Electric and Magnetic Properties of Ultra Thin (Ga,Mn)As Epilayers

Ph.D. Thesis

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Abstract

This is a study of the electric and magnetic properties of low temperature grown GaAs capped ultra thin (Ga,Mn)As epilayers, by low temperature electrical transport measurements and Superconducting Quantum Interference Device (SQUID) magnetometry. Post-growth annealing has an impact on these properties and has been investigated.

The lower thickness limit for the ferromagnetic phase to appear has been studied by resistance vs. temperature measurements and shows that it is around 5 nm for a set of $Ga_{0.95}Mn_{0.05}As$ samples having the same resistivity. The value of the $J_{pd}$ exchange integral has been found from these experiments by assuming the Magnetoimpurity model to be centred around $67 \text{ meV nm}^3$.

Hall measurements has been used to obtain the charge carrier density from the ordinary Hall effect and the Curie temperature and magnetization vs. temperature curve from the anomalous Hall effect, which arise from the magnetization of the sample itself. The Curie temperatures found by resistance vs. temperature measurements and Hall measurements has been compared and show that the latter is the largest. The anomalous Hall effect depends on different scattering mechanisms, which has also been studied.

Anomalies in the Hall resistance, that can not be explained by the ordinary and anomalous Hall effect, are caused by the planar Hall effect. These anomalies has been shown to be caused by the in-plane cubic magnetic anisotropy of the (Ga,Mn)As layers which has also been been studied.

The effects of post-growth annealing on the charge carrier density and Curie temperature as well as the impact dependence on the (Ga,Mn)As layer thickness has been studied. Both charge carrier density and Curie temperature are seen to increase by a magnitude dependent on the thickness of the layer. The Curie temperature is seen to follow the power law of $1/3$ on the charge carrier density as predicted by Dietl et al. [1]. The Curie temperatures for this study has been found by SQUID magnetometry from which the magnetization vs. temperature curves was determined also.
The shape of the magnetization vs. temperature curve depends on both layer thickness and annealing time. These results point towards disorder in the Mn distribution and rearrangement of defects during annealing. The impact of annealing depends on annealing time and temperature as well as the presence of a capping layer and the nature of it. These effects as well as the in-depth profile of the Mn distribution all have an influence on these results, as will be discussed.

The small thickness at which the ultra thin (Ga,Mn)As epilayers are still ferromagnetic has been utilized in the attempt to create two magnetic domains separated by a nm sized bridge. This was done with the ambition of studying the electric transport properties of two magnetic domains in series with opposite direction of magnetization. This has unfortunately not been done with success.

The degree of charge carrier spin-polarization of the ultra thin (Ga,Mn)As epilayers was tried to be obtained by studying the electrical transport properties of tunnel junctions. The tunnel junctions consist of a nm thick superconducting aluminium layer on the top of an insulating aluminium oxide barrier on the (Ga,Mn)As layer. The results indicate that the desired tunnel structure has not been obtained and that additional effects obscure the possibility of obtaining a realistic value of the charge carrier spin-polarization.
Preface

This is a Ph.D. thesis submitted to the Faculty of Science at the University of Copenhagen on the electric and magnetic properties of ultra thin (Ga,Mn)As epilayers. This work was started May 2001 and has been financed by the Danish Research Council of Engineering Sciences (STVF) through the framework program: ”Nanomagnetism”. Besides the work presented here, I have taught 1. year physics students, advised a Bachelor project, completed graduate and Ph.D. courses and participated in international summerschools.

The research area of spintronics was entered during the spring of 2001 at the Ørsted Laboratory, Niels Bohr Institute fAFG and is lead by Assoc. Prof. Poul Erik Lindelof. In collaboration with Dr. Janusz Sadowski, two Ph.D. works kicked off the experimental side of this initiative; the present work is one of them. The starting point was on the III-V diluted magnetic semiconductor (Ga,Mn)As grown at Max-Lab in Lund in Sweden for spin-injection and spin-detection devices. Later, other people has joined and beside characterization of this material, a spin-light emitting diode with a (Ga,Mn)As spin-injector and successful incorporation of single walled Carbon nanotubes in a (Ga,Mn)As based structure, have been some of the achievements.

During my Ph.D. study I visited Toshiba Research Europe Ltd. laboratories in Cambridge, UK for a period of four months in the summer of 2003, during which, I also got the opportunity to use the facilities at the Cavendish Laboratories, University of Cambridge. Here I grew and characterized layered structures of Co$_2$GaMn and various metals for Giant Magnetoresistance (GMR) studies. Dr. Anke Husmann and Dr. Stuart Holmes were my hosts and advisors during that time, and I would like to thank them for the good collaboration and especially the caring hospitality they showed my family and me. The work I performed there, has been left out of my thesis for various reasons, of which the main reason is the lack of time to complete the work. Collaboration between the Niels Bohr Institute with the Danish Technical University and Toshiba Research Europe Ltd. on the Co$_2$GaMn Heusler alloys is still going on.
During my work, I have been in contact with a number of people that I would like to thank.

First I would like to thank my advisor Assoc. Prof. Poul Erik Lindelof for leading me into this exiting field of physics and thank him for his continuous help, inspiration and patience in listening to me.

Dr. Søren E. Andresen, with whom I started on empty grounds, for numerous discussions and inspiration. Dr. Janusz Sadowski for always being there for me and sharing his broad and deep insight of magnetic semiconductors with me. I would also like to thank all my colleagues at the Ørsted Laboratory, especially Dr. Ane Jensen for many inspiring discussions and help, as well as M. Sc. Martin Ågesen for his attempts in saving me at the final hour. Thanks to Dr. Kurt Gloos for operating the Kelvinox cryostat.

I would especially like to thank Dr. Roland Mathieu for a very good collaboration and his generous hospitality during my stay in Uppsala.

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For help during the process of writing, I would like to thank my co-supervisor Assoc. Prof. Finn Berg Rasmussen for discussions, encouraging words and his thorough comments as well as Dr. Janusz Sadowski and M. Sc. Betina Axelsen for their comments and corrections.

Thanks to my beloved wife Betina, carrying our second son, and my son Angus, for the cheers and countless happy moments in good, as well as stressed times. I love You.
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Chapter 1

Introduction

What is and what is known about (Ga,Mn)As? This chapter elucidates the currently known properties of (Ga,Mn)As as well as why I, in a group effort with advisors and collaborators, have chosen to study this material.

(Ga,Mn)As is epitaxially grown by Molecular Beam Epitaxy (MBE) on GaAs and the effect of growth conditions and post-growth annealing on the electric and magnetic properties are discussed.

What actually is going on in (Ga,Mn)As from a solid-state physics point of view, is still very much debated. The popularity of the theoretical results depends on their ability to describe experimental observations even though questionable simplifications are made. This chapter contains a section that outlines the theoretical results that are relevant for the experimental findings made during this work. It is not the intention of this section to discuss the degree of validity of the individual theoretical approaches.

1.1 Motivation

The field of Spintronics (spin electronics) was initiated by the proposal of Datta and Das on a field effect spin transistor back in 1990 [2]. The idea is to utilize the spin-degree of freedom of the charge carriers to take care of the transistor action instead of the charge. This idea in itself has many advantages but the idea of combining the areas of electronics and magnetism kicked off a rapidly increasing research area, where there seems to be no end of the line of ideas on possible applications [3]. The exciting physics as well as the industrial success in combining the areas of electronics and optics is an encouraging factor and the results of a combination of all three areas are impossible to predict.

In realizing the spin-transistor there are several independent tasks to be overcome, each leading to a deeper insight of solid state physics. One task is to inject
a spin-polarized current from a magnetic material into a non-magnetic material. Another is to detect this spin-polarized current. Two unambiguously very important parameters in realizing spintronic devices are the use of materials and the properties of the interface between these materials. For an extensive review on spintronics see the special issue on the subject in ‘Semiconductor Science and Technology’ vol. 17, num. 4, 2002.

(Ga,Mn)As is a diluted magnetic semiconductor (DMS) that has shown to be a good model system for spintronics devices. Since the first observation of ferromagnetism in this III-V compound in 1996 [4], several research groups have contributed to the understanding of this material. Firstly it is grown by the same method as standard III-V compounds, which makes it possible to incorporate it into III-V heterostructures with perfect interfaces. Secondly it is a semiconductor that overcomes the problem of conductivity mismatch and the resulting effect on spin-injection efficiency for ohmic contact between a ferromagnetic metal and a non-magnetic semiconductor [5].

The application of spintronic devices depends heavily on the ferromagnetic ordering temperature ($T_c$, Curie temperature) of its magnetic constituents. Currently $T_c$ for (Ga,Mn)As is around 160 K [6, 7, 8], and hence a doubling of $T_c$ is necessary for realizing spintronic devices containing this material, to operate at room temperature. The pursuit of increasing the Curie temperature, where post-growth annealing has shown to be very important, has led to an increasingly deeper understanding of (Ga,Mn)As.

Superlattices (SL), which contain tens to hundreds of nm thick alternating magnetic and non-magnetic layers, have been suggested as a way to increase the Curie temperature because of the strong confinement of the charge carriers in the magnetic layers [9]. The growths of SL require high quality growth conditions and experience. (Ga,Mn)As/GaAs SL with (Ga,Mn)As layers down to 8 – 10 atomic monolayers (ML) (2.3 – 4.5 nm) in thickness, has been made by J. Sadowski with $T_c \approx 60$ K [10].

The lower thickness limit of (Ga,Mn)As for the ferromagnetic phase to occur in single layers has been theoretically predicted to be around 2.5 nm [11, 12]. We found it interesting to investigate this lower thickness limit in single layers of (Ga,Mn)As and study the electric transport- and magnetic properties of these ultra thin epilayers. Post-growth annealing has an effect on these properties and has been investigated. This work is the main core of this thesis, where these ultra thin (Ga,Mn)As epilayers with thicknesses down to 3 nm have been studied by means of low temperature electrical transport measurements and Superconducting QUantum Interference Device (SQUID) magnetometry.
A straightforward advantage of a small sample thickness is the possibility of creating small structures by wet chemical etching. We did this in order to create two spatially separated magnetic areas connected by a nm sized bridge, aiming to study the electric transport properties of two electrically connected magnetic domains.

The degree of charge carrier spin-polarization in the magnetic material is a very important parameter for spintronics devices. When we started, no experimental observations on the degree of spin-polarization in (Ga,Mn)As had been published. Theoretically, bandstructure calculations have predicted (Ga,Mn)As to be half-metallic [13, 14], meaning that the charge carriers are polarized in one direction only, whereas mean-field calculations based on the GaAs bandstructure, predict a spin-polarization of about 80% [15]. This latter number is in agreement with new experimental findings [16, 17]. We have studied the degree of charge carrier spin-polarization in the ultra thin (Ga,Mn)As epilayers by utilizing the Zeeman splitting in the superconducting aluminium (Al) in an Al/Al2O3/(Ga,Mn)As (SC/I/DMS) tunnel junction, along the line of P. Meservey and P. M. Tedrow [18].

1.2 Outline

The rest of this Chapter is devoted to a presentation of the current understanding of (Ga,Mn)As from a theoretical and experimental point of view as well as how (Ga,Mn)As is made.

Chapter 2 is about the fabrication of the individual devices investigated during the course of my Ph.D. study, together with the descriptions of the experimental setups.

The experimental findings on these devices are divided into four chapters. The electric transport properties of the ultra thin (Ga,Mn)As epilayers and the effect of annealing are presented in Chapter 3. The magnetic properties of the ultra thin (Ga,Mn)As epilayers measured by SQUID magnetometry and the effect of annealing are presented in Chapter 4. Some of the results in these two chapters are closely related, especially the results on the effects of annealing. Therefore some interpretations and conclusions belonging to Chapter 3 are postponed to the end of Chapter 4, where the (Ga,Mn)As thickness dependence on annealing is summarized.

The results on geometrically constricted ultra thin (Ga,Mn)As layers are presented in Chapter 5 followed by the theory and experiments on the spin-polarized electron tunneling in SC/I/DMS tunnel junctions in Chapter 6.

All results are summarized in Chapter 7.
The Appendixes contain the details of the device processing, short descriptions of the cryostats used as well as equations used for calculations.

A list of publications made during my Ph.D. study is placed at the end of this thesis.

1.3 Ferromagnetic (Ga,Mn)As

The understanding of (Ga,Mn)As is still a subject of controversy in the semiconductor community, but some basic mechanisms are generally accepted.

(Ga,Mn)As is called a diluted magnetic semiconductor because Mn is dilutely distributed in the GaAs Zinc-blende lattice and acts as an acceptor when substituting a cation. The two 4s electrons of the Mn atom create covalent bonds to the surrounding As atoms, leaving a negatively charged Mn$^{2+}$ ion with a half-filled 3d shell. The Mn$^{2+}$ is negatively charged in the GaAs lattice due to its acceptor nature in GaAs. The 5 electrons in the 3d shell give the Mn$^{2+}$ ion a total moment of $J = L + S = 0 + 5/2 = 5/2$. The ferromagnetic ordering in (Ga,Mn)As between the localized magnetic moments of Mn$^{2+}$ is mediated by the conduction holes ($S = 1/2$) in the (Ga,Mn)As valence band, through an antiferromagnetic coupling to the Mn$^{2+}$ ions.

Mean-field theory calculations have shown very good agreement with experiments [15, 19, 20]. The main approach is the above-described scenario with an antiferromagnetic exchange interaction between charge carriers in the host semiconductor valence band and the Mn$^{2+}$ ions, including effects such as spin-orbit coupling and various Coulomb interactions. In these models it is assumed that the d-electrons are strongly localized and do not contribute to the electrical conduction. Within the Zener model [1, 15] a quantitative expression for the Curie temperature has been found and is given by: $T_c \propto x_{eff} J_{pd}^2 p^{1/3}$, where $x_{eff}$ is the effective acceptor concentration and $J_{pd}$ is the exchange integral between the localized d-states and the p-type valence band. $p$ is the charge carrier density. This expression has been shown to be in good agreement with experiments although there is an uncertainty in determining the magnitude of the individual parameters experimentally. Agreement on magnetic anisotropy and the anomalous Hall effect has also been demonstrated as well as a possible explanation of the experimentally observed non-mean-field-like concave shape of the magnetization vs. temperature curve [20].

Bandstructure calculations [13, 14] have shown that with increasing doping concentration of Mn, an impurity/defect band is created at the Fermi energy by the increasing mixing of the p-type valence band and Mn d-states, leading to an
antiferromagnetic coupling between the charge carriers and the Mn$^{2+}$ ions. Furthermore, these calculations predict a half-metallic band structure where the Fermi energy lies in the band gap for one of the two spin directions. Several experiments stress the importance of an existing impurity band [21, 22, 23, 24].

Beside the exchange interaction, double-exchange has been proposed as the mechanism of ferromagnetic ordering in (Ga,Mn)As [25, 26].

1.4 Properties of (Ga,Mn)As

This section briefly describes the physical properties of (Ga,Mn)As. (Ga,Mn)As is grown by MBE under conditions that deviate from MBE growth of regular GaAs. There is an induced strain in the (Ga,Mn)As layer, depending on the substrate on which it is grown, and defects are formed during growth that have a strong impact on the electric and magnetic properties. There are different kinds of defects and post-growth annealing can reduce some of them. This latter effect will be described in some detail.

1.4.1 Molecular Beam Epitaxy (MBE)

MBE is a technique of depositing single atomic layers (mono layers (ML)) with very high accuracy, from single element sources under high vacuum that makes it possible to create perfect crystal structures containing different compositions of the elements.

Because of the low solubility of Mn in GaAs, (Ga,Mn)As has to be grown under low temperature conditions in order to incorporate a sufficient amount of Mn to obtain ferromagnetic ordering and avoid segregation of unwanted specimens such as MnAs. The typical growth temperature of GaAs is between 500 °C and 600 °C, but temperatures in the range of 200 °C to 300 °C are necessary in order to obtain single-crystalline (Ga,Mn)As. The highest obtainable concentration of Mn is about 8 %, and in the temperature and Mn content range available for single-crystalline growth, there are different areas where (Ga,Mn)As is either metallic or insulating [27]. The magnitude of the lattice constant of (Ga,Mn)As is in between the lattice constants of (In,Ga)As and GaAs and depends linearly on the Mn content [27]. There are other parameters than mentioned here, which are of importance when growing high quality (Ga,Mn)As. For a discussion on this matter see e.g. ref. [28] and references therein.
1.4.2 Effect of lattice-mismatch

The strain induced in the (Ga,Mn)As layer depends on the substrate on which it is grown and affects its magnetic anisotropy. This lattice-mismatch induced strain has a strong effect on the valence band and does not relax even for layers with thicknesses up to $2 \, \mu m$ [27]. (Ga,Mn)As grown on a GaAs substrate is under compressive strain that leads to an in-plane magnetic anisotropy, whereas (Ga,Mn)As grown on (In,Ga)As is under tensile strain, which leads to an out-of-plane magnetic easy-axis [29, 15, 19].

