. The MEA of sample (c) and (e) resembles (In,Al,Mn)As and (In,Ga,Mn)As respectively; while the MEA of sample (d) pointing in the [1-10] direction indicates that the larger effective magnetic moment per unit volume of (In,Ga,Mn)As dominates the magnetic anisotropy of equally spaced (In,Al,Mn)As/(In,Ga,Mn)As superlattices.
Figure 5-4 shows the temperature dependence of the magnetization $M(T)$ for the same series of samples (a) – (e), where each sample was first cooled down from room temperature to $T = 5$ K with 1 tesla magnetic field applied along its magnetic easy axes. The sample magnetization was then measured while warming up in 50 Oe. For the (In,Al,Mn)As [sample (a)] and (In,Ga,Mn)As [sample (b)], the Curie temperature is 20 K and 95 K respectively. Surprisingly, for the three SL samples, instead of seeing two
distinct transitions in each of the M(T) data curve, only one \( T_C \) is observed. Also the \( T_C \) of the SLs increases qualitatively with the volume ratio of \((\text{In},\text{Ga},\text{Mn})\text{As}\) and is distributed between the transition temperature of the two alloys (20 K and 95 K).

Figure 5-4: Remanent magnetization of \((\text{In},\text{Al},\text{Mn})\text{As}\), \((\text{In},\text{Ga},\text{Mn})\text{As}\) and three lattice-matched superlattices based on these two quaternary alloys [samples (a) – (e)] plotted as a function of temperature along the corresponding magnetic easy axis of each sample.

Similar behavior is observed in the effective ferromagnetic moment of the corresponding SLs, which is defined as the average magnetic moment contributed by each Mn ion. Their values are calculated by normalizing the magnetization of each sample along its MEA at \( T = 5 \) K and \( H = 0 \) T. For example, \((\text{In},\text{Ga},\text{Mn})\text{As}\) has 2.2 Bohr magneton (\( \mu_B \)) per Mn ion, which is 2.5 times larger than that of \((\text{In},\text{Al},\text{Mn})\text{As}\). We plot the \( T_C \) and the effective ferromagnetic moment as a function of the \((\text{In},\text{Ga},\text{Mn})\text{As}\)
composition in Figure 5-5, which clearly shows that these two parameters have a strongly correlated dependence on the volume ratio of (In,Ga,Mn)As in each SL period.

Figure 5-5: The effective ferromagnetic moment and Curie temperature plotted as a function of (In,Ga,Mn)As composition for the samples (a) – (e) as shown in Figure 5-4.

In our (In$_{1-y}$Al$_{y}$Mn$_{x}$)As, (In$_{1-x}$Ga$_{x}$Mn$_{x}$)As and superlattice samples, the incorporated Mn is relatively rich (x ~ 0.11), which indicates that the prediction of $T_C \sim x^* p^{1/3}$ ($p$: carrier density) based on the mean-field theory is applicable.[10] This would lead to a good estimate of the carrier density ratio of (In,Ga,Mn)As and (In,Al,Mn)As (denoted $P_{\text{InGaMnAs}}$ and $P_{\text{InAlMnAs}}$ respectively) using their Curie temperature

$$\frac{P_{\text{InGaMnAs}}}{P_{\text{InAlMnAs}}} = \left[ \frac{T_C(\text{InGaMnAs})}{T_C(\text{InAlMnAs})} \right]^3 = 55$$

(5.1)
This value will be used later as a comparison to show that the following assumption is valid: the Mn acceptor level is tied largely to the vacuum level, which is independent of the valence band edge of the host semiconductor InAlAs or InGaAs. That is, the Mn acceptor level $E_{A(\text{InAlAs})}$ of (In,Al,Mn)As deepens as the band gap increases as illustrated in Figure 5-6, which can be written as

$$E_{A(\text{InAlAs})} = E_{A(\text{InGaAs})} + \Delta E_{vb}$$ (5.2)

where $E_{A(\text{InGaAs})}$ is the acceptor energy of Mn-doped InGaAs known to be 0.077 eV.[11] \(\Delta E_{vb}\) is the valence band discontinuity between InAlAs and InGaAs. We can calculate the value of $E_{A(\text{InAlAs})}$ by finding $\Delta E_{vb}$, which is found to be approximately 30% of the total band gap discontinuity in the valence band.[12] The room-temperature band gaps of In$_{0.5}$Ga$_{0.5}$As and In$_{0.5}$Al$_{0.5}$As are 0.74 and 1.47 eV respectively,[13] which will give $\Delta E_{vb} = 0.22$ eV. Therefore $E_{A(\text{InAlAs})} = E_{A(\text{InGaAs})} + \Delta E_{vb} = 0.077 + 0.22 = 0.297$ eV.

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![Diagram](image.png)

Figure 5-6: Illustration of the Mn acceptor level in (In,Al,Mn)As and (In,Ga,Mn)As.
We now check if the carrier density ratio of \((\text{In},\text{Al},\text{Mn})\text{As}\) and \((\text{In},\text{Ga},\text{Mn})\text{As}\) based on our assumption is consistent with the results of Eq.(5.1). The Mn acceptor activation energy of \((\text{In},\text{Ga},\text{Mn})\text{As}\) and \((\text{In},\text{Al},\text{Mn})\text{As}\) is 77 meV and 297 meV respectively, so their carrier density ratio at \(T = 300\) K calculated by\[14\]

\[
p \sim \exp(-E_A/2k_BT)
\]

(5.3)

gives

\[
\frac{P_{\text{InGaMnAs}}}{P_{\text{InAlMnAs}}} = 70
\]

(5.4)

The results obtained by mean-field theory [Eq.(5.1)] and our assumptions here [Eq.(5.4)], which differs only by approximately 20%, prove that it is reasonable to assume that the Mn acceptor level is pinned in the vacuum.

