Magnetic Tunnel Junctions
Based on Fe$_3$O$_4$

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Abstract

A magnetic tunnel junction consists of two metal electrodes separated by an insulating barrier thin enough for electrons to tunnel across. With ferromagnetic electrodes, a spin dependent tunneling (SDT) effect i.e., electrons of one spin tunneling preferentially compared to those of the other, is observed. When the magnetization of the ferromagnetic electrodes are switched from a parallel to anti-parallel alignment, the tunneling current at a given voltage across the barrier changes, thus giving rise to tunneling magnetoresistance (TMR).

In this work, the influence of magnetite ($\text{Fe}_3\text{O}_4$) on the magnetoresistance of a TMR thin films stack has been investigated. The critical parameters involved in the epitaxial growth of magnetite thin films on MgO substrates have been optimized. The tunneling barrier Al$_2$O$_3$ has been used in different thicknesses and is grown under different conditions to study the effect of these parameters on the value of tunneling magnetoresistance. Magnetotransport measurements have been carried out across mesoscopic tunnel junctions to study the applicability of magnetite as efficient spin polarizer in the field of magnetoelectronics.

The thin films have been prepared in an ultra high vacuum system by pulsed laser deposition and electron beam evaporation on MgO(001) single crystal substrates. The surface and growth analysis has been made with the help of in-situ reflection high energy electron diffraction and atomic force microscopy. High resolution X-ray diffraction method has been used to study the crystal properties, film thickness and interface roughness. The magnetic characteristics, in particular the magnetic coupling within the multilayers, have been measured with a SQUID-magnetometer. Electric transport measurements were carried out at different temperatures and magnetic fields in a cryostat system. The thin films achieved a high quality and showed similar properties as bulk single crystal material.

Using the methods of optical lithography and ion beam etching the micrometer sized tunnel junctions have been fabricated. Mesoscopic tunnel junctions of different sizes and shapes have been prepared to investigate the influence of these parameters on the magnetotransport characteristics. The insulating barrier has been grown in five different thicknesses to optimize the thickness for the maximum TMR effect. Tunneling magnetoresistance values of as high as 8% have been obtained at room temperature. At low temperatures even higher values (up to 11%) have been found.
Contents

1 Introduction 1
  1.1 Introduction .................................................. 1
    1.1.1 Magnetoelectronics ...................................... 1
    1.1.2 Spin Dependent Tunnelling .............................. 2
    1.1.3 Magnetic Tunnel Junction .............................. 2
    1.1.4 Tunneling Magnetoresistance ........................... 4
  1.2 Half Metallic Materials .................................... 5
  1.3 Overview of Thesis ......................................... 5

2 Magnetite 7
  2.1 Chemical properties ...................................... 7
  2.2 Crystal Structure and Magnetism ................. 8
  2.3 Transport Properties .................................... 9
  2.4 Band Structure and Spin Polarization ............ 11

3 Experimental Methods 15
  3.1 UHV-Pulsed Laser Deposition System .............. 15
    3.1.1 Heating Laser .......................................... 16
    3.1.2 Temperature Measurement by Pyrometer .......... 17
    3.1.3 Laser Ablation Process ......................... 17
  3.2 RHEED .......................................................... 17
  3.3 AFM .............................................................. 18
  3.4 Electron Beam Evaporation .......................... 18
  3.5 High Resolution X-Ray Diffraction .............. 19
  3.6 SQUID ........................................................... 20
  3.7 Micropatterning ............................................ 20
    3.7.1 Optical Lithography .................................. 20
    3.7.2 Ar - Ion Beam Etching .............................. 20
    3.7.3 Au - Sputtering ...................................... 21
  3.8 Magnetotransport Measurements .................. 21
## CONTENTS

4 Layer Manufacturing and Characterization 23
  4.1 Theory ........................................ 23
  4.2 Substrate ..................................... 26
  4.3 Buffer layer ................................... 27
  4.4 Magnetite on MgO ............................... 27
  4.5 Insulating Barrier ......................... 28
  4.6 Counter Electrode ............................ 28
  4.7 Structural Analysis by HRXRD ............... 31