The in-plane magnetic anisotropy of ‘metallic’ (Ga,Mn)As grown on GaAs-(001) substrates has been shown to be cubic along the $\langle 100 \rangle$ and equivalent directions with a small uniaxial anisotropy along the $\langle 110 \rangle$ direction [30]. Theory predicts that even in compressively strained (Ga,Mn)As layers, the easy-axis orientation can change from in-plane to out-of-plane with temperature, as a consequence of the change in the carrier density [15, 19]. This effect has been observed experimentally for very small carrier densities [31].

1.4.3 Effect of Annealing

For a long period of time, the highest observed Curie temperature has been 110 K [32] but Curie temperatures as high as 160 K has now been obtained by carefully controlled annealing [6, 7, 8]. In this period of time, a deeper understanding of the nanostructure of (Ga,Mn)As has progressed, so the defect structure and the mechanism behind the removal of these defects is now very well elucidated.

The low temperature conditions under which (Ga,Mn)As is grown, induce different kinds of defects in the crystal that have an impact on the magnetic and electronic transport properties. In (Ga,Mn)As, Mn can occupy different positions in the zinc-blende lattice, where Mn on substitutional sites (Mn$_{Ga}$) acts as an acceptor and possesses the local magnetic moment that is part of the ferromagnetic ordering, as described previously. Mn also occupies interstitial sites (Mn$_{I}$) that are commensurable with the crystal structure. Because of their positive charge, Mn$_{I}$ are preferably in tetrahedral positions surrounded by four As atoms as nearest neighbors. They can passivate Mn$_{Ga}$ by formation of weakly bound Mn$_{Ga}$-Mn$_{I}$ complexes and they act as double donors. Hence Mn$_{I}$, both decreases the density of localized magnetic moments and reduces the hole density [33, 34].

A third possibility is the formation of defects such as MnAs, which is typically formed at high growth- or annealing temperatures. The low temperature growth conditions also create As-antisites, As$_{Ga}$ (As situated on Ga-sites), which acts as a donor.
As described in sec. 1.3, the Curie temperature depends on both hole concentration and non-passivated Mn$_{Ga}$. Annealing at temperatures at or below the growth temperature has been shown by many groups to increase the Curie temperature and the magnitude of magnetization. This is now understood to be a consequence of removal of the highly mobile Mn$_{I}$ and not, as earlier believed, the removal of As$_{Ga}$. This is because As$_{Ga}$ are strongly bound and stable up to above 300 °C [35].

Typical annealing temperatures leading to an increase in $T_c$ are between 160 °C and 280 °C in a nitrogen atmosphere and the most successful results have been at the lowest temperatures with annealing times up to above 100 hours.

The removal of Mn$_{I}$ has been well described by a one-dimensional diffusion model where the out-diffusion of Mn$_{I}$ is governed by a barrier of about 0.7 eV [8]. The out-diffusion is believed to happen both towards the substrate and towards the surface. The diffusion into the substrate is limited by the build-up of a p-n junction by the negatively charged Mn$_{Ga}$ and positively charged Mn$_{I}$. At the surface a similar limitation is not present and the Mn$_{I}$ are believed to be passivated by oxidation or formation of MnN. This mechanism for passivation of Mn$_{I}$ is supported by the experimental observations of a limited effect of annealing on GaAs capped or layered structures [7, 36, 37, 38].
Chapter 2

Devices & measurements

This chapter contains the descriptions of the devices and device processing as well as the different measurement techniques used to characterize the devices. Standard in-house cleanroom facilities for processing III-V semiconductor devices have been used, so has annealing furnaces at different laboratories. The ultra thin (Ga,Mn)As epilayers have been characterized by four-point dc-measurements, whereas tunnel junctions have been studied using standard two-point ac lock-in techniques. The measurements have been performed in several different cryostats in the temperature range between room temperature and 60 mK. The cryostats are described in Appendix B. The magnetization of the ultra thin (Ga,Mn)As layers have been determined by SQUID magnetometry which is described in Chapter 4.

2.1 Devices

The samples studied and presented in this thesis are grown by J. Sadowski at MAX-Lab in Lund, Sweden. They are ultra thin (Ga,Mn)As epilayers encapsulated in low temperature grown (LT) GaAs. They were grown by MBE at a substrate temperature of 230 °C having an intended Mn content of either 5 % or 6 %. LT GaAs has a resistivity that is typically more than three orders of magnitude larger than well conducting (Ga,Mn)As and the measured electrical transport properties is thus dominated by that of the (Ga,Mn)As layer [39].

The samples were made by the following growth sequence: 200 nm standard high-temperature GaAs buffer layer and 20 nm LT GaAs is grown on semi-insulating epi-ready GaAs(100) wafers followed by a ultra thin (Ga,Mn)As layer. The (Ga,Mn)As layer is then capped by a 3 nm thick LT GaAs layer. This capping is added in order to prevent degradation of the ultra thin epilayers by e.g. oxidation.

The samples were grown while the thickness was monitored by RHEED oscillations. The (Ga,Mn)As layer was made by opening the shutters of the Mn and Ga...
Figure 2.1: Device processing. a) Cleaned and resist covered wafer surface is subjected to UV-light through mask-aligner. b) After developing, the desired areas are exposed. c) Etching removes material to the desired depth. d) Cleaning removes the resist. e) Cleaned and resist covered wafer is subjected to UV-light through mask-aligner. f) After developing the desired areas are exposed. g) Contact metallization. h) Cleaning removes the resist and leaves metal contacts at the desired areas.
2.1 Devices

Figure 2.1: Flowchart illustrating the device processing steps.

Figure 2.2: Top-view illustration of the final Hallbar geometry with typical electrical wiring.

effusions cells, keeping the As shutter open before, during and after growth. See ref. [40] for details on the growth conditions and procedures by J. Sadowski as well as other results on samples containing ultra thin (Ga,Mn)As epilayers grown in the same MBE system.

The processing of the samples was made at the III-V Nanolab at the Ørsted Laboratory using the in-house facilities to create standard III-V semiconductor device designs.

For MBE growth the samples were soldered by Indium on the backside to the sample holder in the MBE chamber. This was removed before any processing of the samples was made, by soaking the sample with resist-covered surface into HCL (18 %) for about an hour.

For four-point dc-transport measurements the samples were formed into 100 µm wide and 1000 µm long Hallbars by wet chemical etching through windows in the photoresist covered surface, defined by UV-lithography. Au/Zn/Au was deposited in a thermal evaporator at a pressure of about $10^{-7}$ mbar and the samples were annealed in a Hot-plate furnace at 240 °C for one hour, in order to create ohmic p-type contacts. The Hot-plate furnace will be described in the following section. It later turned out that this annealing is not necessary, even though the (Ga,Mn)As layer is capped. This is because of the high carrier density in the (Ga,Mn)As layer and an indication of penetration of the capping layer during metal deposition.

The etching and metallization process are outlined in Figure 2.1 and a top-view of the final Hallbar is shown in Figure 2.2. The chemical constituents and a more detailed outline of the device processing is described in Appendix A.
In order to perform measurements in the cryostats, the samples were mounted on a 14-pin ceramic chip-carrier to which the sample is electrically connected by Au-wire bonding.

2.1.1 SC/I/DMS tunnel junction device

In order to study the degree of charge carrier spin-polarization in (Ga,Mn)As, tunnel junctions has been made. The tunnel junctions consist of a metallic Al-layer and an electric insulating AlO$_2$-layer on top of the LT GaAs capped (Ga,Mn)As epilayer (SC/I/DMS). Several approaches have been tried, but only one recipe gave devices with a good tunnel barrier. The Ga$_{0.94}$Mn$_{0.06}$As sample was cleaned and Au/Zn/Au contacts were deposited for ohmic contact to the (Ga,Mn)As. The tunnel junction was created by depositing approximately 2 nm of Al on-top the (Ga,Mn)As in the thermal evaporator, which was left to oxidize in ambient air for 24 hours. This was followed by deposition of 50 nm of Al and 200 nm of Au in the same run, in order to avoid oxidation of the Al-layer. When depositing this latter metal sequence, deoxidation and O$_2$ plasma etch was left out. A schematic illustration of the sample is shown in Figure 2.3. In the metallization chamber used, it is very difficult to deposit metal in the $1 - 5$ nm range with high accuracy, and the listed metal thickness in this range is thus a rough estimate from the thickness monitor of the metallization chamber.
2.1 Devices

2.1.2 Geometrically constricted devices

Geometrically constricted devices have been made by using Single Electron Microscopy (SEM) lithography on the (Ga,Mn)As surface. This has been done in the attempt to create constrictions with widths in the sub-micrometer range.

When etching lines/trenches in III-V compounds, the width of the line is not only determined by the line width defined by the lithographic process, but also on the etch depth. Considering wet chemical etching, lateral etching continues to increase the width of the line until the desired etch depth is reached and the etching is stopped. We therefore wanted to utilize the small etch depth necessary for creating very narrow geometrical constrictions in the ultra thin (Ga,Mn)As epilayers, in the attempt to create electrically connected geometrically confined magnetic domains.

Device processing using SEM lithography in general follows the same line of processing as with UV-lithography, as shown in Figure 2.1. A 20 µm wide Mesa is defined along the <110> crystallographic direction following step a) to d). This sequence is repeated using a different resist for SEM lithography in order to define the constrictions. Contacts are deposited following step e) to h). For details, please see Appendix A.

Figure 2.4 is a SEM-image showing the SEM-defined constrictions, the Mesa and some part of the contacts. The path of the current is between two neighbouring contacts through a small opening between two SEM-defined trenches. The smallest openings obtainable, as determined from SEM-images, were in the range between 150 nm and 250 nm. A 150 nm wide and 300 nm long opening is shown as an insert in Figure 2.4.

Complete control of the etching parameters was never obtained and functional devices were found at random between many different opening widths, as defined by SEM lithography. A closer look at the openings revealed that etching under the resist reduced the thickness of the (Ga,Mn)As layer in the opening or completely removed it. Figure 2.5 shows AFM-images of two different openings. The upper image is an example of an intact bridge and the lower is an example of how etching under the resist can remove parts of the (Ga,Mn)As layer.
Figure 2.4: Top-view SEM-image of a (Ga,Mn)As Mesa containing 9 devices with a constriction. The bright areas at the edge of the image are contacts. The dark areas are regions in which the (Ga,Mn)As has been etched away. The current path when measuring one device is between two neighboring contacts through an opening between two constrictions. The smallest opening on this Mesa is marked by the dark circle. The insert is a magnification of the opening marked by the circle, having a width and length of 150 nm and 300 nm respectively.

Figure 2.5: False colored AFM-images of two devices made by SEM lithography. The upper image shows an intact bridge whereas the lower one shows how etching under the resist can destroy the opening between the constrictions.
2.2 Annealing furnaces

Annealing of the samples has been performed in three different furnaces. For the major annealing studies presented in this thesis, the annealing was performed in a Hot-plate furnace controlled by a thermocouple at the III-V Nanolab and in a glass-tube furnace at the Department of Material Chemistry at Uppsala University, Sweden. For the low temperature - long time annealing experiments, a glass-tube furnace at the Danish Technical University (DTU) in Lyngby, Denmark, was used.

The annealing procedure has been the same in all three cases. Before annealing the furnace was evacuated and flushed with N\textsubscript{2} gas for an appropriate period of time. A continuous flow of N\textsubscript{2} gas was provided during annealing and was not stopped until the sample had reached room temperature again.

The difference in annealing conditions between the different furnaces is mainly the time of which the furnace is to reach the desired annealing temperature. Since the annealing was to be performed close to the MBE growth temperature, overshoot was not desired. The temperature was therefore slowly and carefully step-wise increased. The rise-time of the temperature also varied from time to time, but in general the rise-time was around 10 minutes.

The temperature in the different furnaces is monitored in different ways. Especially in tube furnaces the temperature gradient through the furnace can make it difficult to know the exact temperature at the position of the sample. For the main annealing studies two different kinds of furnace were used, but we believe that the desired annealing temperature was the same in both the Hot-plate furnace and the glass-tube furnace in Uppsala. For annealing in the Hot-plate furnace the sample was placed directly on the hot plate and must thus have a temperature very like the hot plate. The glass-tube furnace at Uppsala is typically used for growth of functional oxides by Chemical Vapour Deposition (CVD) and is for this use very well calibrated, so the temperature gradient down through the furnace is known with very high accuracy. Dr. Jonas Sundqvist, who is an established expert in this setup, operated the furnace. The temperature in the glass-tube furnace at DTU was monitored close to the sample by a thermocouple.
2.3 Measurement techniques

For all the experiments, Labview programs on a PC have been used to control the experimental equipment and to collect the data. The PC communicates with the experimental equipment through GPIB connections or through a DA- and AD converter unit.

2.3.1 dc-measurements

Two dc-measurement setups have been used. One is built around the Cryocooler, and will throughout the thesis be referred to as the Cryocooler setup. This setup is indicated in Figure 2.2. A Keithley 224 current supply is used to apply a current $I_{DC}$, along the Hallbar, and a HP 3478A Multimeter is used to measure the voltage drop either along the Hallbar ($V_x$) or across the Hallbar ($V_H$, Hallvoltage), controlled by a Keithley 705 scanner.

As shown in Figure 2.2, the ratio of the distance between the voltage probes and the width of the Hallbar is an integer. This makes it easy to calculate the square resistance or sheet resistance $R_{\text{sheet}}$ that is used in this thesis and is given by:

\[ R_{\text{sheet}} = R_{\text{meas}} \frac{W}{L} = \frac{\rho_{xx}}{d}, \quad R_{\text{meas}} = \frac{V_x}{I_{DC}} \] (2.1)

where $W$ is the width of the Hallbar and $L$ is the distance between the voltage probes. $d$ is the thickness of the (Ga,Mn)As layer and $\rho_{xx}$ is the resistivity. The Hall resistance is given by:

\[ R_H = \frac{V_H}{I_{DC}} \] (2.2)

The four-point dc-measurements performed in other cryostats, mainly for Hall measurements at magnetic fields above 1 T, were carried out using a Keithley KE-2400 SourceMeter. The current in both dc-setups was set to 10 $\mu$A.
2.3 Measurement techniques

2.3.2 ac-measurements

The interesting physical parameter in the study of the SC/I/DMS tunnel junction is the differential conductance, since it reflects the density of states of the SC. In this measurement, the differential conductance is measured as a function of dc-bias, hence mapping out the overlap in energy of the spin density of states of the SC and the DMS. This effect will be described in detail in Chapter 6.

The basic outline of the measurement setup, which is shown in Figure 2.6, is as follows. An ac- and dc-voltage is applied across the sample and the current response due to the resistance of the sample is measured via a current amplifier by the lock-in amplifier and an AD-converter. The differential conductance \( \frac{dI}{dV} \) is the ac-response \( dI \) to the ac-input \( dV \) and is measured as a function of the dc-bias.

In order to be in the linear response regime the applied ac-voltage has to be less than \( k_B T \), leading to ac-voltages of about 1\( \mu \)V at mK temperatures. Having such small signals, the impact of noise on the measurements becomes important and precautions to minimize this has to be made. As shown in Figure 2.6, the entire measurement setup is situated inside a shielded room having only battery driven units inside. The sample is isolated from the surroundings by having all lines in and out of the shielded room to pass through battery powered Burr-Brown ISO-100 optical isolation amplifiers (opto-couplers) and Ferroperm ceramic low-pass filters (\( \pi \)-filters).

Figure 2.6: Experimental setup for measuring the differential conductance of the SC/I/DMS devices. For a description of this setup, see the text. (DAC) digital to analogue converter, (ADC) analogue to digital converter, (Oscillator) lock-in amplifier oscillator, (opto) opto-couplers, (\( \pi \)) \( \pi \)-filter.
Going through the setup in more detail, the ac-voltage is supplied by a Stanford SR530 lock-in amplifier and the dc-voltage is supplied by a 16-bit National Instruments DA/AD converter. The signals are passed into the shielded room to a potential divider box that adds the two signals and divide the dc- and ac-signals with 1000 and 10000 respectively. This added signal is the source (S) and is connected via the electrical wires in the cryostat to the sample.

The drain (D) current is amplified with an Ithaco DL1211 current pre-amplifier with a typical amplification of $10^{-7}$ A/V, that converts the current signal to a voltage. The RMS amplitude of the ac-signal is picked up by the lock-in amplifier and its dc-output is read by the AD-converter.

All the connections are made by coaxial cables. The ground lines are not shown in Figure 2.6.