For the superlattice samples, we propose that the bandgap varies as a Mn-doped alloy \(\text{In}_{0.5}(\text{Ga}_{1-w},\text{Al}_w)_{0.5}\text{As}\), which increase with the Al content. As the activation energy increases with the Al ratio (closer to \((\text{In},\text{Al},\text{Mn})\text{As}\)), hole-carriers are more localized and decrease their overlap with the \(3d^5\) Mn ions. This could qualitatively explain the trend of an increasing \(T_C\) and effective ferromagnetic moment of these superlattices which decrease with the \(\text{Al}/(\text{Al+Ga})\) ratio in the sample composition.
5.3 Conclusion and future work

In summary, we have studied a novel quaternary ferromagnetic semiconductor (In,Al,Mn)As in the class of III-Mn-As compounds. The magnetization studies of closely lattice-matched (In,Al,Mn)As/(In,Ga,Mn)As superlattices on InP substrates show that the Curie temperature, effective ferromagnetic moment and magnetic anisotropy are strongly correlated with the thickness ratio of the constituents in each SL period. The unambiguous single phase transition for all the SLs regardless of the thickness ratio indicates that these SLs behave like homogeneous ferromagnetic alloys. We attribute the increase of the Curie temperature and effective ferromagnetic moment with the reduction of the Al/(Al+Ga) ratio to the pinning of the Mn acceptor level to the vacuum level, which is independent of the valence band edge of the host semiconductor. We note that studies on the electric properties of these superlattice samples were carried out, although more measurements will be needed to confirm the results.
5.4 References


7. TEM image taken by William Fadgen et al.


Appendix A

Supplemental Materials

This appendix contains supplemental contents related to our research finding, as well as additional or preliminary data that are not included in the thesis chapters.

A.1 Derivation of the hopping energy from Mott’s VRH conduction model

In this section, we derive the mathematical expression [Eq.(4.8)] which we have used to calculate the hopping energy of our low Mn-doped (Ga,Mn)As samples. The following three equations describe Mott’s assumptions for variable-range hopping (VRH) conduction model,[1][2] where $W$, $R$, $N(E_F)$, $\alpha$, and $T_0$ are the hopping energy, hopping distance, density of states at the Fermi energy, exponential decay rate of a localized wave function, and the coefficient of the VRH conduction formula [Eq.(4.2)] respectively.

$$W = \left[ \frac{4}{3} \pi R^3 N(E_F) \right]^{-1}$$  \hspace{1cm} (1.1)

$$R = \frac{3^{1/2}}{(8\pi \alpha N(E_F)k_B T)^{1/4}}$$ \hspace{1cm} (1.2)

$$k_B T_0 = 1.5\alpha^3 / N(E_F)$$ \hspace{1cm} (1.3)

From Eq.(1.3) we could get

$$N(E_F) = 1.5\alpha^3 / k_B T_0$$ \hspace{1cm} (1.4)
and from Eq.(1.2) we could obtain

\[ R^3 = \left( \frac{9}{8\pi} \right)^{\frac{3}{4}} \left( \frac{1}{\alpha N(E_F)k_B T} \right)^{\frac{3}{4}} \]  \hspace{1cm} (1.5)

Combining Eq.(1.4) and Eq.(1.5) gives us Eq.(1.6)

\[ R^3 N(E_F) = \left( \frac{9}{8\pi} \right)^{\frac{3}{4}} \left( \frac{1}{\alpha k_B T} \right)^{\frac{3}{4}} \left( \frac{1}{N(E_F)} \right)^{\frac{3}{4}} \] 
\[ = \left( \frac{9}{8\pi} \right)^{\frac{3}{4}} \left( \frac{1}{\alpha k_B T} \right)^{\frac{3}{4}} \left( \frac{1.5\alpha}{k_B T_0} \right)^{\frac{1}{4}} \] 
\[ = \left( \frac{9}{8\pi} \right)^{\frac{3}{4}} \left( 1.5 \right)^{\frac{1}{4}} \left( \frac{1}{k_B T_0^{1/4}T^{3/4}} \right) \]  \hspace{1cm} (1.6)

We then insert Eq.(1.6) into Eq.(1.1) to get

\[ W = \left( \frac{3}{4\pi} \right)^{\frac{3}{2}} \left( \frac{9}{8\pi} \right)^{\frac{3}{2}} \left( 1.5 \right)^{\frac{1}{4}} k_B T_0^{1/4}T^{3/4} \] 
\[ = 0.466k_B T_0^{1/4}T^{3/4} \]  \hspace{1cm} (1.7)

which is the Eq.(4.8) in Chapter 4.

A.2 Supplemental data for GaAs/(Ga,Mn)As/GaAs nanowires

This section contains additional data for the GaAs/(Ga,Mn)As/GaAs nanowire study that are not published or included in Chapter 3 of the thesis.
Figure A-1: A zoomed out version of the FESEM image Figure 3-1, which shows the layout of a four-probe resistance measurement for a 70 nm wide single wire patterned on GaAs / (Ga,Mn)As (50 nm) / GaAs (10 nm).

Figure A-2: FESEM image of typical four-probe resistance measurement design to study the resistance of a single nanowire. The center part of the image is shown in detail in Figure A-1, where the four GaAs/(Ga,Mn)As/GaAs leads expand out toward the four corners. Then a thin layer of gold was deposited on top of these leads at the corners, so annealed indium could be used to create four ohmic contacts.
A.3 Supplemental data for low Mn-doped (Ga,Mn)As

This section contains additional data for the low Mn-doped (Ga,Mn)As study that are not published or included in Chapter 4 of the thesis.

Figure A-3: Temperature dependence of the resistivity of the same wires as shown in Figure 3-4. The annealing time is 1 hour at the same condition (190 °C in nitrogen gas).
Figure A-4: Curie temperature of low Mn-doped Ga$_{1-x}$Mn$_x$As ($x \leq 0.015$) samples plotted as a function of the electric conductivity at $T = 25$ K, 30 K and 300 K. Non-ferromagnetic samples are labeled with $T_C = 0$ K for the guide of eye. Rainbow color gradient is used to indicate the carrier concentration. This figure is plotted to show that the cutoff dependence of ferromagnetism on the electric conductivity is independent of the temperature.
Figure A-5: Electric conductivity at $T = 25$ K plotted as a function of the hopping energy at $T = 25$ K for the low Mn-doped $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($x \leq 0.015$) samples. Rainbow color gradient is used to indicate the Curie temperature or the carrier concentration of the samples.
Figure A-6: Carrier concentration of the low Mn-doped Ga$_{1-x}$Mn$_x$As ($x \leq 0.015$) samples plotted as a function of the electric conductivity at $T = 25$ K. Rainbow color gradient is used to indicate the Curie temperature of the samples. Notice that both axes are in logarithmic scale.
The relation between $\ln(\rho)$ and the actual sample resistance ($R$) is described by

$$\ln(\rho) = \ln(R \times (400 \mu m \times 100 nm / 700 \mu m)),$$

where $R$ has the unit of $\Omega$ and $\rho$ has the unit of $\Omega$-cm. The normalization factor used was based on the dimensions of the hall bars as described in Figure 2-2 (two neighboring leads) and the film thickness of 100 nm.