5 Magnetic Tunnel Junctions 37
  5.1 Theory .......................................... 37
  5.2 Simmons - Model ............................. 38
  5.3 Patterning of TMR Turrets .................... 39
    5.3.1 Optical Lithography ...................... 39
    5.3.2 Ion Beam Etching ......................... 41
    5.3.3 Au-Sputtering ............................. 44

6 Transport Measurement 47
  6.1 Magnetic Properties .......................... 48
  6.2 R(H) - Measurement .......................... 53
  6.3 R(T) - Measurement .......................... 56
  6.4 V(I) - Measurement .......................... 58
  6.5 Conclusions ................................... 61

7 Appendix 63

    Bibliography 73
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Sketch of the energy bands in ferromagnetic materials. Spin-up and spin-down electrons have different densities of states at the Fermi energy.</td>
</tr>
<tr>
<td>1.2</td>
<td>Tunneling through a trilayer MTJ system: The antiparallel resistance $R_{\uparrow\downarrow}$ is higher than the parallel resistance $R_{\uparrow\uparrow}$.</td>
</tr>
<tr>
<td>1.3</td>
<td>Tunneling phenomenon of majority and minority spins in parallel and antiparallel alignment. Resistance is lower in case of parallel alignment.</td>
</tr>
<tr>
<td>2.1</td>
<td>The inverse spinel structure of Fe$_3$O$_4$, consisting of an fcc oxygen lattice and Fe$^{3+}$ ions filling 1/8 of the tetrahedral sites and equal amounts of Fe$^{3+}$ and Fe$^{2+}$ ions filling half of the octahedral sites.</td>
</tr>
<tr>
<td>2.2</td>
<td>Electronic configuration of Fe [(Ar)3d$^6$4s$^2$].</td>
</tr>
<tr>
<td>2.3</td>
<td>Electronic configuration of Fe$^{2+}$ [(Ar)3d$^6$] and Fe$^{3+}$ [(Ar)3d$^5$]. In Fe$^{2+}$ the two 4s electrons are omitted, whereas in Fe$^{3+}$ one more spin down electron is missing from 3d.</td>
</tr>
<tr>
<td>2.4</td>
<td>Density of states of Fe$_3$O$_4$ in the ferrimagnetic state, (a) calculated using the LDA, (b) calculated using the LDA+U, from [6].</td>
</tr>
<tr>
<td>2.5</td>
<td>Photoemission spectra from 5 nm magnetite film at room temperature. (a), (c) Spin polarized photoemission spectra and photoemission intensity and (b), (d) spin polarization as function of binding energy, from [17].</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic diagram of Pulsed Laser Deposition Process.</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic diagram of X-Ray Diffraction.</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic diagram of atomic processes in the nucleation of three-dimensional clusters of deposited film atoms on a substrate surface.</td>
</tr>
<tr>
<td>4.2</td>
<td>Nucleation of three-dimensional cluster and corresponding energies.</td>
</tr>
<tr>
<td>4.3</td>
<td>Thornton Diagram, from [18].</td>
</tr>
<tr>
<td>4.4</td>
<td>Schematic illustration of thin film growth method, showing the change in RHEED information as the growth mode changes from ”step-flow” to 2-D nucleation, from [18].</td>
</tr>
<tr>
<td>4.5</td>
<td>Crystal structure of MgO, from [28].</td>
</tr>
<tr>
<td>4.6</td>
<td>RHEED patterns obtained during Pulsed Laser Deposition of TiN and Fe$_3$O$_4$.</td>
</tr>
<tr>
<td>4.7</td>
<td>RHEED patterns obtained during Pulsed Laser Deposition of TiN and Fe$_3$O$_4$.</td>
</tr>
</tbody>
</table>
4.8 X-ray diffraction: Bragg condition if \( n\lambda = 2d \sin\theta \) .......................... 31
4.9 \( \theta-2\theta \) scan of a sample with 30nm Fe\(_3\)O\(_4\) layer on MgO(001). .................. 32
4.10 \( \theta-2\theta \) scan of a sample with 30nm Fe\(_3\)O\(_4\) layer on MgO(001). The (004)-Fe\(_3\)O\(_4\) peak is present just besides the MgO(002). .................. 33
4.11 \( \theta-2\theta \) scan of a sample with 30nm Fe\(_3\)O\(_4\) layer on MgO(001). The small figure shows the rocking curve for the (004)-Fe\(_3\)O\(_4\) peak. .................. 33
4.12 Rocking curve for the (004)-Fe\(_3\)O\(_4\) peak. The FWHM is 0.0338\(^\circ\). .................. 34
4.13 X-ray reflectometry graph of a sample with a 30nm Fe\(_3\)O\(_4\) layer. .................. 35
4.14 Actual and simulated x-ray reflectometry curves. .................. 35
4.15 Actual and simulated x-ray reflectometry curves. .................. 36
4.16 Actual and simulated x-ray reflectometry curves. .................. 36