The different amplifiers have offsets that need to be compensated for. There are dc offsets from the opto-couplers and from the input of the current pre-amplifier, which have to be compensated for each time the experimental setup is changed or on a regular basis, since the offset of these battery-driven amplifiers tends to drift. The calibration of the in-put signal is made by using a test resistor as a sample and zero the dc-voltage on an oscilloscope, inserted before the lock-in amplifier, when the amplification of the current pre-amplifier is at its lowest. The DAC voltage is then changed until an increased amplification of the current pre-amplifier has no effect on the dc-signal monitored on the oscilloscope. At this point there is no dc-bias on the sample and this DAC voltage is used as the zero-point. The test resistor is then used to calibrate the out-put signal at finite biases.
Chapter 3

Electrical transport measurements

This chapter contains the electrical transport measurements on the ultra thin (Ga,Mn)As epilayers. The samples are shaped like Hallbars for four-point dc-measurements as described in section 2.1 and 2.3.1. The results are from measurements on a collection of high quality samples containing 5 % of Mn with thicknesses ranging from 3 nm and up, as well as a few samples containing 6 % of Mn with a thickness of 10 nm.

The magnetization of the sample has an impact on the electrical transport properties and from these, it is possible to determine the magnetic characteristics such as Curie temperature, magnetization vs. temperature curve and magnetic anisotropy. Hall measurement is a widely used tool for looking at the magnetic properties of (Ga,Mn)As, since the magnetization of the sample has an impact on the Hall resistance which makes it a good magnetometer. It is especially an important characterization tool when looking at magnetic samples with thicknesses in the range studied here, since the magnitude of the magnetic signal is so small that it is difficult to detect using other methods.

In this chapter, the lower thickness limit for the ferromagnetic phase to occur is determined for (Ga,Mn)As samples containing 5 % of Mn and the $pd$-exchange integral is evaluated assuming the Magnetoimpurity scattering model. Hall measurements are used to determine the Curie temperature and magnetization vs. temperature curve.

Anomalies in the Hall resistance are seen in these measurements and studies of the magnetic anisotropy reveal that this stems from a strong in-plane anisotropy and an unusually large planar Hall effect. The impact on the electric and magnetic properties upon annealing is studied and the observed changes are in correspondence with the currently known mechanisms. Though the impact on Hall resistance of the magnetization of the sample is very high, the carrier density can still be estimated when the applied magnetic field is sufficiently high. Findings on all the layers containing 5 % of Mn show, that there is a good correspondence be-
tween the carrier density and Curie temperature, as predicted by Dietl et al. [15].

When annealing (Ga,Mn)As, the annealing temperature and time is of great importance. The chapter ends with a discussion on these effects on the capped ultra thin epilayers. The discussion is continued in the following chapter.

## 3.1 Curie temperature and magnetization

(Ga,Mn)As epilayers, with thicknesses ranging from 3 nm and up, have been grown by LT MBE in order to determine a lower thickness limit for the ferromagnetic phase to occur. This has been done by resistance versus temperature measurements at zero magnetic field, from which the para- to ferromagnetic phase transition can be seen. By using the Magnetoimpurity model, it is possible to determine the value of the exchange integral $J_{pd}$ from these measurements. The Curie temperature can also be determined from Hall measurements and the values obtained by the two different methods will be compared. The Hall resistance is dominated by the anomalous Hall effect as a consequence of the magnetization of the sample. This effect will be discussed.

All the samples presented in this section have a Mn content of 5 % and have been annealed for one hour at 240 °C in the Hot-plate furnace unless otherwise stated.

### 3.1.1 Determination of lower thickness limit on ferromagnetism

The following results have been obtained by standard four-point dc-measurements in the Cryocooler setup (section 2.1, Appendix B).

The resistance as a function of temperature with no applied magnetic field for five different thicknesses of (Ga,Mn)As is presented in Figure 3.1. The 3 nm thick sample shows an insulating behavior whereas the thicker samples exhibit a metallic-like behavior with a local maximum in the resistance near 100 K. This latter behavior is commonly seen in ferromagnetic semiconductors where the maximum is known to lie close to the para- to ferromagnetic phase transition temperature [32, 41, 42]. The resistance of the ‘metallic’ samples decreases with increasing layer thickness and they all have a resistivity of $\approx 3.5 \, \text{m}^2\text{cm}$ at $T = 300$ K. This is a powerful indication of high quality growth, and it can therefore be assumed that the samples are very much alike in terms of impurity and acceptor density, and that the diffusion of Mn into the surrounding layers is the same. From these findings it can therefore be concluded, that the lower thickness limit for the ferromagnetic phase to occur is above 3 nm for samples grown under these conditions. Growth conditions have a huge impact on the properties of (Ga,Mn)As, as discussed in section 1.4, so a change in growth conditions or annealing may result in another thickness limit.
3.1 Curie temperature and magnetization

![Graph showing sheet resistance as a function of temperature with zero applied magnetic field for different thicknesses of the Ga$_{0.95}$Mn$_{0.05}$As layer annealed at 240 °C for one hour.]

The resistance is a sum of different contributions, containing impurity and phonon scattering as well as a magnetic term [43]. It is the magnetic term that gives the observed shape with two resistance extremes. The Magnetoimpurity model [44] describes similar behaviour of Manganites and other conventional ferromagnetic semiconductors such as e.g. EuO, and has been used to obtain an estimate of the exchange integral $J_{pd}$ in (Ga,Mn)As [45]. We have used the same approach to analyze our results.

The Magnetoimpurity model has been argued to be suitable for all degenerate ferromagnetic semiconductors, although it is derived on the basis of double-exchange systems [44]. The Magnetoimpurity model can qualitatively be described as follows: Increasing the temperature from below $T_c$, leads to an increase in resistivity due to a gain in the effective local magnetic moment of the ionised acceptors, that is absent when the material is fully magnetised. This gain is increased up to near $T_c$, beyond which the local moment is reduced again. The reason is, that the negatively charged Mn acceptors attract the conduction holes leading to an increased charge carrier density around the Mn acceptor ions. This again, leads to a local increase in the indirect exchange interaction and hence a non-uniform magnetization of the material. Since the holes lower their energy in regions of high magnetization a ‘magnetic’ force additional to the Coulomb force,
Electrical transport measurements

attracts the conduction holes toward the Mn acceptors. This correlation between fluctuations in the electrostatic potential and spatial magnetic fluctuations leads to a maximum in the resistance near $T_c$ where the effective local magnetic moment peaks. Since an external magnetic field diminishes the spatial differences in the magnetization it would decrease the magnitude of the resistance maximum. This effect can be seen in the measurements by F. Matsukura et. al. [32]. For a more detailed description of the Magnetoimpurity model, see ref. [44].

With the expressions from Sh. U. Yuldashev et al. [45], the resistivity is given by:

$$\rho(T) = \frac{\rho_0}{(1 - \Gamma)^2}$$

(3.1)

where for

$$T > T_c : \quad \Gamma \approx \frac{J_{pd}^4 S^2 (S + 1)^2 m^* N_0 x^2 k_F p}{4 \pi^2 E_F^2 h^2 k_B T} \left[1 - \frac{3 k_F a_i}{4 \pi}\right] = \kappa_1 \frac{T}{T_c}$$

$$T < T_c : \quad \Gamma = \frac{3 k_B T N_0 x}{2 E_F^2 p} = \kappa_2 T$$

$\rho_0$ is the background resistivity and $J_{pd}$ is the exchange integral. $S = 5/2$ is the Mn spin, $m^*$ is effective hole mass and $k_F$ is the Fermi wave vector. $N_0 x$ is the Mn concentration, where $N_0$ is the concentration of cation sites and $x$ is the fraction of Mn. $E_F$ is the Fermi energy, $k_B$ is the Boltzmann constant and $a_i$ is the lattice constant. $E_F^+ = 2^{2/3} E_F$ is the Fermi energy in the completely spin-polarized subband of free holes. $p$ is the hole concentration.

Using $\rho_0$ and $\kappa_1$ as fitting parameters, values of the exchange integral have been obtained from eight samples in the thickness range between 5 nm and 20 nm using eq. (3.1). Some of them have been annealed for an additional hour at 240 °C. The effective hole mass has been taken as $m^* = 0.5m_0$, where $m_0$ is the electron rest mass. The Fermi wave vector, $k_F$, and the Fermi energy, $E_F$, are determined from the carrier density $p$, which has been determined from Hall measurements at $T = 300$ mK assuming a spherical Fermi surface. See section 3.3.2 and Appendix C for measurements and formulas.

The value of the exchange integral shows a tendency to grow with increasing layer thickness, but no effect of annealing can be seen. The obtained values lie in
3.1 Curie temperature and magnetization

Figure 3.2: Sheet resistance as a function of temperature with zero applied magnetic field for the 10 nm thick Ga$_{0.95}$Mn$_{0.05}$As layer annealed at 240 °C for one hour (dots). The data-point at $T = 300$ mK is from a measurement performed in a different cryostat (13T). The full lines shows fits to eq. 3.1 using $\rho_0$ and $\kappa_1$ or $\kappa_2$ as fitting parameters. $R_0 = \rho_0/d = 3.35$ kΩ for $T > T_c$.

The range of $J_{pd} \in [65 \text{ meV nm}^3 ; 73 \text{ meV nm}^3]$, with a mean value of $\langle J_{pd} \rangle = 67 \text{ meV nm}^3$. Figure 3.2 is a blow-up of Figure 3.1 and shows the resistance of the 10 nm thick (Ga,Mn)As layer together with the fits to eq. (3.1).

Using the same model Sh. U. Yuldashev et. al. [45] found $J_{pd} = 70 \text{ meV nm}^3$, which is similar to the value of 68 meV nm$^3$ obtained by assuming intrinsic fluctuations of the localised spin, leading to spin disorder scattering [46]. A value of $55 \text{ meV} \pm 10 \text{ meV nm}^3$ has been reported by photo-emission experiments [47]. Comparing these values of the exchange integral, the values obtained assuming the Magnetoimpurity model correspond reasonably well to the values obtained by other methods or assumed scattering mechanisms, and it can be concluded that there is no observed difference in the magnitude of $J_{pd}$ between thick and thin (Ga,Mn)As layers.

A more common way of listing the value of the exchange integral, is in units of eV. The values of $J_{pd}$ determined for these samples are in this unit between $| N_0 / \beta | = 1.4$ and $1.6 \text{ eV}$ (here $\beta$ is the exchange integral).
The expression for the resistivity below $T_c$ assumes a fully spin-polarized sub-band of free holes, which may not be a realistic assumption for (Ga,Mn)As. Nevertheless the expression has been fitted to the data in Figure 3.2, showing that the resistance exhibits the same temperature dependence. The fitting parameter $\kappa_2$ is more than a factor of ten too small from the value of $3k_B N_{0x}/2E_F p$ when inserting the experimentally observed quantities.

The minimum of the resistance below $T_c$ is still of unknown origin, but can be a consequence of localization of the charge carriers, due to the increasing magnetization with decreasing temperature, as proposed by Van Esch et al. [48].

A different view on the mechanism behind the resistivity peak near $T_c$ is presented by K. Hirakawa et al. [49], where the partially localised holes have a decreasing hopping probability between Mn$^{2+}$ ions with decreasing temperature, until $T_c$ is reached. When $T_c$ is reached, the double exchange interaction modifies the 3d impurity band so that the holes get an increasing kinetic energy, and hence increase the charge transport.

### 3.1.2 Hall effects

An estimate of the Curie temperature has been obtained for the (Ga,Mn)As epilayers with thicknesses of 5 nm, 10 nm and 15 nm by Hall measurements in a magnetic field up to 2 T. The following results are obtained by standard four-point dc-measurements in the Heliox cryostat (Appendix B) with the applied magnetic field normal to the sample surface.

The sheet resistance as a function of applied magnetic field at different temperatures is shown in Figure 3.3 for the 5 nm thick sample. The sheet resistance shows an overall decrease with increasing magnetic field, with the exception of an increase at low magnetic fields at the lowest temperatures.

The overall negative magnetoresistance has been attributed to a reduction of random spin-flip scattering, due to the alignment of spins by the applied magnetic field. This has been described for thick (Ga,Mn)As samples at temperatures above $T_c$ by the spin disorder formula, as a decrease in scattering of charge carriers by spin fluctuations via the exchange coupling with increasing magnetic field [32].

Well below $T_c$ this model is not valid [50]. The negative magnetoresistance is observed to sustain to very high magnetic fields at very low temperatures, way above the value where the magnetization is saturated. From Figure 3.4 it is seen, that the Hall resistance is saturated at about 1 T, whereas the negative magnetoresistance continues beyond this point. The signature of a fully magnetized sample at the highest magnetic fields thus rejects spin-disorder scattering as the driving mechanism, and the magnetoresistance behaviour is instead proposed to
be caused by weak localization. F Matsukura et al. [50] stresses the importance of phase breaking scattering at low temperatures and writes that the negative magnetoresistance is: ‘an orbital effect resulting from the destructive influence of the magnetic field on interference of scattered waves’.

At temperatures below the Curie temperature, a positive magnetoresistance appears at low magnetic fields. This is caused by the anisotropic magnetoresistance and is due to an in-plane magnetic easy axis, where the positive magnetoresistance is caused by the turning of the magnetization direction from the spontaneous in-plane direction to the perpendicular direction by the applied magnetic field [32, 51, 30]. The anisotropic magnetoresistance will be discussed in section 3.3.1.

The behaviour of the magnetoresistance shown for the 5 nm thick sample is representative for all the (Ga,Mn)As layer thicknesses.
The Hall resistance for the 5 nm thick sample at different temperatures is shown in Figure 3.4. The Hall effect is seen to be strongly non-linear in magnetic field, a behaviour that is caused by the magnetization of the sample itself. This is a common behaviour in ferromagnetic materials where the Hall Resistance is given by [43]:

\[
R_H = \frac{R_0}{d} B + \frac{R_s}{d} 4\pi M
\]  

(3.2)

d is the sample thickness, \(M\) is the sample magnetization and \(B\) is the magnetic induction. \(R_0 = 1/ep\) is the ordinary Hall coefficient, where \(e\) is the electron charge and \(p\) is the charge carrier density and \(R_s\) is the anomalous Hall coefficient. The Hall resistance is dominated by the second term, called the anomalous Hall effect, since the ordinary Hall term for the present sample geometry is of the order of 1 \(\Omega\) for typical carrier densities in metallic (Ga,Mn)As in this magnetic field range.
3.1 Curie temperature and magnetization

The expression for the Hall resistance given above can be deduced from the general expression for the electric current density $J$ in a ferromagnetic metal with cubic symmetry, which is given by [52]:

$$J_x = \sigma_0 E_x + \sigma_H (E_y B_z - E_z B_y) + \sigma'_H (E_y M_z - E_z M_y), \quad x \rightarrow y \rightarrow z \quad (3.3)$$

$E$ is the electric field strength. From this expression the Hall resistivity $\rho_H$, in the usual Hall geometry, where $J = (J_x, 0, 0)$ and $B = (0, 0, B_z)$, is given by:

$$\rho_H \equiv \frac{E_y}{J_x} = \frac{\sigma_H}{\sigma_0^2} B_z + \frac{\sigma'_H}{\sigma_0^2} M_z \quad (3.4)$$

neglecting higher order terms of $M$ and $B$. $\sigma_0$ is the normal electrical conductivity, $\sigma_H$ is the Hall conductivity and $\sigma'_H$ is the anomalous Hall conductivity. The first term on the right hand side of eq. (3.4) is the ordinary Hall coefficient $R_0$ as given earlier, and the second term is the anomalous Hall coefficient, $R_a$. Notice, that it is only the $z$-component of the sample magnetization that has an impact on the anomalous Hall term.

The origin of the anomalous Hall effect is still debated [53], but the mechanism is known to be a consequence of spin-orbit interaction. The spin-orbit interaction between the magnetic moment of the charge carriers and the magnetic field induced by moving charged impurities in the charge carrier rest frame (intrinsic spin-orbit coupling), or the interaction between a localized magnetic moment and the free charge carrier angular moment (extrinsic spin-orbit coupling), removes the spatial symmetry in a scattering event. Because of this asymmetry the charge carriers in the ferromagnetic phase will be scattered preferably to one side, creating a transverse current that leads to the anomalous Hall effect. The anomalous Hall coefficient is given by [52]:

$$R_a = a \rho_{xx} + b \rho_{xx}^2 \quad (3.5)$$

The linear term in resistivity $\rho_{xx}$, on the right hand side of eq. (3.5), is due to skew-scattering, where the trajectory of the scattered charge carrier has an angle to the incoming trajectory. The quadratic term in $\rho_{xx}$ is from side-jump scattering.
Figure 3.5: Hall resistance as a function of applied magnetic field at $T = 10$ K for the 5 nm thick (Ga,Mn)As layer annealed at 240 °C for one hour. The arrows indicate the sweep direction of the magnetic field.

where the trajectory of the scattered charge carrier is displaced from the incident one. For a detailed discussion on the anomalous Hall effect see ref. [52, 54, 55]. The relative importance of the two scattering mechanisms depends on the material and the temperature. For (Ga,Mn)As both scattering mechanisms seems to be of importance [4, 51, 27, 56].