Figure A-7: $\ln(\rho)$ versus $T^{-1/4}$ data shown for the ferromagnetic Ga$_{1-x}$Mn$_x$As samples in the $x = 0.0125$ series of non-rotated samples. A deflection in the slope of the curves is observed at temperatures near the $T_C$ of each sample (though less pronounced in more resistive samples). Note that linear fits were performed between 25 K and 80 K (which correspond to the $T^{-1/4}$ values of 0.447 and 0.334) to obtain the $T_0$ term in the variable-range hopping model for all of the low Mn-doped (Ga,Mn)As.
Figure A-8: Ln(ρ) versus $T^{-1/4}$ data shown for the ferromagnetic Ga$_{1-x}$Mn$_x$As samples in the $x = 0.010$ series of non-rotated samples.

Figure A-9: Ln(ρ) versus $T^{-1/4}$ data shown for the ferromagnetic Ga$_{1-x}$Mn$_x$As samples in the $x = 0.0075$ series of non-rotated samples.
Figure A-10: The remanent magnetization of Ga$_{1-x}$Mn$_x$As samples with $x =$ 0.0125, 0.010 and 0.0075 that show changes of magnetic easy axis from the sample in-plane to the out-of-plane (normal) direction as found in samples from the $x =$ 0.015 series (Figure 4-8).
Figure A-11: This figure is essentially a combination of Figure 4-11 and Figure 4-14, except that data points taken from the “Ga-rich” part of the non-ratated Ga_{1-x}Mn_{x}As wafers are excluded. The definition of “Ga-rich” samples is described in reference [3] and Appendix C. Note that the dependence of ferromagnetism on the hopping energy and the electric conductivity observed in Ga-rich samples are consistent with the results from stoichiometric and As-rich samples, although Ga-rich samples are structurally less homogeneous.
Figure A-12: This figure is essentially a combination of Figure 4-10, Figure 4-12 and Figure 4-13, except that there are no data points from “Ga-rich” samples.
Figure A-13: Curie temperature of low Mn-doped Ga$_{1-x}$Mn$_x$As ($x \leq 0.015$) samples plotted as a function of the hopping energy at $T = T_C$, denoted $W(T_C)$. Non-ferromagnetic samples are not shown in this graph. Rainbow color gradient indicates the carrier concentration of the samples. There are no data points from “Ga-rich” samples. This figure shows that all ferromagnetic samples in this low Mn-doped regime have $W(T_C)$ between 3 and 10 meV.
A.4 Supplemental data for (In,Al,Mn)As/(In,Ga,Mn)As heterostructures

This section contains preliminary transport data for the ongoing study of the (In,Al,Mn)As/(In,Ga,Mn)As thin films and superlattices that are not included in Chapter 5 of the thesis. We caution that more samples are needed to confirm the results and speculations summarized as follows:

(i) The features of a metallic carrier-mediated ferromagnetic semiconductor, such as the local characteristic peak in the resistivity near its Curie temperature, was observed.

(ii) Hall effect measurements at T = 300 K have shown that the majority carrier of InAlAs or InGaAs with up to 11% Mn-doping is “n-type”. Similar measurements for our (In,Ga,Mn)As sample at lower temperatures have shown that the majority carrier changed to “p-type” at above T = 200 K. For other highly-resistive samples such as (In,Al,Mn)As, unintended contribution of the large longitudinal resistance at low temperatures makes reliable Hall effect measurements difficult.

(iii) Interesting magneto-resistance effects were observed in (In,Al,Mn)As samples for a specific temperature range below T = 100 K, which has not been reported in other III-Mn-As systems such as (Ga,Mn)As. This may be related to the simultaneous transition of “n-type” majority carrier to “p-type” in the semiconductor host. Further studies are certainly needed to better understand the phenomena.

Note that similar to the magnetization studies, all the samples used for transport measurements were annealed at 250 °C for 30 minutes in high purity forming gas (95% N2 + 5% H2).
Figure A-14: Temperature dependence of the resistivity of annealed (In,Al,Mn)As sample with approximately 11% Mn. Since the sample resistance is too large for the PPMS electronics, this was measured using the high resistance measurement setup mentioned in Appendix B. We caution that there can be a large uncertainty at the resistivity peak.

Figure A-15: Temperature dependence of the resistivity of annealed (In,Ga,Mn)As epilayer as well as (In,Al,Mn)As and (In,Ga,Mn)As superlattices (SLs). “Al:Ga” denotes the thickness ratio of (In,Al,Mn)As and (In,Ga,Mn)As in each SL period. Notice that the peak of $\rho(T)$ near $T_C$ still exists as observed in metallic (Ga,Mn)As.
Figure A-16: Magnetic field (H) dependence of the resistivity of annealed (In,Al,Mn)As sample. H is along the out-of-plane direction of the sample. Measurements were taken using the high resistance measurement setup mentioned in Appendix B. Data taken at T = 2 K, 30 K and 50 K were not shown here due to the larger uncertainty.

Figure A-17: Magnetic field dependence of the resistivity of annealed (In,Al,Mn)As and (In,Ga,Mn)As superlattice sample (031107E, Al:Ga = 3:1). The magnetic field and the source current were applied along the in-plane [110] direction.
Figure A-18: Magnetic field dependence of the resistivity of annealed (In,Al,Mn)As and (In,Ga,Mn)As superlattice sample (031107E, Al:Ga = 3:1). The source current was applied along the in-plane [1-10] direction; the magnetic field was applied along [1-10] and out-of-plane respectively.
References


Appendix B

Measurement and Sample Preparation Techniques

This appendix contains the experimental details of this thesis work, such as the instrumentation setup used to measure high resistance and recipes for photolithography.

B.1 High Resistance Measurement Setup (HRMS)

This section contains supplemental information on the details of the high resistance measurement setup (HRMS) as described in section 4.2, which was designed to measure samples with high resistance (up to 1 GΩ resistance and above). The circuit diagram of the setup was shown in Figure 4-6, and more realistically in the Figure B-1, which includes the following instruments used to perform the differential four-probe measurements.