In eq. (3.2) the Hall resistance is defined through the magnetic induction, but since $B = H_{appl} + 4\pi(1 - N)M$ where $H_{appl}$ is the applied magnetic field strength and $N$ is the demagnetization factor, $B = H_{appl}$ because $N = 1$ in the Hall geometry [57]. $B$ will hence be the notation for the applied magnetic field throughout this thesis.

Returning to the Hall resistance in Figure 3.4, which is dominated by the anomalous Hall effect and hence the magnetization in the available magnetic field range, the magnitude of the Hall resistance is seen to increase with decreasing temperature until $T = 73$ K, from where it starts to decrease again at $B = 2$ T.

This behaviour has not been reported for thick (Ga,Mn)As layers and the effect is observed to decrease with increasing layer thickness. Looking at eq. (3.5) this temperature dependence must be a result of either the temperature dependence of the resistivity, temperature dependence of the factors $a$ and/or $b$ or reflect the magnetization. From the resistance measurements, the observed temperature dependence of the Hall resistance cannot be explained by the temperature depen-
3.1 Curie temperature and magnetization

dence of the resistance alone, leaving the other two possibilities to account for this behaviour. This issue will be addressed later.

With decreasing temperature an increasing offset of the Hall resistance at $B = 0$ T is observed. Figure 3.5 is a blow-up of the Hall resistance at $T = 10$ K, showing both sweep directions of the magnetic field. Here the offset at $B = 0$ T is clearly seen. It is caused by an increasing contribution from the planar Hall effect, as will be shown in section 3.2.2. There are two additional features that deviate from the anomalous Hall effect. One of them is symmetric around $B = 0$ T and depends on the sweep direction of the magnetic field. The other is only seen at positive magnetic fields and independent of sweep direction. The first is a contribution from the planar Hall effect and the latter is an unexplained reproducible anomaly that is only seen in this sample. The planar Hall effect will be described in more detail with other experimental results showing this effect in section 3.2.2.

The Curie temperature can be found from a so-called Arrot plot. This is a technique widely used for ferromagnetic semiconductors and assumes that the internal field may be described by $H_I = H_{appl} - 4\pi N M = \chi^{-1} M + \alpha M^3$, where $\chi$ is the susceptibility [58].

Assuming only skew scattering, the Curie temperature can be found from the intersection with the ordinate of the back-extrapolated linear part at high magnetic fields in a $(R_H/R_{sheet})^2$ vs. $B/(R_H/R_{sheet})$ plot (Arrot plot).

The value of the intersection at positive values on the ordinate, represents a finite magnetization with a value proportional the value of $R_H/R_{sheet}$. See eq. (3.2). The Arrot plot of the 5 nm thick sample is shown in Figure 3.6. The intersection with the abscissa is equal to the susceptibility $\chi^{-1}$, but higher temperatures for obtaining information on the temperature dependence of $\chi^{-1}$ was not possible in this cryostat.

The value proportional to the magnetization $R_H/R_{sheet} = M_H$ deduced from the Arrot plot, is presented in Figure 3.7 for the three (Ga,Mn)As layer thicknesses. The magnetization vs. temperature curves show a strong deviation from the usual Brillouin function shape, with an initial increase in magnetization followed by a small decrease. This effect is observed to become less pronounced with increasing layer thickness.

The shape of the magnetization curves cannot be explained by the temperature dependence of the resistance as discussed earlier. Therefore, this must be a consequence of either a temperature dependent anomalous Hall coefficient or a mere expression of the actual sample magnetization in the $z$-direction. Comparing this with both theory and experimental findings on (Ga,Mn)As, a decreasing magnetization with temperature has been observed when looking at the remanent
Figure 3.6: Arrot plot using the measured sheet- and Hall resistance for the 5 nm thick (Ga,Mn)As layer annealed at 240 °C for one hour.

Figure 3.7: Magnetization curves for the 5, 10 and 15 nm thick (Ga,Mn)As layers, annealed at 240 °C, obtained from Arrot plots. The negative values of $M_H$ have no physical meaning but are shown to illustrate the tendency around $T_c$. 
3.1 Curie temperature and magnetization

Figure 3.8: Curie temperature for the 5, 10 and 15 nm thick (Ga,Mn)As layers, annealed at 240 °C, obtained from resistance vs. temperature measurements (circles) and Hall measurements (triangles).

magnetization. This effect is caused by the possible reorientation of the magnetic easy-axis with charge carrier concentration [15, 31]. Here \( M_H \) is an expression of the saturated magnetization, where magnetic anisotropy have no impact. The behaviour of the magnetization curve is thus likely to be found in a temperature dependence of the anomalous Hall coefficient [52, 54, 55]. It should be emphasized, that the magnetization vs. temperature curves shown in Figure 3.7 are obtained by assuming only skew scattering and that the general shape of the curves is unchanged by assuming only side-jump scattering.

The Curie temperatures determined from the resistance vs. temperature measurements and Hall measurements are compared in Figure 3.8. The deviation is seen to be large but fairly constant and the Curie temperature always lies on the low-temperature side of the resistance-maximum. This is indeed the case for the resistance vs. temperature dependence as described by the Magnetoimpurity model [44]. From Figure 3.8 it can be seen that there is a tendency of decreasing Curie temperature with increasing layer thickness. The connection between (Ga,Mn)As layer thickness and Curie temperature will be addressed in greater detail in Chapter 4.

Because of the limitation in the available magnetic field range for these experiments, it was not possible to determine the Curie temperature with an acceptable accuracy for thicker (Ga,Mn)As layers by Hall effect. Since the anomalous Hall effect depends on the resistivity, the magnetoresistance causes the linear part of the Arrot plot to become either short or non-existing. This leads to an underestimated value of the Curie temperature.
3.2 Magnetic anisotropy

Magnetic anisotropy arises from the spin-orbit interaction of the localized electrons in the d-shell. Since \( L = 0 \) for five electrons in the d-shell, it is the orbital momentum of free charge carriers that is believed to be of importance in (Ga,Mn)As \cite{15}. As a consequence of the spin-orbit interaction, the symmetry of the charge carrier system is lowered and the scattering probability becomes dependent on the relative orientation between the sample magnetization and the current direction \cite{59}. This effect is studied here. From this study, it is possible to determine the magnetic anisotropy.

The magnetic anisotropy of the ultra thin (Ga,Mn)As epilayers has been studied in detail by electrical transport measurements on two 10 nm thick (Ga,Mn)As layers containing 6 % of Mn. The only difference between the two samples is the annealing time. Sample A has been annealed for 136 hours and Sample B for 266 hours at 180 °C in the glass-tube furnace at DTU. The extra annealing time for Sample B leads to a decrease in resistivity of about 13 % and an increase in Curie temperature from 113 K to 126 K, as determined from the resistance maximum in resistance vs. temperature measurements. The annealing study of these samples is treated in section 3.4.

3.2.1 Anisotropic magnetoresistance

The following results are obtained by standard four-point dc-measurements in the 2T-dipstick magnet (section 2.3.1, Appendix B). Figure 3.9 and 3.10 show the sheet resistance at \( T = 4.2 \) K as a function of applied magnetic field in the plane of the sample, with an angle \( \theta \) to the direction of the current for Sample A and B respectively.

For a single domain ferromagnetic layer, the resistivity \( \rho_{xx} \) can be written as \cite{59}:

\[
\rho_{xx} = \rho_\perp + (\rho_\parallel - \rho_\perp) \cos^2(\phi)
\]

(3.6)

where \( \phi \) is the angle between the sample magnetization and the current direction. \( \rho_\perp \) and \( \rho_\parallel \) are the resistivities for the current perpendicular and parallel to the sample magnetization.

Common for both plots in Figure 3.9 and 3.10 is the overall negative magnetoresistance at high magnetic fields, which was described in sec. 3.1.2.
Figure 3.9: (Sample A) Sheet resistance as a function of applied magnetic field at $T = 4.2$ K for 10 nm thick Ga$_{0.94}$Mn$_{0.06}$As layer, annealed for 136 hours at 180 °C. $\theta$ is the angle between the current and the magnetic field in the plane of the sample. Hall is for the magnetic field applied perpendicular to the sample surface.

Figure 3.10: (Sample B) Sheet resistance as a function of applied magnetic field at $T = 4.2$ K for 10 nm thick Ga$_{0.94}$Mn$_{0.06}$As layer, annealed for 266 hours at 180 °C. $\theta$ is the angle between the current and the magnetic field in the plane of the sample. Hall is for the applied magnetic field perpendicular to the sample surface.
For both samples the resistance is higher for $\theta = 90^\circ$ than for $\theta = 0^\circ$ with the resistance for $\theta = \pm 45^\circ$ in between. From eq. (3.6) this leads to the relation that $\rho_\perp > \rho_\parallel$, as is typically seen in (Ga,Mn)As [30, 60, 61]. This relation is the opposite of what is observed in other ferromagnetic materials [59], but agrees with mean-field calculations on (Ga,Mn)As [62].

For both samples as well, the magnetoresistance at low magnetic fields is positive when $\theta = 90^\circ$ and negative when $\theta = 0^\circ$, but the sign of the magnetoresistance when $\theta = \pm 45^\circ$ is different. Furthermore, the magnitude of the magnetoresistance when $\theta = 0^\circ$ or $\theta = 90^\circ$, is also different.

As described in section 1.4.3, a cubic in-plane anisotropy along the $\langle100\rangle$ and equivalent directions, with a small uniaxial anisotropy along $\langle110\rangle$ or $\langle100\rangle$ is expected. In the literature only uniaxial anisotropy in the $\langle110\rangle$ direction have been reported [22, 30, 61].

Remembering that the direction of the current in these Hallbars is randomly chosen to be in the $\langle110\rangle$ direction or orthogonal to this, the magnitude of the magnetoresistance when $\theta = 0^\circ$ and $\theta = 90^\circ$ would be equal and the magnetoresistance would be zero when $\theta = \pm 45^\circ$, if there is cubic in-plane anisotropy only or no anisotropy at all.

Focusing on the behaviour of Sample B, it corresponds to the scenario with the current running parallel to the easy-axis of magnetization. This is because the resistance change for $\theta = 0^\circ$ is less than for $\theta = 90^\circ$ and because the magnetoresistance for $\theta = \pm 45^\circ$ is positive as it should be for an increasing angle between the current and the magnetization, when looking at eq. (3.6), if there is a small uniaxial anisotropy along $\langle110\rangle$. From these findings, the current in this sample must run in the $\langle110\rangle$ direction when comparing with the reported results in the literature.

The difference in the magnitude of the magnetoresistance between $\theta = 0^\circ$ and $\theta = 90^\circ$ for Sample A is less pronounced. It is in fact so small (6 $\Omega$), that these measurements suggest a purely cubic anisotropy with no uniaxial anisotropy.

The only difference between Sample A and B is the annealing time. Annealing has an impact on both charge carrier density and lattice constant, which has both been observed to increase [63]. Since the magnetic anisotropy depends on these two parameters [15], the observed difference between Sample A and B is due to a change in the magnetic anisotropy upon annealing.

The strong in-plane anisotropy of compressively strained (Ga,Mn)As can be seen from the resistances in Figure 3.9 and 3.10 when the magnetic field is applied perpendicular to the sample surface (Hall). Here the resistance increases less rapidly with magnetic field and the turning point of the magnetoresistance
is about 7 times bigger than for in-plane applied magnetic fields. Contrary to the magnetoresistance measured with the applied magnetic field in-plane of the (Ga,Mn)As layer, the magnetoresistance exhibits hysteretic behaviour when the magnetic field is applied perpendicular to the sample surface. This effect is not due to a magnetic remanence perpendicular to the sample surface, but is caused by the planar Hall effect as will be shown in the next section.

### 3.2.2 Planar Hall effect

The resistances of the two samples shown in Figure 3.9 and 3.10 are shown in Figure 3.11 together with the corresponding Hall resistances, when the magnetic field is applied perpendicular to the sample surface. Here it is seen, that the hysteretic behaviour of the resistances appears at the same values of the applied magnetic field as ‘bumps’ appear in the Hall resistance, when the magnetic field is swept from zero and out.

Assuming that only the anomalous Hall effect contributes to the Hall resistance, the Hall resistance at these small magnetic fields depends solely on the magnetization perpendicular to the surface and the sample resistance (see section 3.1.2). First it should be noted that the Hall resistance has an offset at $B = 0$ T. This offset increases with decreasing temperature as described in section 3.1.2. Second, the values of the Hall resistance at $B = 0$ T coincide for the two sweep directions, showing that there is no magnetic remanence perpendicular to the sample surface. Third, the difference in the resistance between the two sweep directions is the opposite of the difference between the Hall resistances. Hence the observed ‘bumps’ cannot be attributed to the anomalous Hall effect.
The observed effect can be described by the planar Hall effect. Because of the difference between $\rho_\perp$ and $\rho_\parallel$, the resulting electric field in the plane of the sample will not be completely parallel with the current direction, but have a transverse component. The resulting Hall resistivity $\rho_y$, is given by [30]:

$$\rho_y = (\rho_\parallel - \rho_\perp) \cos(\phi) \sin(\phi)$$  

(3.7)

where the quantities are the same as in eq. (3.6). The planar Hall effect has been observed to be orders of magnitude larger in (Ga,Mn)As than in other metallic ferromagnets [30] and can qualitatively be described as follows.

Figure 3.12 (a) is a schematic drawing of the (Ga,Mn)As (001)-plane. The current density $\mathbf{J}$ is set to be in the $\langle 110 \rangle$ direction and the sample magnetization $\mathbf{M}$ with an angle $\phi$ to the current direction. The cubic magnetic easy axis is along the $\langle 100 \rangle$- and equivalent directions. The black and grey dots indicate respectively the maxima and minima directions in the Hall resistivity as given by eq. (3.7). Figure 3.12 (b) is an illustration of the Planar Hall resistance from the results of H. X. Tang et al. [30], that shows the general behaviour as a function of an applied magnetic field in the plane of the sample with an angle $\theta$ to the current.
3.2 Magnetic anisotropy

Figure 3.13: (Sample A) Hall resistance as a function of applied magnetic field perpendicular to the sample surface at $T = 4.2$ K for 10 nm thick Ga$_{0.94}$Mn$_{0.06}$As layer annealed for 136 hours at 180 °C. Grey and black curves corresponds to two small but different intentionally induced in-plane components of the applied magnetic field.

The angle $\theta$ has to be only a few degrees before these double switching events take place [30]. The magnitude of the planar Hall effect is comparable with the anomalous Hall term at low magnetic fields, as observed by H. X. Tang et al.. A very small misalignment of the sample, causing an unintended in-plane component from the magnetic field applied perpendicular to the sample surface, will give rise to the observed ‘bumps’ in the Hall resistance. It is seen from from Figure 3.13 that this is indeed the case for these samples.

Figure 3.13 show the Hall resistance for Sample A in the Cryocooler setup at $T = 10$ K. Here, the sample is intentionally rotated by a small angle relative to the applied magnetic field, so that the in-plane transverse component (y-direction)
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is changed. The graphs in Figure 3.13 show two different situations and can be explained by an initial small in-plane component with a small angle to the current direction, that is altered by the intentional rotation. Comparing with Figure 3.12 (b) it illustrates the transition from having $\theta < 0$ to $\theta > 0$. From these findings it can also be seen that it is indeed the Planar Hall effect that is responsible for the offset in the Hall resistance at $B = 0$ T.

The misalignment of the applied magnetic field perpendicular to the sample surface only has to be a few percent in order to see the 'bumps', since not only the angle but also the magnitude of the in-plane component only have to be very small [30]. The magnitude of the turning field depends very much on temperature, ranging from a few mT at high temperatures to tens at low temperatures. To illustrate this evolvement with temperature, results from Sample A obtained in the Cryocooler setup is shown in Figure 3.14. H. X. Tang et al. [30] have deduced the in-plane anisotropy fields from their experiments on the Planar Hall effect to be 240 mT and 16 mT for the cubic and uniaxial anisotropy, respectively.

The offset in the Hall resistance at $B = 0$ T is commonly seen in Hall experiments, but the 'bumps' have not been reported in the literature for thick (Ga,Mn)As layers. The bumps are seen in almost every measured ultra thin (Ga,Mn)As epilayer and the summary of these findings could therefore be, that the samples are always badly aligned to the applied magnetic field. The bumps have been impossible to get rid of by patient adjustments and they appear in different cryostats. The double switching is a single domain event and taking into account the findings by H. X. Tang et al. on the magnitude of the planar Hall effect and at which magnetic fields it can be measured, it must be concluded that these ultra thin (Ga,Mn)As epilayers are single- or few domain structures. The bumps are seen here because of a small misalignment of the applied magnetic field and comparing numerical values, it is a misalignment of about 5 %.
3.2 Magnetic anisotropy

Figure 3.14: (Sample A) Hall resistance as a function of applied magnetic field perpendicular to the sample surface at different temperatures for 10 nm thick Ga$_{0.94}$Mn$_{0.06}$As layer annealed for 136 hours at 180 °C. (Full line) sweep up, (dotted line) sweep down.
3.3 Dependence of Curie temperature on charge carrier density

Post-growth annealing at temperatures at or below the growth temperature, is known to have an effect on the charge carrier density, Curie temperature and magnetization. This was described in detail in section 1.4.3. We have studied the effect of annealing at 240 °C in a Nitrogen atmosphere for different spans of time on the ultra thin (Ga,Mn)As epilayers, having a Mn content of 5 %, with thicknesses in the range from 5 nm to 25 nm. See section 2.2 for a detailed description of the annealing procedure. The effect of annealing on the Curie temperature and magnetization has been investigated by SQUID magnetometry, and will be presented in the next chapter. Here the effect of annealing on the transport properties, by means of Hall measurements, is presented. The charge carrier density can be determined from the Hall measurements at low temperatures and at high magnetic fields, where the influence of the anomalous Hall effect with magnetic field is sufficiently small. The relation between the Curie temperature and the charge carrier density is compared with the theoretical prediction by Dietl et al. [1, 15] as presented in section 1.3. All measurements in this chapter are standard four-point dc-measurements and are performed in the 13T cryostat. (See section 2.3.1 and Appendix B).

3.3.1 Magnetoresistance

Figure 3.15 and 3.16 shows the relative change in resistance and the Hall resistance of the 5 nm thick layer, annealed for one and four hours respectively, as a function of applied magnetic field perpendicular to the sample surface at $T = 300$ mK.

The resistance is seen to increase at low magnetic fields as a consequence of the in-plane magnetic anisotropy followed by a negative slope. Besides this behaviour, which was described in section 3.1.2, an additional oscillating feature can be seen at around $B = 3$ T for the sample annealed for one hour and two around $B = 3$ T and $B = 4.5$ T for sample annealed for four hours. This feature, varying in magnitude, is seen in all the samples with thicknesses below 20 nm. Annealing has some effect on the magnitude and magnetic field dependence of this oscillation, but it has not been possible to find a direct connection or address this feature to a physical mechanism.

Classical Size effects can have an impact on the magnetoresistance as well as on the Hall resistance [52]. If the charge carrier mean free path is comparable to the thickness of the sample, surface scattering becomes important and oscillations in both the resistance and the Hall resistance with magnetic field can arise.
3.3 Dependence of Curie temperature on charge carrier density

Figure 3.15: The relative change in resistance and the Hall resistance of the 5 nm thick Ga$_{0.95}$Mn$_{0.05}$As layer, annealed for one hour at 240 °C, as a function of applied magnetic field perpendicular to the sample surface at $T = 300$ mK.

Figure 3.16: The relative change in resistance and the Hall resistance of the 5 nm thick Ga$_{0.95}$Mn$_{0.05}$As layer, annealed for four hours at 240 °C, as a function of applied magnetic field perpendicular to the sample surface at $T = 300$ mK.
The oscillating behaviour stems from the relative magnitude of the cyclotron orbit to the thickness of the sample and is commonly seen in metals. The mean free path of the charge carriers, determined from the zero field resistivity and the charge carrier density obtained from the Hall measurements, lies below 1 nm for all the (Ga,Mn)As layers (see Figure 3.20 (d)). Therefore, it is very doubtful that this effect is the source of the observed oscillations.

The oscillation weakly appears in the Hall resistance with the same magnetic field dependence as in the magnetoresistance. This originates from the resistance dependence of anomalous Hall term as will be show in section 3.3.3.

As presented in section 3.1.2, the 5 nm sample showed an anomaly in the Hall resistance at $T = 10$ K at low magnetic fields in only one magnetic field sweep direction. This anomaly is still seen at $T = 300$ mK and from Figure 3.15 and 3.16 it can be seen that it decreases in magnitude upon annealing. The anomaly could be a consequence of the turning point of the magnetoresistance, but it is evident that the increase in $\Delta R/R$ with annealing time does not lead to a bigger anomaly in the Hall resistance.

The oscillating feature in the resistance and Hall resistance disappears at higher temperatures. Figure 3.17 shows the relative change in resistance and the Hall resistance for the 15 nm thick (Ga,Mn)As annealed for two hours as a function of applied magnetic field perpendicular to the sample surface at $T = 300$ mK and $T = 8$ K.
3.3 Dependence of Curie temperature on charge carrier density

The charge carrier density depends on the temperature and for the samples presented in Figure 3.17 the charge carrier density (determined from the Hall data) decreases with decreasing temperature by approximately 8%. The resistance minimum lies about 8 – 10 K (see Figure 3.1), so the resistance increment from 8 K to 300 mK is in agreement with a decreasing charge carrier density.

3.3.2 Carrier density

As shown in Chapter 3.1.2, the Hall resistance is given by:

\[ R_H = \frac{R_0}{d} B + \frac{R_s}{d} 4\pi M \]  (3.8)

where \( R_0 \) is the ordinary Hall coefficient and \( R_s \) is the anomalous Hall coefficient. Below \( T_c \), the anomalous Hall term leads to a rapid increase in Hall resistance with increasing magnetic field, often followed by a small decrease due to the negative magnetoresistance. Therefore it is often necessary to apply high magnetic fields at very low temperatures, in order to determine the carrier density from the ordinary Hall term. Magnetic fields of more than 16 T are often necessary, but for these ultra thin epilayers 12 T is enough due to their unusually small negative magnetoresistance, that is just a fraction of 1 %, compared to thick (Ga,Mn)As layers.

It has been possible to determine the carrier density \( p \), for samples with (Ga,Mn)As layer thickness up to 20 nm, assuming either skew or side-jump scattering, by fitting the data to eq. (3.8) rewritten as:

\[ \rho_H - \Lambda \rho_{xx}^{\alpha} = R_0 B \]  (3.9)

\[ \Lambda = 4\pi M_{sat}a \quad \text{for} \quad \alpha = 1 \quad \text{(skew scattering)} \]
\[ \Lambda = 4\pi M_{sat}b \quad \text{for} \quad \alpha = 2 \quad \text{(side-jump scattering)} \]

by using eq. (3.5). \( \Lambda \) is the fitting parameter. \( \rho_H \) is the measured Hall resistivity and \( \rho_{xx} \) is the measured resistivity. \( M_{sat} \) is the saturated magnetization of the sample. The negative magnetoresistance increases with increasing layer thickness, and the carrier density could not be determined to a satisfying accuracy for the 25 nm thick layer in the available magnetic field range.
There is a difference in the determined carrier density depending on the assumed scattering mechanism, where skew scattering gives the highest values. This can be seen in Figure 3.18 that shows the fit to eq. (3.9) for the 10 nm thick sample annealed for one hour. The difference increases with increasing layer thickness but depends only weakly on annealing time as can be seen in Figure 3.19. This deviation will be discussed in the next section.

The results for the carrier density assuming only skew scattering are shown in Figure 3.20 (b). The carrier density increases upon annealing, except for the 5 nm layer, where it decreases. The increase upon annealing is consistent with the reported decrease in the amount of Mn interstitials as described in sec. 1.4.3.

The Curie temperatures, shown in Figure 3.20 (a), are also seen to increase during annealing. This observation is contrary to reported results, where the presence of a capping layer tends to reduce $T_c$ in layers thinner than 50 nm upon annealing [64]. The Curie temperatures have been determined by SQUID magnetometry, except for the 5 nm thick layer that was determined from Hall measurements.

The mean free path $l$, calculated from the measured resistivity at $B = 0T$ and carrier density at $T = 300$ mK, is shown in Figure 3.20 (d) (see Appendix C). The obtained $l$ values are in the range between 0.4 and 0.65 nm, which is shorter...
3.3 Dependence of Curie temperature on charge carrier density

Figure 3.19: The charge carrier density for Ga$_{0.95}$Mn$_{0.05}$As layers with thicknesses between 5 nm and 20 nm at $T = 300$ mK obtained by fitting the Hall data to eq. (3.9) assuming either skew- or side-jump scattering. In the graph on the right side, the 15 nm thick sample has been annealed for 3 hours. See text for details.

than the average distance between Mn ions in (Ga,Mn)As with 5% of Mn (1.1 nm). These low values for the mean free path is expected due to the high degree of disorder in low temperature grown (Ga, Mn)As. The increasing mean free path upon annealing is a consequence of reduced disorder by the removal of Mn$_I$.

The Curie temperature, carrier density and the effect of annealing depends on the thickness of the layer, as can be seen from Figure 3.20. This will be discussed in the next chapter, since the magnetization curves of the individual layers presented there adds to this discussion. Here, the clear correspondence between the Curie temperature and carrier density seen in Figure 3.20 will be discussed. This clear correspondence suggests that the Curie temperature is governed by the concentration of charge carriers and not directly related to the thickness of the layer.
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Figure 3.20: Ga$_{0.95}$Mn$_{0.05}$As parameters at $T = 300$ mK as a function of layer thickness for samples annealed at 240 °C for 1 h (open squares), 2 h (filled squares), and 3 h (circle).

(a) Curie temperature; (b) carrier density as determined from Hall data assuming only skew scattering; (c) resistivity; (d) mean free path. See Appendix C for equations used for calculations.
Within the Zener model, Dietl et al. has predicted a relation between the Curie temperature and carrier density given by [1, 15]:

$$T_c = x_{eff}N_0S(S + 1)\beta^2 A_F m^* \frac{\hbar^2 \pi^{2/3} 3^{1/3}}{12k_B} p^{1/3}$$

$$= x_{eff}Cp^{1/3} \quad (3.10)$$

for a strongly degenerate carrier liquid ($E_F \gg k_B T$), neglecting spin-orbit coupling in an III-V compound. $x_{eff}N_0$ is the effective Mn concentration where $x_{eff}$ is the fraction of Mn participating in the magnetic ordering and $N_0$ is the concentration of cation sites. $S = 5/2$ is the Mn$^{2+}$ spin and $\beta$ is the pd-exchange integral. $A_F$ is the Fermi-liquid parameter, which has been evaluated to be about 1.2. $m^*$ is the effective hole mass, which is set to $0.5m_0$. $m_0$ is the electron rest mass.

The data of all the samples presented in Figure 3.19 or 3.20 spans only the range of half a decade. This makes a fit using a log-log plot in order to determine whether or not the power law holds and at the same time determine the magnitude of the material parameters $x_{eff}$ and $C$, very questionable. But, in doing so, the obtained power law was 0.36 and 0.255 for skew- and side-jump scattering respectively, with $x_{eff}C_{skew} = 6.5 \cdot 10^{-6}$ Km and $x_{eff}C_{side-jump} = 6.66 \cdot 10^{-4}$ Km. The uncertainty on the product of the material parameters is higher than 60 %. Assuming the given power law in eq. (3.10), accurate fits can be made yielding a value for $x_{eff}C$ equal to about $1.1 \cdot 10^{-5}$ Km, independent of the scattering mechanism used. The Curie temperature is plotted as a function of charge carrier density for the two sets of samples in Figure 3.21, where the carrier density has been determined assuming either skew- or side-jump scattering. The full lines show the $p^{1/3}$ dependence.

Using the values given in ref. [15], where $\beta N_0$ is set equal to 1.2 eV, the value of $C$ is equal to $3.41 \cdot 10^{-4}$ Km and results in a value of $x_{eff} = 3.24 \%$. Using the mean value of $\beta N_0 = 1.48$ eV obtained for these samples using the magnetoimpurity model on the resistance vs. temperature measurements, one gets $x_{eff} = 2.12 \%$. 

The amount of Mn in these ultra thin epilayers is intended to be 5%. Assuming that each and every Mn ion contributes with a conduction hole, the carrier density should be $11.1 \times 10^{20}$ cm$^{-3}$. The value of the carrier density determined from the Hall measurements lies between $5 \times 10^{20}$ cm$^{-3}$ and $8 \times 10^{20}$ cm$^{-3}$, which corresponds to an effective acceptor concentration between 2.3% and 3.6%. These values correspond very well to the values found above.

There are uncertainties in some of the parameters in eq. (3.10) that determines the value of $C$, and some values may even depend on the charge carrier density itself. Focusing on $x_{eff}$ alone does in principle not make sense when looking at the estimated value of $x_{eff}C$, since it probably changes during annealing. But from the carrier density it can be seen that only about half of the intended Mn ions act as an acceptor, and that this fraction corresponds very well to the resulting value of $C$ when the relation between $T_c$ and $p$ is assumed to be the 1/3 power law.
3.3 Dependence of Curie temperature on charge carrier density

3.3.3 Skew- or side-jump scattering?

Returning to the issue on the dominant scattering mechanism in the anomalous Hall effect, there are different results in the literature [4, 27, 51]. Using the coefficient $\Lambda$, which was used as a fitting parameter in determining the carrier density, and the determined carrier density, the measured Hall resistivity is compared with the calculated Hall resistivity given by:

$$\rho_{H,\alpha}^{\text{calc}} = \Lambda \rho_{xx}^{\alpha} + B/ep$$  \hspace{1cm} (3.11)

where $\alpha$ is equal to one for skew scattering and two for side-jump scattering.

The result depends strongly on the layer thickness and for the thinnest layers, the calculated Hall resistivities almost co-inside, but describes the Hall resistance at low magnetic fields ($B < 7$ T) very badly. For the 5 nm thick sample $\rho_{H,\alpha}^{\text{calc}}$ are both below the measured one whereas the opposite is seen for the 7 nm thick sample.

For the 10 nm thick layer (see Figure 3.22), $\rho_{H,2}^{\text{calc}}$, assuming only side-jump scattering, lies perfectly over the measured Hall resistivity, and it can bee seen, that the oscillations in the Hall resistance originate from the oscillations in the resistance. The evolution of the oscillations upon annealing is also clearly seen. Another interesting feature to notice, is the accuracy of the fit all the way down to about 2 T. This shows, that the magnetization is completely saturated in the

Figure 3.22: Hall resistivity at $T = 300$ mK for the 10 nm thick Ga$_{0.95}$Mn$_{0.05}$As layer together with plots of eq. (3.11) assuming either skew scattering (dotted line) or side-jump scattering (full line).
As the layer thickness is increased from 10 nm, both calculated Hall resistivities are above the measured one and skew-scattering starts to be a better candidate for the dominant scattering mechanism.

The anomalous Hall effect in Ferromagnets depends on the temperature and the composition of the Ferromagnet [52, 59], and the anomalous Hall effect in (Ga,Mn)As probably consists of both scattering mechanisms as is the case for other Ferromagnets. By comparing the anomalous Hall resistance and the resistance at different temperatures, K. W. Edmonds et al. [51] have found that side-jump scattering in a wide range of Mn content is the dominant scattering process, but they also see evidence of both scattering mechanisms having importance in other samples.

The results presented above suggests, that the dominant scattering mechanism depends on the layer thickness, with side-jump being dominant at small layer thicknesses and skew for thicker layers. No definitive conclusion on the dominant scattering mechanism is possible from these measurements.

It is a possibility, that the impact on the dominant scattering mechanism by the thickness of the layer is through the composition of the layer. As will be shown in the next chapter, the composition, in terms of the distribution of the Mn ions that participate in the ferromagnetic ordering, depends on the layer thickness as well as on annealing time.

### 3.4 Impact of annealing temperature and time

As described in section 1.4.3, the understanding of the annealing process has developed during the recent years. The optimum annealing temperature and time has changed as deeper insight was achieved, and currently long annealing times at temperatures well below the growth temperature are the most effective in increasing the Curie temperature. This observation led us to try to decrease the annealing temperature from 240 °C to 180 °C and prolong the annealing time as well.

Four different samples from the same wafer with a 10 nm thick (Ga,Mn)As layer containing 6 % of Mn were annealed at 180 °C in a Nitrogen atmosphere. The detailed description of the annealing procedure is to be found in section 2.2. Four-point dc-measurements were performed in the cryocooler cryostat (see section 2.3.1 and Appendix B). The measured resistivities are shown in Figure 3.23 as a function of temperature. With increasing annealing time the shape of the curves is slightly changed toward a less pronounced resistivity peak near $T_c$. 
3.4 Impact of annealing temperature and time

Figure 3.23: Resistivity as a function of temperature with zero applied magnetic field for different annealing times of the 10 nm thick Ga$_{0.94}$Mn$_{0.06}$As layer annealed at 180 °C.