(i) Keithley 2400 source meter: this was used to source electric current between 2 nA and 1 μA through the patterned hall bar geometry of our samples. It is capable of supplying a large compliance voltage (up to 210 V). Note that in our experiments, the maximum compliance voltage applied was 21 V (to avoid electric arching inside the PPMS or destroying the leads). The use of compliance voltage higher than 21 V was not tested and should be treated with extreme caution.
(ii) Unity-gain buffers: we have employed two high-Z unity-gain buffers assembled in the lab using commercially available electrometer op amps (Texas Instruments OPA129U). Note that DC working voltages of +15 V (red cable), -15 V (white cable) and common ground (black cable) need to be connected for the op amps to function. The input and output voltage of each unity-gain buffer will be the same for input voltages between +13.8 V and -13.8 V (slightly below the applied working voltage),

Figure B-1: Diagram of the high resistance measurement setup (HRMS).
but when the input voltage exceeds this upper or lower limit, the output voltage will saturate at +13.8 V or -13.8 V. In this case, we will need to replace this unit with a Keithley 6514 electrometer and use the unity-gain buffer mode (linearity up to 21 V). The circuit diagram (Figure B-2) for the home-built unity-gain buffer was designed by John Passaneau from the Physics Electronics Shop.

Figure B-2: Circuit diagram of the lab assembled unity-gain buffer using an electrometer op amp (Texas Instruments OPA129U).
(iii) HP 34401A digital multimeter: two of these standard digital multimeters were used behind the unity-gain buffers to read their output voltages. The difference between voltage #1 and #2 is the electric potential difference ($\Delta V$) across the two leads (as indicated in Figure B-1). The sample resistance can be obtained by dividing this potential difference by the actual source current.

We compared the accuracy of our HRMS with commercially available electrometers (Keithley 6514 and Keithley 616, two-probe measurements) by using a 1.0 G$\Omega$ resistor with +/- 5% error manufactured by Vishay Dale mounted on insulating epoxy filled dip sockets. Measurements were performed inside and outside of the PPMS.

![Figure B-3: Measured resistance of a standard 1.0 G$\Omega$ resistor with +/- 5% error plotted as a function of the measurement time using the HRMS. The fluctuation of the resistance reading is smaller than 0.5%.

---

Figure B-3: Measured resistance of a standard 1.0 G$\Omega$ resistor with +/- 5% error plotted as a function of the measurement time using the HRMS. The fluctuation of the resistance reading is smaller than 0.5%. 

---
In the following figures, we will show data to verify that our HRMS provides consistent and precise results when used with both the 9 tesla and 14 tesla PPMS. Temperature-dependent resistivity data taken from low Mn-doped (Ga,Mn)As samples using the HRMS and PPMS electronics also show good consistency.

Figure B-4: Measured resistance of the 1.0 GΩ resistor and the source current (which depends on the Keithley 2400 compliance voltage) as a function of temperature. Note that the 1.0 GΩ resistor value of the resistor is specified at room temperature, so the change in its value at lower temperatures is normal.
Figure B-5: Temperature-dependent resistivity data of a low Mn-doped (Ga,Mn)As. The data was taken using the HRMS with the sample mounted in both the 9 tesla and 14 tesla PPMS cryostats.

Figure B-6: Temperature-dependent resistivity data of a low Mn-doped (Ga,Mn)As sample, where the data were taken using the HRMS with the sample mounted inside the 9 tesla PPMS, and with the 14 tesla PPMS electronics (two different resistivity puck used for the 14 T PPMS measurements).
The following temperature-dependent resistivity data of a few low Mn-doped (Ga,Mn)As samples with different Mn concentration and carrier density (in particularly non-ferromagnetic and low carrier density ones) measured using a range of source currents (e.g., 20 nA, 100 nA and 1 μA) show that the contacts prepared by annealed indium (650 °F) are ohmic between $T = 2$ K and 300 K. We note that the sample resistance can increase quickly to above 1.0 GΩ before the temperature drops to 2 K. In this case, no data are shown due to the large uncertainty. Table B-1 shows a list of representative samples we have used to verify that annealed indium contacts are ohmic.

Table B-1: List of (Ga,Mn)As samples with different Mn concentration and carrier density that were used to verify that annealed indium contacts are ohmic.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn concentration (%)</th>
<th>Carrier density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>051011B #4</td>
<td>1.5</td>
<td>1.77e17</td>
</tr>
<tr>
<td>051011C #9</td>
<td>1.25</td>
<td>1.36e18</td>
</tr>
<tr>
<td>051018A #5</td>
<td>1.0</td>
<td>6.44e17</td>
</tr>
<tr>
<td>051018A #10</td>
<td>1.0</td>
<td>1.97e17</td>
</tr>
<tr>
<td>051018B #6</td>
<td>0.75</td>
<td>7.11e17</td>
</tr>
</tbody>
</table>
Figure B-7: Temperature dependence of the resistivity of Ga$_{1-x}$Mn$_x$As (051011B #4, x = 0.015) and the actual current value of different source current settings applied to the sample. The top and bottom figures show the same data in different temperature range. Solid and open symbols represent the resistivity and current data points respectively. The current drops with the increase of the sample resistance due to a limited compliance voltage.
Figure B-8: Temperature dependence of the resistivity of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ (051011C #9, $x = 0.0125$) and the actual current value of different source current settings applied to the sample. The top and bottom figures show the same data in different temperature range. Solid and open symbols represent the resistivity and current data points respectively. The current drops with the increase of the sample resistance due to a limited compliance voltage.
Figure B-9: Temperature dependence of the resistivity of Ga$_{1-x}$Mn$_x$As (051018A #5, x = 0.010) and the actual current value of different source current settings applied to the sample. The top and bottom figures show the same data in different temperature range. Solid and open symbols represent the resistivity and current data points respectively. The current drops with the increase of the sample resistance due to a limited compliance voltage.
Figure B-10: Temperature dependence of the resistivity of Ga$_{1-x}$Mn$_x$As (051018A #10, x = 0.010) and the actual current value of different source current settings applied to the sample. The top and bottom figures show the same data in different temperature range. Solid and open symbols represent the resistivity and current data points respectively. The current drops with the increase of the sample resistance due to a limited compliance voltage.
Figure B-11: Temperature dependence of the resistivity of Ga$_{1-x}$Mn$_x$As (051018B #6, x = 0.0075) and the actual current value of different source current settings applied to the sample. The top and bottom figures show the same data in different temperature range. Solid and open symbols represent the resistivity and current data points respectively. The current drops with the increase of the sample resistance due to a limited compliance voltage.
B.2 Etching recipe for (Ga,Mn)As

To prepare (Ga,Mn)As hall bars for transport measurements, use 1813 photoresist (PR) for wet chemical etching and 3012 PR for dry etching (reactive ion etching). For wet chemical etching:

1. Sample cleaning
   (a) Clean samples with acetone, IPA and DI-water.
   (b) Use ultrasonic if needed (not necessary most of the time).
   (c) Dehydrate sample surface with pressurized N₂ gas or air.
   (d) Bake for 2 minutes on hot plate at 90 °C if needed.