Figure 3.24: Room-temperature resistivity and $T_c$ determined from the resistivity maximum in resistance vs. temperature measurements as a function of annealing time at 180 °C for the 10 nm thick Ga$_{0.94}$Mn$_{0.06}$As layer.
The resistivity decreases and the resistivity maximum moves toward higher temperatures.

Figure 3.24 show the resistivity maxima, interpreted as $T_c$, and the resistivity at room temperature as a function of annealing time. $T_c$ increases from about 90 K for the as-grown sample to about 125 K for the sample annealed for 233 hours. This increase is accompanied by a decrease in room-temperature resistivity by 20%. Though the evaluated Curie temperatures from these measurements are with some uncertainty (see Figure 3.8), the increase in $T_c$ with annealing time does not seem to saturate. This result was encouraging, so a Bachelor project was initiated with the purpose of continuing these experiments under my supervision.

For this project, new samples were made. The students carried out similar experiments as presented above on 10 nm thick layers with a Mn content in the range between 3% and 7%. These layers were also capped with LT GaAs. The students reached annealing times up 500 hours, but saw only small effects on the evaluated Curie temperature. The highest obtained $T_c$ was 76 K for a sample with 5% of Mn. Their results can be found at the Ørsted Laboratory Library in their report: ‘Electrical transport properties of magnetic semiconductors.’

The capping layer is, on the basis of the current understanding, known to limit the effect of annealing (section 1.4.3). As will be discussed in the next chapter, this limitation is observed for the samples annealed at 240 °C and is also observed in the samples investigated by the students.

It is not unlikely for one sample to deviate from this behaviour, but the change in the resistivity vs. temperature curve upon annealing seen in Figure 3.23, may lead to a change in the deviation between the resistivity maximum and the Curie temperature. If this is the case, Figure 3.24 gives a wrong picture of the $T_c$ dependence on annealing time and saturation of $T_c$ might happened for this sample as well.

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1’Elektriske transportegenskaber af magnetiske halvledere’ by C. P. Ryder and A. Thorseth. Ørsted Laboratory Library, Universitetsparken 5, DK-2100 Copenhagen Ø.
Chapter 4

Magnetization by SQUID magnetometry

The samples, from which the carrier density has been determined and presented in the previous chapter, originally come from an annealing study where SQUID magnetometry was used to determine the magnetization vs. temperature curve (magnetization curve) and Curie temperature. These results are the object of this chapter.

To recapture the foundation of this study; samples with thicknesses between 5 nm and 25 nm containing 5 % of Mn were successively annealed for one hour in a Nitrogen atmosphere at 240 °C up to a maximum of three hours. The field-cooled (FC) magnetization of the layers was recorded when re-heating the sample using a Quantum Design MPMS5 SQUID in a small in-plane applied magnetic field of 20 or 50 Gauss depending on the layer thickness. The experiments were performed at the Department of Materials Science, Uppsala University, Sweden, in collaboration with Dr. Roland Mathieu.

The SQUID consists of a superconducting ring interrupted by two Josephson junctions. The number of flux quanta through the superconducting ring is directly related to the current in the ring. The basic concept is, that by applying a constant current in the superconducting ring it is possible to detect a change in the magnetic flux through the center of the ring as a change in voltage across the Josephson junctions. In real systems the magnetic flux through the superconducting ring is detected by the SQUID electronics using a modulation-feed back technique. The magnetization in this chapter is given in units of Bohr magneton $\mu_B$ pr. Mn atom and calculated by knowing the volume of magnetic material and the amount of Mn in the GaAs zinc-blende lattice. See Appendix C for equations.
4.1 Effect of annealing

Figure 4.1 shows the temperature dependence of the FC magnetization for the different layer thicknesses and annealing times. A magnetic signal could not be recorded from the 5 nm thick sample. A magnetic signal from the 7 nm thick sample could only be recorded after one hour of annealing.

Focusing on the data from the as-grown samples, the shape of the magnetization curve is seen to depend on the thickness of the layer. The magnetization curve of the 25 nm thick layer looks similar to what is observed for thick layers [42]. With decreasing layer thickness the magnetization curves become broader. The onset of ferromagnetism is followed by an almost constant magnetization until the lowest temperatures are reached. Here it starts to increase again, having a saturated magnetization value below $2 \mu_B$.

This shape of the magnetization curve resembles the prediction by Berciu and Bhatt in case of a large inhomogeneity in the Mn distribution [65]. The difference in hole density in different areas of the sample leads to a spatial inhomogeneity in the magnetization, since the strength of the exchange coupling between Mn and hole spins depends on the hole concentration. The resulting wide distribution of exchange couplings leads to a broader magnetization curve where regions of low Mn concentration only get ferromagnetic ordered at the lowest temperatures.

Mean-field calculations in the regime of degenerate holes has predicted the same shape of the magnetization curve when there is inhomogeneity in the Mn distribution and the charge carrier to Mn$_{Ga}$ ratio is low [20]. In the same paper, percolation theory, which applies in a regime of localized holes, including disorder in the Mn distribution, again leads to a similar behaviour of the magnetization curve. An interesting result from this paper is the evolvement of the shape of the magnetization curve from a linear-like to a more Brillouin function-like shape when the carrier density - Mn$_{Ga}$ ratio is increased.

Upon annealing, the shape of the magnetization curve for the 25 nm thick sample is unchanged, whereas the shape of the magnetization curves of the thinner samples are gradually changed towards the shape of the 25 nm sample. This change suggests, on the basis of the results of ref. [65] and [20], that annealing leads to a higher degree of homogeneity in the magnetization of the sample, and/or is a consequence of an increased charge carrier density (Figure 3.20).

As we proposed in the paper by R. Mathieu et al. [38], the observed change in magnetization curve upon annealing may be explained as a rearrangement of the compensating donors, not only during post-growth annealing, but also during MBE growth.

Experiments have shown an in-depth gradient in the density of holes with the highest hole density at the surface [66]. On the other hand it has been shown theoretically, that Mn should preferentially occupy interstitial sites in the surface
4.1 Effect of annealing

Figure 4.1: Temperature dependence of the FC magnetization of Ga$_{0.95}$Mn$_{0.05}$As samples with different thicknesses. The samples are annealed as indicated in the box in the upper right corner. The magnitude of the applied magnetic field is shown to the right.
Magnetization by SQUID magnetometry

region [67]. These two findings seem contradicting, since Mn$_I$ act as compensating donors. But there is experimental evidence of segregation of Mn at the surface [68] and assuming that the Mn$_I$ are passivated at the surface, an in-depth gradient in the hole density can be explained by out-diffusion of Mn$_I$ during growth.

If the out-diffusion of Mn$_I$ is slower than the MBE growth rate, the highest impact of this depletion process of Mn$_I$ during growth, must be for thin layers. For layers with thicknesses beyond a critical thickness, determined by the growth process, a density profile of Mn$_I$ would be ‘frozen in’. This picture is consistent with our experimental findings, which also suggests that the critical thickness is about 15 nm. This will be elaborated later.

Experiments on a set of uncapped samples by Ku et al. [64] annealed for one and a half hour at 250 °C, found the highest Curie temperature of 150 K for a 15 nm thick sample. This Curie temperature is one of the highest observed until now, and it is interesting to note that others reaching Curie temperatures this high, are observing it in thick (Ga,Mn)As layers which have been annealed for much longer periods of time. These observations are also in good agreement with the idea of Mn$_I$-diffusion during growth.

The thickness dependent effect of annealing is summarized in Figure 4.2, where the magnetization curves for all the samples after two hours of annealing are shown. Though the shape of the magnetization curves differs, they all have approximately the same value of the magnetization at low temperatures.

The Curie temperature is determined by the onset of ferromagnetic ordering and is shown for all the samples in Figure 4.3. For all thicknesses the Curie temperature is seen to increase during annealing. The Curie temperature for the 25 nm thick sample is vaguely affected, whereas samples with thicknesses below 20 nm all are affected with the highest change for the 15 nm thick sample.

Comparing with Figure 3.20, not only does the Curie temperature decrease for increasing layer thickness beyond 15 nm, but the electric transport properties also degrade. These findings thus suggest 15 nm as the critical thickness limit.

The presence of a capping layer, which we at that time believed to be necessary in order to prevent degradation of the ultra thin (Ga,Mn)As epilayers, seems to cause a limit in the possible obtainable $T_c$ upon annealing. A third annealing was performed on the 15 nm thick layer and, as can be seen in Figure 4.1 and 4.3, had very little effect on the shape of the magnetization curve and $T_c$. This result is along the line of several others [7, 36, 37, 38] and again points to the importance of passivation of Mn$_I$ at the surface in obtaining a high $T_c$. 
4.1 Effect of annealing

Figure 4.2: Temperature dependence of the FC magnetization of Ga$_{0.95}$Mn$_{0.05}$As samples with different thicknesses after two hours of annealing at 240 °C.

Figure 4.3: Curie temperature determined from the onset of ferromagnetism in Figure 4.1 as a function of layer thickness.
Figure 4.4: (a) SIMS Mn distribution profiles from the 1200 nm thick Ga$_{0.93}$Mn$_{0.07}$As layer. The dotted line indicates the LT GaAs - (Ga,Mn)As interface. (b) Cross-sectional TEM image of the surface region of an uncapped Ga$_{0.933}$Mn$_{0.067}$As layer.

As presented in the paper by R. Mathieu et al. [38], Secondary Ion Mass Spectroscopy (SIMS) was used to investigate the assumption of Mn diffusion during annealing. A 1200 nm thick Ga$_{0.93}$Mn$_{0.07}$As layer capped with a 100 nm LT GaAs layer was used in this study and annealed in vacuum at 280 °C for one hour and four hours. The result is shown in Figure 4.4 (a). There are four important features to notice. The in-depth profile of Mn is not constant, and the bulk value is not reached until 15 nm below the LT GaAs - (Ga,Mn)As interface. The Mn profile is shifted towards the surface upon annealing, and even stretches throughout the capping layer. These findings thus confirm the assumption of Mn$_I$ diffusion but raise the question: How come the ultra thin epilayers presented in this thesis are so alike in resistivity (Figure 3.1) and all fall on the same $T_c - p$ dependence (Figure 3.19)? The answer must be, that even though the desired Mn content is not achieved, the Mn in-depth profile for layers with thicknesses below 15 nm is reproducible from growth to growth. It is interesting to note, that the 15 nm is the same as the critical thickness for the ultra thin epilayers found from the shape of the magnetization curves and transport properties. This shows, that for layers with thicknesses above 15 nm, the inhomogeneous surface region becomes decreasingly dominant and hence less significant for the magnetic properties, as seen from the magnetizations measurements in Figure 4.1.

Considering uncapped (Ga,Mn)As, very recent experimental findings by K. W. Edmonds et al. on the nature of the surface have been published [69]. Figure 4.4 (b) is a cross-sectional Transmission Electron Microscope (TEM) image,
from ref. [69], of the surface region of a Ga$_{0.933}$Mn$_{0.067}$As layer with very high $T_c$, annealed in air. The surface layer is seen to be about 3 nm thick and very oxide rich, containing several times more Mn than in the bulk, as determined by x-ray absorption spectroscopy. On this basis, the oxidation seems to be the mechanism for passivating Mn$_I$. In this paper they also note the importance of Mn diffusion during growth.

To recapture the findings and interpretations made in this chapter; the magnetization curves can qualitatively be explained by disorder in the Mn distribution and the change of shape of the magnetization curves upon annealing as a decrease in Mn inhomogeneity and/or as an increase in carrier density. It is furthermore evident that Mn diffusion happens towards the surface during annealing and a similar diffusion is likely to happen during MBE growth. Mn diffusion during growth will lead to an inhomogeneous in-depth distribution of Mn, that depends on the thickness of the (Ga,Mn)As layer and growth conditions. If this Mn diffusion is slower than the growth rate, it will have the largest impact on the electric and magnetic properties of (Ga,Mn)As layers below a certain thickness. Above this critical thickness the in-depth distribution of Mn will be the same over a large range, which then dominates the electric and magnetic properties of the layer. Adding to this the in-depth profile of Mn obtained by SIMS, the electric transport properties and the thickness dependent impact of annealing, the critical thickness is about 15 nm.

The presence of a LT GaAs capping layer is now known to have a limiting effect in obtaining high Curie temperatures by post-growth annealing, an effect we also have observed.

The effect of annealing and different annealing techniques is still studied in the aim of achieving a high Curie temperature. As mentioned in the introduction, (Ga,Mn)As has the advantage that it can be incorporated into III-V heterostructures with very good interfaces, but its current Curie temperature is too low for it to be considered as a good candidate for room-temperature operating devices. Since the way of increasing the Curie temperature is by post-growth ex situ annealing, additional epitaxial overgrowth with a good interface is not possible. Very resent experimental findings by M. Adell et al. [70], show that it is possible to obtain Curie temperatures compared to the ones obtained by ex situ annealing, by annealing in situ. Here an As cap layer act as a sink for trapping the Mn$_I$ during annealing in the MBE chamber. This method prevents oxidation of the surface and thus opens for the possibility of incorporating (Ga,Mn)As with high $T_c$ in multilayered structures as is likely to be the structure of future room-temperature operating devices.
Chapter 5

Geometrically constricted ultra thin (Ga,Mn)As epilayers

We have wanted to utilize the small thickness, to which the ultra thin (Ga,Mn)As epilayers still are ferromagnetic, to fabricate geometrically constricted devices. The intention was to separate two magnetic domains by etching a line across a Mesa, leaving a small bridge for electric transport. Since the magnetic domains in (Ga,Mn)As are microns in size [71], sub-micrometer wide openings should be able to achieve this. The nature of a possible domain wall between such two separated magnetic domains in terms of e.g. domain wall width and hence magnitude of the magnetoresistance [72] is not known. The ambition was to separate the two magnetic domains by an opening so small that the bridge between them is no longer ferromagnetic. This scenario could perhaps lead to spin-valve effect or a sizeable tunneling magnetoresistance. The observation that (Ga,Mn)As can be ferromagnetic down to a thickness of 5 nm will probably make this task difficult.

We used SEM-lithography to create such devices, as described in section 2.1.2. The devices were characterized by two-point dc-measurements, as described in section 2.3.1.

As stated in section 2.1.2, it proved difficult to create functional devices with very small openings due to etching under the resist that covers the opening. Figure 5.1 is a top-view SEM-image of a device that conducts and which has a magnetoresistance that is representative for all the devices that conducted. The sample was roughly characterized before insertion into the 2T-dipstick magnet (Appendix B) for resistance vs. magnetic field measurements. The creation of the constriction increased the resistance of the device by a factor of two. An I-V characteristic was performed at 4.2 K after the magnetic field had been swept from zero to 2 T and back again, showing a linear dependence.
The results with the applied magnetic field in-plane of the sample with an angle \( \theta \) to the direction of the current are shown in Figure 5.2.

Comparing these results with the results on magnetic anisotropy in section 3.2, it resembles the behaviour well as a function of \( \theta \), with a small hysteretic behaviour from bulk anisotropic magnetoresistance of about 20 mT. Additional reproducible features are seen, especially at \( \theta = -45^\circ \). Since the results at \( \theta = \pm 45^\circ \) are different and the change in resistance is negative for \( \theta = -45^\circ \), these features are likely to be a consequence of the cubic in-plane magnetic anisotropy and the possible switching between these directions, dependent on the relative orientation of magnetic field, current and magnetization, as discussed in section 3.2. There is no obvious sign of additional domain wall resistance on top the bulk-like behaviour.

The desired behaviour of large magnetoresistance has been achieved by C. Rüster et al. [73] using SEM-lithography. By sequential etching of two constrictions in series, separated by a couple of hundred nm, an increase of the magnetoresistance from 8 % to 2000 % have been observed by reducing the widths of the constrictions to a point where the charge carriers begin to tunnel on and off the island. From these encouraging results we have initiated the attempt to create similar devices with lithography by Atomic Force Microscopy (AFM). The acquisition at the Nanoscience center in Copenhagen of a Dimension 3100 AFM from Veeco with a close loop scanner in the x-y direction, also called NanoMan AFM, capable of making accurate AFM-lithography, inspired the idea of a possible re-
alization of the ambition using this method. At the deadline of this Thesis, M. Sc. Martin Ågesen and I have realized devices that showed several switching events and with a magnetoresistance of the order of 0.5 %. One advantage of AFM lithography is, that it is possible to modify the device geometry with very high precision even after the sample has been tested in a cryostat. The future intention is thus to narrow the constrictions down in the aim of increasing the magnetoresistance. For a description of lithography by AFM, see ref. [74] and references therein.
Geometrically constricted ultra thin (Ga,Mn)As epilayers
Chapter 6

(Ga,Mn)As - Superconductor tunnel junction

Knowing the degree of spin polarization of the charge carriers in (Ga,Mn)As is not only important for elucidating its properties. It is also an important number for interpreting the results of spin-injection devices, where the spin-life time in the different compounds in the device and the effect of the interfaces between the different compounds on the spin-transport, are crucial in obtaining high degree of spin-injection.