2. Spin 1813 photoresist on 4 mm x 4 mm substrate material
   (a) Use a pipet to withdraw the PR, and use only one droplet (~ 2 mm³) of the PR to avoid unnecessary residues accumulating at the corners of the sample. Avoid bubbles in the droplet.
   (b) Spin at 5000 rpm with acceleration of 500 rpm/sec for 40 secs.
   (c) Bake sample at 105°C for 2 minutes and cool it on aluminum plate.

3. Exposure with mask aligner (Karl Suss MA6)
   (a) Use channel 1 power setting (12 mW/cm²-sec, wavelength 365 nm).
   (b) Align the preferred hall bar geometry on the mask to the substrate.
   (c) Make sure there is enough gap before the actual contact and exposure, so the sample does not stick to the mask and could be moved around for finer alignment.
   (d) Expose for 3.4 seconds.
4. Develop the sample with MF CD-26
   (a) Develop the sample with CD-26 for at least 90 seconds.
   (b) Rinse in DI-water (> 60 seconds).
   (c) Blow dry with pressurized N₂ gas or air.
5. Etch the sample with III-V etch (K₂Cr₂O₇:HBr:H₂O = 15g:150ml:300ml)
   (a) Etch rate: 300 nm/min.
   (b) Rinse in DI-water after etching (> 60 seconds).
   (c) Blow dry with pressurized N₂ gas or air.
6. Remove the photoresist on the sample with acetone, IPA and DI-water (use ultrasonic if needed)

For dry etching (reactive ion etching, RIE), the following adjustments need to be made:

1. Use 3012 PR instead of 1813 PR for RIE, and spin at 4000 rpm with acceleration of 1000 rpm/sec for 40 secs.
2. Expose for 5.0 seconds using channel 1 power setting on MA6.
3. An additional “post-exposure bake” of the sample PR at 115°C for 1 minute is required after PR exposure (step 3). Sample cool down also needed.
4. In step 5, etching method is then replaced by standard Cl₂ etching recipe in Plasma Therm 720. The etch rate for GaAs or (Ga,Mn)As is approximately 500 nm/min.
B.3 Etching recipe for (In,Al,Mn)As, (In,Ga,Mn)As and MnAs

The photolithography process for etching hall bars on (In,Al,Mn)As, (In,Ga,Mn)As and MnAs materials are basically the same as for (Ga,Mn)As. The only difference is the etching recipes listed as follows:

1. For (In,Al,Mn)As and (In,Ga,Mn)As thin films grown on InP substrates: use the 1813 PR and etch the material with the etchant $\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:1:20$ solution. The etch rate is ~ 200 nm/min.

2. For MnAs thin films grown on GaAs substrates: use the 3012 PR and etch the material using the standard Cl$_2$ recipe in the RIE etcher (Plasma Therm 720). The etching rate is ~ 8 nm/min (relatively slow compared to the 500 nm/min for GaAs), so cooling cycles are needed between the Cl$_2$ etching periods.
Appendix C

Sample Profiles

This appendix contains the complete list of samples that we have used in this thesis research.

C.1 GaAs-capped (Ga,Mn)As nanowire samples

This section lists the samples used for the GaAs-capped (Ga,Mn)As nanowire study. The sample names indicate the date which they were grown in the sequence of year, month and date. The wires on each sample were patterned along the in-plane [110] direction unless otherwise stated. The standard annealing condition used was 190 °C in ultrahigh purity nitrogen gas (5N).

Table C-1: Substrate material used to fabricate GaAs-capped (Ga,Mn)As nanowires.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>As-grown $T_C$ (K)</th>
<th>Annealed $T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>040816B</td>
<td>GaAs(10 nm)/GaMnAs(15 nm)/GaAs</td>
<td>68</td>
<td>66</td>
</tr>
<tr>
<td>040816C</td>
<td>GaAs(10 nm)/GaMnAs(50 nm)/GaAs</td>
<td>62</td>
<td>60</td>
</tr>
</tbody>
</table>
Table C-2: List of GaAs-capped (Ga,Mn)As nanowire samples from which data were taken for publication and thesis work.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Substrate Sample</th>
<th>Fabrication Date</th>
<th>Wire Description</th>
</tr>
</thead>
</table>
| 10       | 040816C          | 041008           | (1) 1 μm wide, 6 μm long along [110]  
(2) 70 nm wide, 4 μm long along [110] & [1-10]  
(3) 70 nm wide, 5.6 μm long along [010] & [100]  
(4) van der Pauw geometry |
| 11       | 040816C          | 041008           | (1) 1 μm wide, 6 μm long along [110]  
(2) 70 nm wide, 4 μm long along [110] & [1-10]  
(3) 70 nm wide, 5.6 μm long along [010] & [100]  
(4) van der Pauw geometry |
| 12       | 040816B          | 041028           | (1) 1 μm wide, 6 μm long along [110]  
(2) 70 nm wide, 4 μm long along [110]  
(3) 70 nm wide, 5.6 μm long along [100] |
| 13       | 040816B          | 041028           | (1) Miscellaneous feature  
(2) 70 nm wide, 4 μm long along [1-10]  
(3) 70 nm wide, 5.6 μm long along [100] |
| 14       | 040816B          | 041028           | (1) 1 μm wide, 6 μm long along [110]  
(2) 70 nm wide, 4 μm long along [110]  
(3) 70 nm wide, 4 μm long along [1-10] |

Note that since the chip carriers we used for the PPMS resistivity puck have only 12 available connection pins, which enable three sets of four-probe measurements, therefore for samples that have more than three sets of wires or features (such as sample #10 and #11), only three sets of them could be connected to the chip carrier at a time.
C.2 Low Mn-doped (Ga,Mn)As samples

This section lists the low Mn-doped (Ga,Mn)As samples used for the study of paramagnetic to ferromagnetic transition of (Ga,Mn)As. Summaries of the sample characteristics are also included. Unlike all the other samples used in this thesis, these low Mn-doped (Ga,Mn)As samples were grown by Roberto Myers from University of California Santa Barbara. Sample wafers from UCSB have a scribed “X” to label the back of the sample (no indium residue), and the “_” marker below the “X” indicates the orientation of the wafer major flat (the major flat is also parallel to the “_” marker).