Mean-field calculations by T. Dietl [15] have predicted a charge carrier spin-polarization of up to 80 %, while bandstructure calculations have shown that (Ga,Mn)As is half-metallic [13, 14]. Very little experimental investigation has been made on this subject and it seems to be a rather difficult task [16]. J. G. Braden et al. [16] have probed Ga$_{0.95}$Mn$_{0.05}$As using a superconducting Ga contact directly on top the DMS, by Andreev reflection spectroscopy, obtaining a charge carrier spin-polarization of 85 %. In a (Ga,Mn)As/GaAs/(Ga,Mn)As tunnel junction D. Chiba et al. have determined the spin-polarization to be 77 % by tunnel magnetoresistance measurements [17].

We have used yet another approach, initially invented by Meservey, Tedrow and Fulde [75], using a superconductor - insulator - ferromagnet (SC/I/FM) tunnel junction. Here the Zeeman splitting of the energy levels on each side of the superconducting gap provides the mechanism to selectively probe the two different spin orientations of the charge carriers in the ferromagnet. We have used Al and AlO$_x$ as SC and I, respectively. The fabrication process of the SC/I/DMS tunnel junctions has been described in section 2.1.1.

After the following theoretical background, the results on a 30 nm thin (Ga,-Mn)As layer with 6 % Mn, will be presented.
6.1 Spin-polarized electron tunneling

This section is based on the publications of R. Meservey and P. M. Tedrow [18], emphasizing the relevant physical mechanisms for obtaining a basic understanding of the results on the SC/I/DMS tunnel junctions.

Al-films with thicknesses in the nm range have a higher Superconducting ordering temperature ($T_{sc}$) and a higher breakdown field than bulk Al, when the magnetic field is applied in-plane of the film. The high breakdown field enables creation of a significant Zeemann splitting of the energy levels on each side of the superconducting gap before the superconducting state is destroyed. It is this ability, in addition to the natural formation of AlO$_x$, that have made Al very suitable for determining the degree of charge carrier spin-polarization in many metals and semiconductors. The natural formation of a 1 – 2 nm thick AlO$_x$ layer on top of the Al gives a good tunnel barrier between the Al and the ferromagnet you want to study. This property can not be used here, due to the growth conditions of (Ga,Mn)As.

Al is a type I superconductor with $T_{sc} = 1.18$ K and a critical field of 10 mT. These numbers can be as high as 2.5 K and 5 T for thin films with thicknesses in the nm range. Below $T_{sc}$ Cooper-pairs are formed and an energy gap $2\Delta$ in the density of states is created at the Fermi energy. Cooper-pairs are of the form $(k_\uparrow, -k_\downarrow)$, where $k$ is the electron wave vector and the arrows indicate the direction of the spin. The opposite spin of the two electrons forming a Cooper-pair has a major limiting effect on the magnitude of the critical field, as will be described later.

In a magnetic field, the SC is penetrated to a depth $\lambda$ (penetration depth), by the magnetic field. The magnetic field generates a current in the surface region of the SC, creating a magnetic field directed opposite to the applied magnetic field, canceling the applied magnetic field in the interior of the superconductor (Meissner effect). At some value of the applied magnetic field, called the critical field, the energy associated with the induced current destroys the superconducting state. The coherence length $\xi$, is the size of the Cooper pairs and if the thickness of the superconducting film is less that these two parameters, $\lambda$ and $\xi$, the applied magnetic field penetrates the film uniformly, if it is applied in the plane of the film. The induced current is therefore greatly reduced compared to thick films, leading to a higher critical field.

The high critical field for thin superconducting films enables the Zeemann energy, equal to $2\mu B$, to reach the same order of magnitude as the superconducting gap, before the superconducting state is destroyed. Here $B$ denotes the applied
6.1 Spin-polarized electron tunneling

Figure 6.1: SC/I/FM tunnel junction. (a) The spin-split density of states of the SC. (b) Derivative of the Fermi function weighted by the fraction of spin-polarized electrons along the magnetic field direction in the FM. (c) Theoretical differential conductance for each spin direction (dotted/dashed) and the total differential conductance (solid). All are a function of voltage, measured from the Fermi energy of the FM. The Figure is partly reproduced from [18].

magnetic field and \( \mu \) the spin magnetic moment. Still being in the superconducting state, the Cooper-pairs are split in energy on both sides of the superconducting gap, leading to a density of state profile as shown in Figure 6.1 (a).

The Zeemann energy competes with the binding of the Cooper pairs, and having opposite spin, the Cooper-pair at some point will be torn apart by the applied magnetic field. This de-pairing effect, depending on the film thickness, is the limiting mechanism (Pauli or Paramagnetic limit) for the magnitude of the critical field in thin Al films.
Reciting the model by Meservey and Tedrow, the tunnelling current through a SC/I/FM tunnel junction is determined by the alignment of filled states on one side of the junction with empty states on the other side, as well as the tunnelling probability. As the bias across the junction is changed, the two Fermi levels on each side of the junction are moved relatively to each other, mapping out the density of states overlap as a function of bias. Assuming spin-conservation in the tunnelling process and no spin-orbit scattering and de-pairing effect in the SC, their model shows that the differential conductance is exactly proportional to the sum of the two spin-density of states of the superconductor at \( T = 0 \), each weighted by the spin dependent tunnelling probability. The differential conductance is given by:

\[
\frac{dI}{dV}(V) \sim \int_{-\infty}^{\infty} \{a \rho_+ + (1 - a) \rho_-\} dE \quad (6.1)
\]

where \( \rho_\pm = \rho_{sc}(E \pm \mu H) K(E + eV) \)

and

\[
\rho_{sc}(E) = \begin{cases} 
\rho_n(E) E / (E^2 - \Delta^2)^{1/2} & \text{if } |E| \geq \Delta \\
0 & \text{if } |E| < \Delta 
\end{cases}
\]

\( K(E) \) is the derivative of the Fermi function with respect to \( V \) and \( \rho_n(E) \) is the density of states of the SC in the normal state. \( a \) is the fraction of electrons with spin parallel to the applied magnetic field.

With the mentioned assumptions, the density of states for each spin direction in the SC has the same functional form, as shown in Figure 6.1 (a). In a ferromagnet \( a \) is different from \( 1/2 \) and the value of \( aK(E) \) and \( (1 - a)K(E) \) hence differ as depicted in Figure 6.1 (b), leading to a differential conductance as a function of bias as shown in Figure 6.1 (c).

The assumption of no spin-orbit scattering in the SC, is essential in determining the spin polarization from these kinds of measurements. Spin-orbit scattering is caused by charged impurities and modifies the density of states, leading to different functional forms for the two spin directions.
Now, having the same functional form, the spin polarization $P$, is simply given by the relative difference between the conduction peaks:

$$P = 2a - 1 = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} = \frac{(\sigma_4 - \sigma_2) - (\sigma_1 - \sigma_3)}{(\sigma_4 - \sigma_2) + (\sigma_1 - \sigma_3)}$$

(6.2)

$n_{\uparrow,\downarrow}$ are the number of electron spins (anti)parallel to the applied magnetic field. $\sigma_{1,2,3,4}$ are as defined in Figure 6.1 (c).

The effects of spin-orbit scattering and de-pairing will be discussed in greater detail at the end of the next section, since these effects are believed to be observed in the $\frac{dI}{dV}(V)$-curves for the SC/I/DMS tunnel junctions.

### 6.2 Measurements on SC/I/DMS tunnel junctions

Several different approaches have been tried in the attempt to realize a SC/I/DMS tunnel junction, but only one gave devices that showed tunnel properties. This successful approach is described in section 2.1.1. Out of twelve devices made in the same run on the same wafer, three showed tunneling characteristics like the one presented in the previous section. The remaining nine had a very weak bias dependence on the differential conductance. In two out of the three devices that worked, the Zeemann splitting is clearly visible and it is the result from these two devices that will be presented here. The two devices will be denoted Sample I and Sample II. The measurements carried out are two-point ac-measurements by standard lock-in technique as described in section 2.3.2 and were performed in the Kelvinox, which is described in Appendix B, at around 60 mK. The magnetic field is applied along one of the cubic easy-axis of the (Ga,Mn)As layer.

The differential conduction as a function of bias at different values of the applied magnetic field is shown in Figure 6.2 for Sample I.

As a function of magnetic field, the bias dependence can be divided into three parts. Before the Zeemann splitting appears, when it is visible, and when it disappears again. Different features are visible in the different magnetic field ranges, and focusing on the range between zero and 0.3 T, before the Zeemann splitting appears, several things happen. This magnetic field range is shown in Figure 6.3.

At zero field there are three features symmetric around zero bias. Close to zero bias there is a small dip (see insert of Figure 6.2) followed by a broader shoulder in the superconducting gap. The large peak is the thermally smeared edge of the superconducting gap as described in the previous section.
As the magnetic field is increased the small dip around zero bias disappears, whereas the shoulder, situated at 0.41 T, evolves towards a higher conductance until it disappears at 0.3 T. The magnitude of the large peak decreases rapidly with increasing magnetic field.

The small dip around zero bias at zero field, is a signature of electron tunneling between two SC. In a SC at finite temperatures there are filled states above the superconducting gap and empty states below. This results in two dips around zero bias separated by two times the difference of the magnitudes of the two superconducting gaps: \(2(\Delta_1 - \Delta_2)\). Now, having two SC gaps to overcome, the distance between the two outer peaks is equal to: \(2(\Delta_1 + \Delta_2)\).

As described in the previous section, spin-orbit scattering leads to different functional forms of the density of states of the different spin-directions in a SC.
This deformation of the density of states from the ideal one, can result in peaks or shoulder-like features in the differential conductance in the SC gap in a SC/I/SC tunnel junction [18].

The data of Figure 6.3 can thus be interpreted as a signature of electron tunnelling between two SC, where the superconducting state in one of the SC is destroyed at a approximately 0.3 T and where spin-orbit scattering is present in one or both SC.

The data from Sample I in the magnetic field range showing Zeemann splitting are shown in Figure 6.4. At 0.4 T a small splitting in the differential conductance peak can been seen. This splitting increases for increasing magnetic field, until the superconducting state is destroyed between 4 T and 5 T.

There are two things to be noted here. One is, when looking at the relative magnitudes of the differential conductance peaks the majority of charge carriers are spin-down electrons, meaning electrons having their spin directed opposite the direction of the applied magnetic field. Another is that the magnitude of this difference changes with the magnitude of the applied magnetic field.
Before going into details about the spin-polarization of the charge carriers, the focus will be on the magnetic field dependence of the position of the differential conductance peaks, shown in Figure 6.5. In the case of an ideal SC/I/FM tunnel junction the differential conductance peaks should lie on straight lines with an inclination given by $\mu_B/e$, assuming that the g-factor is equal to 2 and that the electron moment is $1/2$.

The innermost peaks fulfill this behaviour, whereas the outermost only fulfill this in a limited region at high magnetic fields. Starting from zero magnetic fields, the outermost peaks evolve towards smaller energies until 0.4 T where a significant change in magnetic field dependence can be seen. Here the peaks start to move towards bigger energies again, with an inclination of $3\mu_B/e$. At 2 T they begin to follow the inclination given by the Zeemann energy $\mu_B B/e$.

One way to interpret these results is to look at Sample I as a double tunnel junction consisting of two SC and one DMS in series, separated by insulators. This configuration is possible if the deposited Al-layer intended as oxide barrier has been made too thick. In that way, a metallic Al-layer is left un-oxidized on top.
of the LT GaAs under the oxide, thus creating an SC/I/SC/I/DMS tunnel junction. Here, the last insulating layer is the LT GaAs capping layer. Now, the middle SC layer must be very thin and indeed much thinner than the top SC layer. The data may then be explained as a destruction of the superconducting state of the top Al-layer, followed by dominant SC/I/DMS tunnelling with an intermediate region in between.

The magnitude of the superconducting gap in the thinnest Al-layer can be estimated by back-extrapolation of the innermost peaks in Figure 6.5 to zero field, to be about $\Delta = 0.42$ meV. This corresponds very well to the SC gap energies determined in ref. [18] for nm thin Al-layers. When following the $3\mu_B/e$-line of the outermost peaks to zero field, the intersection with the ordinate almost equals $\Delta$. Back-extrapolating the outermost peaks at high fields equals a value of $\delta = 0.65$ meV at zero field.

Figure 6.6 shows the charge carrier spin-polarization $P$, of Sample I as determined from the differential conductance peaks using eq. (6.2), as a function of applied magnetic field. The spin-polarization is seen to be negative, meaning that
Figure 6.6: Charge carrier spin-polarization as a function of applied magnetic field calculated using eq. (6.2) on the differential conductance of Sample I at \( T = 60 \) mK.

Spin-down electrons dominate the charge carrier spin polarization. This is rather surprising since the ferromagnetic ordering in (Ga,Mn)As is mediated by spin-down holes and hence spin-up electrons in the (Ga,Mn)As valence band. Another thing is that the charge carrier spin polarization depends on the applied magnetic field, which is not expected to reflect the behaviour of the (Ga,Mn)As, whose magnetization is saturated at about \( 1.5 - 2 \) T (See section 3.2.1).

The presented data of Sample I gives a rather complicated picture, compared to the ideal one presented in the previous section. One obvious explanation for this is the possible existence of a second superconducting layer. Assuming that this second superconducting layer is not superconducting above \( 0.3 \) T, the differential conductance peak dependence on magnetic field still acts very different from what is expected. Furthermore, the spin-polarization depends on the applied magnetic field.

In the previous section, spin-orbit scattering and de-pairing was mentioned as possible mechanisms for destroying the simple picture given by eq. (6.1) and (6.2). Spin-orbit scattering is believed to be present in at least one of the SCs. This is an indication of the presence of charged impurities and affects the magnitude of the calculated spin-polarization given by eq. (6.2). The de-pairing effect causes a critical field, at which the superconducting state is destroyed. Using a formula given by ref. [18], this critical field is given by: \( B_p = \Delta / \sqrt{2} \mu_B \approx 2.5 \) T. Note, that this is approximately the field at which the spin polarization changes rapidly.
Spin-orbit scattering has a huge impact on the actual breakdown field. From the presented data it should be possible to determine the spin-orbit scattering parameter and hence a more accurate value for the degree of charge carrier spin-polarization according to ref. [18]. Taking into account the many unexpected details in this sample, new samples would prove to be a better way of obtaining a more accurate determination of the charge carrier spin-polarization.

Turning to Sample II, other features than seen in Sample I appears. The differential conductance of Sample II as a function of bias at different magnetic fields is shown in Figure 6.7. Here the dip around zero bias does not appear, but a second shoulder-like feature can be seen outside the expected superconducting gap at zero magnetic field. As the magnetic field is increased, this shoulder disappears and the Zeemann splitting becomes visible before the superconducting state is destroyed at around 5 T. In Figure 6.8 the differential conductances at $B = 0$ T and $B = 4.5$ T are shown.

Figure 6.7: Differential conductance as a function of bias at different magnetic fields for Sample II at $T = 60$ mK.
Figure 6.8: Differential conductance as a function of bias at $B = 0$ T and $B = 4.5$ T for Sample II at $T = 60$ mK. The charge carrier spin-polarization $P$ is calculated using eq. (6.2). $\Delta_1$ and $\Delta_2$ are the magnitudes of the superconducting gaps in a SC/I/SC-FM tunnel junction and $B_{ex}$ is the exchange field acting on one of the SC calculated by using the same approach as found in ref. [18].

To a very high degree, these data resemble the results presented in ref. [18] on Al$^a$/AlO/Gd/Al$^b$ tunnel junctions. Here, the ferromagnetic ordering in the Gd layer Zeemann- splits the energy levels in the Al$^b$, which leads to a splitting of the differential conductance equal to the difference in Zeemann splitting of the two superconducting layers: $2\mu_B B_{ex}$. $B_{ex}$ is the exchange field from the magnetic layer. At higher magnetic fields the superconducting state of the Al$^b$-layer is destroyed, resulting in a SC/I/FM configuration with an asymmetry in the differential conductance as a result of the spin-polarization in the ferromagnetic layer.