Table C-3: Low Mn-doped Ga_{1-x}Mn_xAs wafers grown by molecular beam epitaxy with wafer substrate rotated during sample growth for uniformity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x (Mn %)</th>
<th>As flux (Torr)</th>
<th>T_C (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>050809A</td>
<td>0.023</td>
<td>2.5E-6</td>
<td>18</td>
</tr>
<tr>
<td>050809B</td>
<td>0.023</td>
<td>3.5E-6</td>
<td>-</td>
</tr>
<tr>
<td>050809C</td>
<td>0.023</td>
<td>4.5E-6</td>
<td>-</td>
</tr>
<tr>
<td>050809D</td>
<td>0.023</td>
<td>2.0E-6</td>
<td>38</td>
</tr>
<tr>
<td>050811A</td>
<td>0.03</td>
<td>2.0E-6</td>
<td>-</td>
</tr>
<tr>
<td>050811B</td>
<td>0.015</td>
<td>2.0E-6</td>
<td>20</td>
</tr>
<tr>
<td>050811C</td>
<td>0.01</td>
<td>2.0E-6</td>
<td>-</td>
</tr>
<tr>
<td>050811D</td>
<td>0.005</td>
<td>2.0E-6</td>
<td>-</td>
</tr>
</tbody>
</table>

The “-” symbol in the T_C column indicates that the sample is not ferromagnetic.
The low Mn-doped Ga_{1-x}Mn_xAs wafers grown by molecular beam epitaxy (MBE) using the non-rotated growth method as described in section 4.1 are listed in the following table. The structure of these non-rotated samples is: Ga_{1-x}Mn_xAs (100 nm) LT (non-rotated)/GaAs buffer (500 nm) HT (rotated)/SI-GaAs (001) wafer. During the growth of the Ga_{1-x}Mn_xAs layer, the wafer substrate was not-rotated; however, the growth of the GaAs buffer still required wafer rotation for material uniformity. The As flux was also further optimized based on results of the samples listed in Table C-3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x (Mn %)</th>
<th>As flux (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>051011A</td>
<td>0.015</td>
<td>2.0E-6</td>
</tr>
<tr>
<td>051011B</td>
<td>0.015</td>
<td>1.83E-6</td>
</tr>
<tr>
<td>051011C</td>
<td>0.0125</td>
<td>1.83E-6</td>
</tr>
<tr>
<td>051018A</td>
<td>0.01</td>
<td>1.83E-6</td>
</tr>
<tr>
<td>051018B</td>
<td>0.0075</td>
<td>1.83E-6</td>
</tr>
<tr>
<td>051018C</td>
<td>0.03</td>
<td>1.83E-6</td>
</tr>
</tbody>
</table>

The following six figures illustrate the wafer map (not to scale) of the wafers listed in Table C-4, which show the relative position of sample pieces cleaved from these wafers that were used for transport and magnetization studies.
Figure C-1: Wafer map of 051011A and 051011B series of low Mn-doped Ga$_{1-x}$Mn$_x$As samples, $x = 0.015$. 
Figure C-2: Wafer map of 051011C and 051018A series of low Mn-doped Ga$_{1-x}$Mn$_x$As samples, $x = 0.0125$ and 0.010 respectively.
Figure C-3: Wafer map of 051018B series of low Mn-doped $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ samples ($x = 0.0075$), and 051018C series of moderately doped $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($x = 0.03$).
For the study of paramagnetic to ferromagnetic transition of low Mn-doped (Ga,Mn)As, data were taken from the 051011B, 051011C, 051018A and 051018B series of samples. Important parameters of the samples are summarized in the following tables. The columns (from left to right) in the following tables represent: (1) hall bar used for transport measurements (2) sample for magnetization measurements (3) Curie temperature of the sample (4) carrier density at T = 300 K (5) electric conductivity at T = 25 K (6) slope fit of the logarithm of the sample resistivity versus T^{-1/4} plot between T = 25 K and 80 K, which is the T_0^{1/4} term in the variable-range hopping conduction model (7) hopping energy at T = 25 K calculated based on the extracted T_0^{1/4} value and Eq. (4.8). In column (3), T_C labeled with the “-” marker indicates that the sample is not ferromagnetic.

Note that we have excluded data taken from samples that were near the edge of the wafers, since the growth temperature could be non-uniform there (e.g., samples 1R and 2R from the 051011B series). We have also excluded data points from “Ga-rich” samples in cases where we focus only on stoichiometric and “As-rich” (Ga,Mn)As. The “Ga-rich” samples are the non-ferromagnetic sample on the Ga-rich side of the wafer as indicated in Phys. Rev. B 74, 155203 (2006). For example, in the 051011C series of samples, samples 1R, 2R and 3R are considered “Ga-rich”. For samples on the “As-rich” half of the wafers, the hole carriers are highly compensated by As-antisite defects, therefore ferromagnetism was quenched as suggested in Phys. Rev. B 74, 155203 (2006).

We would like to caution that although we have done our best to accurately cleave these samples, there can still be slight misalignment between transport and magnetization data due to the size difference between samples used for transport and magnetization measurements (samples used to prepare hall bars are slightly larger).
Table C-5: Summary table of important parameters of the 051011B series of samples.

<table>
<thead>
<tr>
<th>Hall Piece</th>
<th>Mag Piece</th>
<th>$T_c$ (K)</th>
<th>$p$ (cm$^3$)</th>
<th>$\sigma$ (S/cm)</th>
<th>VRH Slope Fit ($T_0^{1/4}$)</th>
<th>$W_{T=25K}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1R</td>
<td>1 / 2</td>
<td>-</td>
<td>1.83e17</td>
<td>5.6e-5</td>
<td>51.79</td>
<td>23.25</td>
</tr>
<tr>
<td>2R</td>
<td>2 / 3</td>
<td>10</td>
<td>2.41e17</td>
<td>0.001872</td>
<td>38.74</td>
<td>17.39</td>
</tr>
<tr>
<td>3R</td>
<td>4</td>
<td>15</td>
<td>3.45e17</td>
<td>0.01749</td>
<td>31.03</td>
<td>13.93</td>
</tr>
<tr>
<td>4R</td>
<td>5</td>
<td>21</td>
<td>1.47e18</td>
<td>0.4755</td>
<td>18.81</td>
<td>8.445</td>
</tr>
<tr>
<td>5R</td>
<td>6</td>
<td>23</td>
<td>7.11e18</td>
<td>6.944</td>
<td>9.743</td>
<td>4.374</td>
</tr>
<tr>
<td>6R</td>
<td>7</td>
<td>20</td>
<td>1.92e19</td>
<td>7.276</td>
<td>11.44</td>
<td>5.138</td>
</tr>
<tr>
<td>7R</td>
<td>8</td>
<td>-</td>
<td>5.95e17</td>
<td>0.01173</td>
<td>34.50</td>
<td>15.49</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>-</td>
<td>3.17e17</td>
<td>0.003064</td>
<td>35.06</td>
<td>15.74</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>2.29e17</td>
<td>0.00283</td>
<td>35.75</td>
<td>16.05</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>1.96e17</td>
<td>0.00148</td>
<td>36.93</td>
<td>16.58</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>1.77e17</td>
<td>0.001532</td>
<td>36.53</td>
<td>16.40</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>1.59e17</td>
<td>0.001313</td>
<td>36.68</td>
<td>16.47</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>1.45e17</td>
<td>0.000982</td>
<td>37.05</td>
<td>16.63</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1 Samples starting from the top of the table are “Ga-rich”, stoichiometric and “As-rich”.
Table C-6: Summary table of important parameters of the 051011C series of samples.

<table>
<thead>
<tr>
<th>Hall Piece</th>
<th>Mag Piece</th>
<th>$T_C$ (K)</th>
<th>$p$ (cm$^3$)</th>
<th>$\sigma$ (S/cm)</th>
<th>VRH Slope Fit ($T_0^{1/4}$)</th>
<th>$W_{T=25K}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1R</td>
<td>1</td>
<td>-</td>
<td>1.10e17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2R</td>
<td>2</td>
<td>-</td>
<td>8.94e16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3R</td>
<td>3</td>
<td>-</td>
<td>9.61e16</td>
<td>0.000199</td>
<td>45.98</td>
<td>20.64</td>
</tr>
<tr>
<td>4R</td>
<td>4</td>
<td>15</td>
<td>3.28e17</td>
<td>0.009494</td>
<td>32.35</td>
<td>14.53</td>
</tr>
<tr>
<td>5R</td>
<td>5</td>
<td>18</td>
<td>7.79e18</td>
<td>0.605694</td>
<td>17.42</td>
<td>7.821</td>
</tr>
<tr>
<td>6R</td>
<td>6</td>
<td>20</td>
<td>1.12e19</td>
<td>10.15744</td>
<td>7.397</td>
<td>3.321</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>16.5</td>
<td>5.25e18</td>
<td>1.00712</td>
<td>18.91</td>
<td>8.491</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>-</td>
<td>1.36e18</td>
<td>0.004182</td>
<td>36.39</td>
<td>16.34</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>-</td>
<td>2.55e17</td>
<td>0.003967</td>
<td>35.24</td>
<td>15.82</td>
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<tr>
<td>7</td>
<td>10</td>
<td>-</td>
<td>2.30e17</td>
<td>0.003218</td>
<td>34.92</td>
<td>15.68</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td></td>
<td>2.42e17</td>
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<td>35.21</td>
<td>15.81</td>
</tr>
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<td>5</td>
<td>-</td>
<td></td>
<td>1.91e17</td>
<td>0.002223</td>
<td>35.35</td>
<td>15.87</td>
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<td>1.62e17</td>
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<td>35.89</td>
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<td>-</td>
<td></td>
<td>1.51e17</td>
<td>0.001539</td>
<td>35.60</td>
<td>15.98</td>
</tr>
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<td>2</td>
<td>-</td>
<td></td>
<td>1.47e17</td>
<td>0.001095</td>
<td>35.98</td>
<td>16.15</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td></td>
<td>1.47e17</td>
<td>0.001078</td>
<td>35.67</td>
<td>16.01</td>
</tr>
</tbody>
</table>

1 Samples starting from the top of the table are “Ga-rich”, stoichiometric and “As-rich”.
Table C-7: Summary table of important parameters of the 051018A series of samples.

<table>
<thead>
<tr>
<th>Hall Piece</th>
<th>Mag Piece</th>
<th>T_C (K)</th>
<th>( p ) (cm(^{-3}))</th>
<th>( \sigma ) (S/cm)</th>
<th>VRH Slope Fit ( T_0^{1/4} )</th>
<th>( W_{T=25K} ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1R</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2R</td>
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<tr>
<td>4</td>
<td>4R</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5R / 6R</td>
<td>- / 13</td>
<td>6.44e17</td>
<td>0.05342</td>
<td>26.60</td>
<td>11.94</td>
</tr>
<tr>
<td>6</td>
<td>6R / 10</td>
<td>13</td>
<td>1.29e19</td>
<td>6.7875</td>
<td>10.49</td>
<td>4.708</td>
</tr>
<tr>
<td>7</td>
<td>10 / 9</td>
<td>13 / -</td>
<td>4.21e18</td>
<td>0.2266</td>
<td>24.04</td>
<td>10.79</td>
</tr>
<tr>
<td>8</td>
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<td>0.002959</td>
<td>34.79</td>
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<tr>
<td>11</td>
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<td>13</td>
<td></td>
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<td>0.001574</td>
<td>35.10</td>
<td>15.76</td>
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<tr>
<td>14</td>
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<td>15</td>
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<td>16</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Samples starting from the top of the table are “Ga-rich”, stoichiometric and “As-rich”.
2 Most samples in this series have very high resistance at low temperatures and cannot be measured below \( T = 200 \) K with our apparatus.
3 Due to the low Mn-doping (1.0 %) in this regime, it is possible that there is a slight variation in the Mn doping between transport and magnetization wafer strips, which could change the sample electronic property. However, the trend that correlates transport and magnetization data is consistent with those observed in the 1.25 % and 1.5 % series.
Table C-8: Summary table of important parameters of the 051018B series of samples.