Treating the data of Sample II in the same manner as given in ref. [18], assuming that the (Ga,Mn)As layer Zeemann-splits the energy levels in a SC/I/SC-DMS tunnel junction, $B_{ex}$ is equal to 1.734 T and the two SC gaps are 0.57 meV and 0.29 meV, respectively. As seen in Sample I, the charge carrier spin-polarization of Sample II also depends on the magnitude of the magnetic field having a spin-polarization of $-2.4\%$ at 4.5 T.
To summarize the results of these two samples; the tunnel characteristics are far from the ideal picture described in the previous section. The main reason is the probable presence of an unintended second superconducting layer. This superconducting layer affects the tunnel properties in a way that makes it very questionable to use these data to determine a realistic value of the charge carrier spin-polarization. The indication of spin-orbit scattering and de-pairing adds to this uncertainty and the effect of the LT GaAs capping layer is not known. What these experiments do show is, that it is possible to create tunnel junctions with Al and (Ga,Mn)As using the ‘reverse’ tunnel fabrication process and that spin-polarized tunneling can be observed in this way. Together with the possible exchange observed in Sample II, these experiments show that interesting physics in tunnel devices combining SC and (Ga,Mn)As is possible.
Chapter 7

Conclusions

It has proved possible to obtain information about the magnetic properties of ultra thin (Ga,Mn)As epilayers by electrical transport measurements. In combination with SQUID magnetometry, a deeper insight into the effect of annealing has been achieved and the relation between charge carriers and Curie temperature has been confirmed.

By resistance vs. temperature measurements, the lower thickness limit for the ferromagnetic phase to appear, has been found to be between 3 and 5 nm for a set of samples, containing 5 % of Mn and annealed for one hour at 240 °C in a nitrogen atmosphere. Assuming the Magnetoimpurity model, the $pd$-exchange integral has been found from these experiments to be centered around 67 meV nm$^3$. This is in good agreement with results obtained by others.

Hall measurements have been carried out and the behaviour of the magnetoresistance has been discussed. The Hall resistance has three contributions. The ordinary Hall effect, caused by the applied magnetic field through the Lorentz force. The anomalous Hall effect, arising from the magnetization of the sample itself, and the planar Hall effect, a result of the in-plane anisotropic magnetoresistance.

By use of the Hall data Arrot plots has been made. From this the magnetization vs. temperature curves has been found to have a shape that deviates from expected for a ferromagnet. This deviation is most likely to be caused by a temperature dependent anomalous Hall coefficient.

The Curie temperatures obtained by Arrot plots have been compared with the ones obtained by resistance vs. temperature measurements, where the latter are the largest.
The reported in-plane cubic anisotropy with a small uniaxial anisotropy for (Ga,Mn)As grown on GaAs(001) substrates was confirmed for the ultra thin (Ga,Mn)As epilayers and a small change in magnetic anisotropy upon annealing has been observed.

Anomalies in the Hall resistance is caused by the planar Hall effect due to a very small misalignment of the magnetic field applied perpendicular to the sample surface. The large impact of the planar Hall effect on the Hall resistance suggests that the ultra thin (Ga,Mn)As epilayers consists of a single or few magnetic domains.

The effect of post-growth annealing on the electrical transport properties has been studied at low temperatures and high magnetic fields. The resistance and Hall resistance shows additional features of unknown origin, although the additional features in the Hall resistance is shown to be caused by the resistance through the anomalous Hall effect.

The charge carrier density has been found at high magnetic fields and depends on the assumed scattering mechanism in the anomalous Hall effect. The charge carrier density was seen to increase upon annealing and the dominating scattering mechanism has been shown to depend on the thickness of the (Ga,Mn)As layer. The Curie temperature, found by SQUID magnetometry, depends on the charge carrier density and follows the predicted $1/3$-power law to a very good degree. The deduced effective acceptor concentration is in good agreement with the number obtained when looking at the charge carrier density, using published or self obtained values for the material parameter $C$.

The impact of annealing time and temperature has been studied by resistance vs. temperature measurements. The Curie temperature was observed to increase by 35 K to 125 K for a LT GaAs capped (Ga,Mn)As sample containing 6 % of Mn at an annealing temperature of 180 °C and annealing time up to 240 hours. The results indicate, that annealing for a longer period of time could enhance the Curie temperature even more.

The magnetization vs. temperature curve and the Curie temperature has been found by SQUID magnetometry and the dependence on the thickness of the (Ga,-Mn)As layer and annealing time has been studied. The Curie temperature was seen to increase upon annealing by a magnitude that depends on the thickness of the layer.

The shape of the magnetization vs. temperature curve depends on the (Ga,-Mn)As layer thickness. The change of shape from a non-concave like to a more Brillouin-function like upon annealing, is very likely caused by a rearrangement
of the compensating donors (Mn$_I$). The results point towards a more homogenous distribution of magnetically active Mn ions as a result of annealing.

The impact of annealing on the electrical transport properties and shape of magnetization vs. temperature curves has been discussed. In this discussion diffusion of Mn$_I$ and the in-depth profile of the Mn distribution of the as-grown samples together with the possible diffusion of Mn during growth was considered. This discussion point towards 15 nm as the critical limit, for which below surface effects has a major importance. The effect of the LT GaAs layer has been discussed and is now known to have a limiting effect in obtaining a high Curie temperature by post-growth annealing.

Considering these effects, it is very surprising that the samples presented in Figure 3.1 have the same resistivity. This must be assigned to very good growth conditions, where the in-depth profile of the Mn distribution is reproducible from growth to growth.

Beside optimized growth conditions post-growth, annealing is the way of increasing the Curie temperature. Even though the mechanism behind increasing the Curie temperature is well elucidated at this point, new results on As capped (Ga,Mn)As layers, annealed in the MBE, show that new approaches are still to be considered in reaching higher Curie temperatures.

Though a high Curie temperature in itself is a vague incitement for performing research on (Ga,Mn)As from a scientific point of view, the ongoing research in doing so, has contributed to a deeper understanding of this material within the last few years. This evolvement seems to continue, making (Ga,Mn)As a still very competitive candidate for spintronic devices.

The small thickness to which the ultra thin (Ga,Mn)As epilayers are still ferromagnetic, has been utilized in the attempt to create two spatially separated magnetic domains, connected by a nm sized bridge in order to study the electrical transport properties of two magnetic domains with opposite direction of magnetization in series. We consider this attempt unsuccessful.

Al/AlO$_x$/(Ga,Mn)As tunnel junctions has been made and electrical transport measurements at mK temperatures has been performed in order to determine the degree of charge carrier spin-polarization. The measurements indicates that the desired device geometry was not achieved. The presence of a second superconducting Al-layer and the LT GaAs capping layer results in tunnel characteristics that make realistic estimates of the charge carrier spin-polarization impossible. The results are encouraging though, and a continuation of this project has been initiated. At the termination of this thesis, new devices containing no LT GaAs, has been made.
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Appendix A

Device processing

Device processing of (Ga,Mn)As involves different kinds of lithographic methods and handling. The different steps in transforming a piece of wafer into a measurable device are listed below.

**Cleaning method:** Rinse in acetone, methanol and isopropanol followed by blow-drying with N$_2$ gas

**Photoresist covering:** Spinning AZ4511 at 4000 rpm for 40 sec.; bake at 115 °C for 45 sec.

**PMMA covering:** Pre-bake at 180 °C for 5 min.; spinning 2 % PMMA at 6000 rpm for 60 sec.; bake at 180 °C for 20 min.

**UV-lithography:** Expose for 20 sec. in mask-aligner

**SEM-lithography:** Exposure settings changed from time to time

**Developing:** Exposed photoresist developed 45 sec. in AZ 400 K.
Exposed PMMA developed in MBIK 1 : 3-propanol for 1 min.; clean in isopropanol; post-bake at 115 °C for 2 – 5 min.; O$_2$ plasma etch for 6 sec.

**Etching:** Etch in H$_3$PO$_4$ : H$_2$O$_2$ : H$_2$O (1:1:3) (100 nm/min.) for a desired amount of time

**Contact metallization:** Clean in O$_2$ plasma for 10 sec.; deoxidize in 2 % NH$_3$ for 20 sec.; evaporate 6 nm Au / 60 nm Zn / 1500 nm Au
Appendix B

Cryostats

Different Cryostats have been used for different purposes depending on the desired temperature range, magnetic field range or temperature control.

For low temperature electrical transport measurements $^3$He, $^4$He and N$_2$ are the key ingredients. At atmospheric pressure liquid N$_2$ and $^4$He have temperatures of 77 K and 4.2 K respectively. Inserting the samples directly into dewars containing one of these elements is one easy way to obtain low temperatures.

Often lower temperatures are desired. By lowering the vapour pressure of liquid $^4$He or $^3$He the temperature of $^4$He can be lowered to about 1.2 K and the temperature of $^3$He can be lowered from 3.2 K to about 300 mK using standard rotary pumps. Obtaining such low temperatures of a sample and doing electrical transport measurements at these temperatures, require big and complicated cryostats. The basic operation of such a cryostat is simple though. It uses the allowed temperature range of the two isotopes of He and is a combination of thermally connected baths containing either liquid $^4$He or $^3$He, connected to rotary pumps. The rotary pumps can lower the temperature of the two liquids and due to the temperature overlap, condensation of $^3$He can be achieved by pumping on liquid $^4$He. The one main reason for using this three-step operation is the extreme cost of $^3$He.

Since these cryostats are commercial systems supplied with detailed manuals, a description of how to operate them is not included here.

In all the cryostats the sample is electrically connected to the measurement setup through a BNC-connector box.
2T-Dipstick magnet

The 2T-Dipstick magnet is a magnet designed for direct insertion into a transport dewar. Inside the magnet the sample can be placed in different angles to the direction of the magnetic field manually. Manually means that the desired angle is fixed and that the sample has to be taken out of the dewar, and hence heated to room-temperature, in order to change the angle.

Cryocooler

The Cryocooler is a cryogenic system that needs no liquid Helium or Nitrogen. It is very well suited for continuous temperature sweeps in the range between room temperature and 8 K and a water-cooled 0.4 T magnet, mounted close to the sample, makes it possible to measure e.g. the magnetoresistance and the Hall effect.

The Cryocooler is a Cryophysics "Extender” closed cycle refrigeration system and its cooling process is similar to that of an ordinary refrigerator but with helium gas as coolant. A typical cool-down process from room temperature to 8 K takes about 2 hours. For measurements at a constant temperature, a heater situated at the sample makes it possible to stay at any temperature in the allowed range to an accuracy of 0.1 K.

For a detailed description and operation manual of the Cryocooler, see the Ph.D. Thesis by Claus B. Sørensen:"MBE-Growth, Processing and Characterization of Low-Dimensional GaAs/AlAs Heterostructures”, Microelectronic Centre, and Niels Bohr Institute fAFG, Nov. 1998. Claus is the creator of this measurement setup.

Heliox

This Cryostat has been used for Hall measurements up to 4 T in the temperature range between 4.2 K and 120 K. It is an Oxford Instruments sorption pumped Heliox\textsuperscript{VL} \textsuperscript{3}He cryostat. It is operated by insertion into a Wessington transport dewar with liquid \textsuperscript{4}He. The sample is shielded from the liquid \textsuperscript{4}He, mounted on a cold-finger from the \textsuperscript{3}He-pot. For the temperature range used in these studies, cooling by \textsuperscript{3}He was not necessary. The ITC-502 temperature controller was used to stabilize the temperature during magnet sweeps.

\footnote{Available in the Ørsted Laboratory Library, H. C. Ørsted Institutet, Universitetsparken 5, 2100 Copenhagen Ø.}
13T

The 13T cryostat is an Oxford Instruments sorption pumped $^3$He cryostat equipped with a 13 T magnet. It is a top-loaded cryostat permanent positioned in the floor and has to be cooled by applying liquid $^4$He from a transport dewar. This cryostat was operated entirely at its base temperature of 300 mK using the cooling process described in the beginning of this Appendix. For a detailed description and operation manual see the Cand. Scient. Thesis by by Guggi Kofod:”Rings and Probes.,” Ørsted Laboratory, August 13, 1998 ².

Kelvinox

A 7 Tesla magnet equipped Oxford Instruments Kelvinox dilution cryostat was used to characterize the DMS/I/SC tunnel junctions at temperatures below 100 mK. It is positioned permanently in the floor and operates with a continuous circulation of $^3$He from a $^3$He/$^4$He mixture, enabling the mixture to reach 20 – 30 mK. Due to the electrical current through the wires to the sample mounted in a vacuum space, the obtainable sample (electron) temperature is about 60 – 70 mK.

²Available in the Ørsted Laboratory Library, H. C. Ørsted Institutet, Universitetsparken 5, 2100 Copenhagen Ø.
Appendix C

Equations

The formulas for obtaining the physical magnitudes calculated from measured ones are given here. The equations as used in Section 3.3.2 and Chapter 4.

Electric transport measurements:

For a free electron gas the relation between the Fermi energy $E_f$, and the Fermi wave vector $k_f$, is given by:

$$ E_f = \frac{\hbar^2}{2m_0} k_f^2 $$  

where $m_0$ is the electron rest mass.

The values of $k_f$ are quantized and having a density of electrons equal to $p$, the Fermi energy is given by:

$$ E_f = \frac{\hbar^2}{2m_0} (3\pi^2 p)^{2/3} $$  

in a three dimensional space.

For a semiconductor the electron rest mass is replaced by the effective electron mass $m^*$. With the values of $p$ between $4 \cdot 10^{20}$ cm$^{-3}$ and $9 \cdot 10^{20}$ cm$^{-3}$, as given in Figure 3.20, the Fermi energy lies in the range between 390 meV and 680 meV for the samples studied, using an effective electron mass of $m^* = 0.5m_0$. 

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The mean-free path \( l \), is given by:

\[
l = v_f \tau \tag{7.3}
\]

where \( v_f \) is the Fermi velocity and \( \tau \) is the momentum relaxation time given by:

\[
v_f = \frac{\hbar k_f}{m^*} = \frac{\hbar}{m^*} (3\pi^2 \rho)^{1/3} \tag{7.4}
\]

\[
\tau = \frac{\mu_m m^*}{e} = \frac{1}{e \rho_{xx}} \frac{m^*}{e^2 \rho_{xx}} \tag{7.5}
\]

using eq. (7.1) and (7.2). \( \mu_m \) is the electron mobility and \( e \) is the electron charge.

From eq. (7.3), (7.4) and (7.5), the mean free path is given by:

\[
l = \frac{\hbar (3\pi^2)^{1/3} \rho^{-2/3}}{e^2 \rho_{xx}} \tag{7.6}
\]

(See e.g. C. Kittel:”Introduction to solid state Physics.” 7’th edition, John Wiley & Sons, Inc., New York 1996.)

**SQUID measurements**

The SQUID records the magnetization \( M \), of the sample. From this the magnetic moment \( \mu \) pr. Mn can be calculated, knowing the density of Mn in the Zinc-blende lattice, \( \rho_{Mn} \):

\[
\mu = M \cdot \rho_{Mn} \tag{7.7}
\]

where

\[
\rho_{Mn} = \frac{(\text{z Ga pr. unit cell}) \cdot (\% \text{ of Ga replaced by Mn})}{\text{unit cell volume}} \tag{7.8}
\]

\[
\Rightarrow \rho_{Mn} = N_0 \cdot x = \frac{4 \cdot x}{(5.653 \cdot 10^{-10} m)^3} = 2.214 \cdot 10^{28} m^{-3} \cdot x
\]

Note that the magnetic moment \( \mu \) pr. Mn in Chapter 4 is given in units of \( \mu_B \) and denoted \( M \).
Publications

This is a list of publications made during the time of my Ph.D. studies and is the basis of many of the results presented in this thesis.

I  Ferromagnetic GaMnAs Thin Films  
B. S. Sørensen, J. Sadowski, S. E. Andresen, P. E. Lindelof, R. Matheu, P. Svedlindh and J. Kanski,  

II  Magnetic anisotropy of tunneling in GaMnAs based structures  
S. E. Andresen, J. Sadowski, B. S. Sørensen and P.E. Lindelof,  

III  Dependence of Curie temperature on the thickness of epitaxial (Ga,Mn)As film  
B. S. Sørensen, J. Sadowski, S. E. Andresen, and P. E. Lindelof,  

IV  Effect of annealing on carrier density and Curie temperature in epitaxial (Ga,Mn)As thin films  
B. S. Sørensen, J. Sadowski, R. Mathieu, P. Svedlindh, and P. E. Lindelof,  

V  Spin-polarized electron tunnelling across a Si delta-doped GaMnAs/n-GaAs interface  
S. E. Andresen, B. S. Sørensen, F. B. Rasmussen, P. E. Lindelof, J. Sadowski, C. M. Guertler, and J. A. C. Bland,  

VI  Magnetization of ultrathin (Ga,Mn)As layers  
R. Mathieu, B. S. Sørensen, J. Sadowski, J. Kanski, P. Svedlindh, P. E. Lindelof, D. Hrabovsky, and E. Vanelle,  