<table>
<thead>
<tr>
<th>Hall Piece</th>
<th>Mag Piece</th>
<th>$T_C$ (K)</th>
<th>$p$ (cm$^3$)</th>
<th>$\sigma$ (S/cm)</th>
<th>VRH Slope Fit ($T_0^{1/4}$)</th>
<th>$W_{T=25K}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1R / 2R</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3R</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4R</td>
<td>-</td>
<td>1.35e17</td>
<td>-</td>
<td>105.6</td>
<td>47.14</td>
</tr>
<tr>
<td>4</td>
<td>5R</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6R</td>
<td>-</td>
<td>3.39e16</td>
<td>-</td>
<td>78.71</td>
<td>35.34</td>
</tr>
<tr>
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<td>7R</td>
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<td>7.11e17</td>
<td>0.07757</td>
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<td>11.54</td>
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<td>7</td>
<td>11</td>
<td>10</td>
<td>1.42e19</td>
<td>2.119</td>
<td>15.28</td>
<td>6.86</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Samples starting from the top of the table are “Ga-rich”, stoichiometric and “As-rich”.
2. Most samples in this series have very high resistance at low temperatures and cannot be measured below $T = 200$ K with our apparatus.
3. The VRH slope fits of samples #3 and #5 were taken from a higher temperature range ($T = 85$ K to 200 K) as a reference. They are also “Ga-rich” samples.
4. Due to the low Mn-doping (0.75 %) in this regime, it is possible that there is a slight variation in the Mn doping between transport and magnetization wafer strips, which could change the sample electronic property. However, the trend that correlates transport and magnetization data is consistent with those observed in the 1.25 % and 1.5 % series.
5. Hall bars #11 through #16 (from the As-rich half of the wafer) are not listed here.
C.3 (In,Al,Mn)As/(In,Ga,Mn)As samples

This section lists the samples used in the study of (In,Al,Mn)As, (In,Ga,Mn)As and superlattices based on these two compounds. Note that since annealing is required to introduce ferromagnetism in the (In,Al,Mn)As samples, all samples studied were annealed at 250 °C for 30 minutes in high purity forming gas (95% N₂ + 5% H₂) for consistency and for optimization of the sample quality. Therefore, the Curie temperature ($T_C$) data listed in the following tables represent the samples annealed in this condition unless otherwise stated. The “Al:Ga” in the description column indicates the thickness of (In,Al,Mn)As and (In,Ga,Mn)As of each SL period in the unit of angstrom.

Table C-9: First set of samples used in the study of (In,Al,Mn)As, (In,Ga,Mn)As and superlattices (SLs) based on these two compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Thickness (nm)</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>031107A</td>
<td>(In,Al,Mn)As</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>031107B</td>
<td>(In,Ga,Mn)As</td>
<td>30</td>
<td>95</td>
</tr>
<tr>
<td>031107C</td>
<td>SL, Al:Ga = 14.4:14.4 (ratio 1:1), 10 periods</td>
<td>30</td>
<td>65</td>
</tr>
<tr>
<td>031107E</td>
<td>SL, Al:Ga = 21.6:7.2 (ratio 3:1), 10 periods</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>031107F</td>
<td>SL, Al:Ga = 7.2:21.6 (ratio 1:3), 10 periods</td>
<td>30</td>
<td>79</td>
</tr>
</tbody>
</table>
Table C-10: Second set of samples used in the study of (In,Al,Mn)As, (In,Ga,Mn)As and superlattices (SLs) based on these two compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Thickness (nm)</th>
<th>T&lt;sub&gt;C&lt;/sub&gt; (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>060803C</td>
<td>(In,Al,Mn)As</td>
<td>30</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>060804B</td>
<td>SL, Al:Ga = 7.2:21.6 (ratio 1:3), 10 periods</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>060804C</td>
<td>SL, Al:Ga = 21.6:7.2 (ratio 3:1), 10 periods</td>
<td>30</td>
<td>25</td>
</tr>
</tbody>
</table>

Note that we have noticed the formation of MnAs clusters in this series of samples (Table C-10), which is perhaps due to the degradation of the materials in the Mn effusion cell and change in the chamber condition. However, the trend of the Curie temperature increasing with the (In,Ga,Mn)As content in these samples is consistent with the observations in the 031107 series of samples. Other (In,Al,Mn)As and (In,Ga,Mn)As samples grown on indium phosphide (InP) are listed in Table C-11 as a reference.
Table C-11: Additional (In,Al,Mn)As and (In,Ga,Mn)As samples grown on InP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Thickness (nm)</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>030911D</td>
<td>(In,Ga,Mn)As, As-grown, $T_{Mn} = 800 \degree C$</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>030911D</td>
<td>(In,Ga,Mn)As, Annealed 250$\degree$C 30 min</td>
<td>30</td>
<td>80</td>
</tr>
<tr>
<td>030911D</td>
<td>(In,Ga,Mn)As, Annealed 250$\degree$C 95 min</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>030911D</td>
<td>(In,Ga,Mn)As, Annealed 250$\degree$C 150 min</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>031015A</td>
<td>(In,Al,Mn)As, $T_{Mn} = 800 \degree C$</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>031015B</td>
<td>(In,Al,Mn)As, $T_{Mn} = 810 \degree C$</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>031016A</td>
<td>(In,Al,Mn)As, $T_{Mn} = 805 \degree C$</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>031016E</td>
<td>(In,Al,Mn)As, $T_{Mn} = 815 \degree C$</td>
<td>12.5</td>
<td>15</td>
</tr>
</tbody>
</table>
VITA

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Education:

- The Pennsylvania State University  Ph.D. Physics, 2007
- National Taiwan University  M.S. Physics, 2001
- National Taiwan University  B.S. Physics, 1999

Selected Publications:


- “Molecular beam epitaxial growth and characterization of (In$_{0.5}$Al$_{0.5}$)$_{1-x}$Mn$_x$As- (In$_{0.5}$Ga$_{0.5}$)$_{1-x}$Mn$_x$As: thin films and superlattices,” O. Maksimov, **B. L. Sheu**, P. Schiffer, N. Samarth, Journal of Vacuum Science and Technology B **23**, 1304 (2005).