5.1 Tunneling through an insulating barrier. .......................... 37
5.2 General barrier in the insulating film between two metal electrodes. .......................... 38
5.3 TMR Multilayer Stack. .......................... 40
5.4 Mask for Step 1. .......................... 40
5.5 Masks for step 2. .......................... 41
5.6 Masks for step 3. .......................... 42
5.7 Patterned Sample. .......................... 43
5.8 Patterned Sample. .......................... 43
5.9 Patterned TMR turrets (a) elliptical with connected Au layer and (b) square with separated Au layer on top. .......................... 44
5.10 Sample with Al bonding wires for electrical connection from outside. .......................... 45
5.11 Complete structure bonded on the copper sample holder ready for transport measurements. .......................... 45

6.1 Tunneling current of spin up and down electrons through the multilayer stack both in parallel and antiparallel alignment. .......................... 48
6.2 Schematic drawing of a stepped hysteresis loop. .......................... 49
6.3 M(H) for a sample with 1.4nm Al\(_2\)O\(_3\) oxidised in one step, the thicknesses of Fe\(_3\)O\(_4\) and Co layers are 20 nm and 40 nm respectively. .......................... 50
6.4 M(H) for a sample with 1.8nm Al\(_2\)O\(_3\) oxidised in two steps, the thicknesses of Fe\(_3\)O\(_4\) and Co layers are 20 nm and 40 nm respectively. .......................... 51
6.5 M(H) for a sample with 1.6nm Al\(_2\)O\(_3\) oxidised in two steps, the thicknesses of Fe\(_3\)O\(_4\) and Co layers are 20 nm and 40 nm respectively. .......................... 52
6.6 8% TMR effect measured across the rectangular turret with dimensions of 37.5\(\mu\)m x 3\(\mu\)m at Room Temperature. The Al\(_2\)O\(_3\) barrier thickness is 2nm. .......................... 53
6.7 Rectangular turret with dimensions of 37.5\(\mu\)m x 3\(\mu\)m (a) at 200 K, (b) at 225 K. The Al\(_2\)O\(_3\) barrier thickness is 2nm for both turrets. .......................... 54
6.8 Square turret with dimensions of 10\(\mu\)m x 10\(\mu\)m (a) at 295 K and (b) at 360 K. The Al\(_2\)O\(_3\) barrier thickness is 1.4nm in both turrets. .......................... 54
6.9 Square turret with dimensions of 18\(\mu\)m x 18\(\mu\)m (a) at 295 K and (b) at 225 K. The Al\(_2\)O\(_3\) barrier thickness is 2nm. .......................... 55
6.10 Elliptical turret with dimensions of 35\(\mu\)m x 15\(\mu\)m (a) at 295 K and with 2nm Al\(_2\)O\(_3\) barrier, (b) at 250 K and with 1.2 nm Al\(_2\)O\(_3\) barrier. .......... 55
6.11 R(T) - curves for tunnel junctions of different sizes and shapes. .......... 56
6.12 R(T) - curves. .................................. 57
6.13 (V-I) - Curves for a sample at different temperatures. ................. 58
6.14 (V-I)- Curves for a sample at different temperatures including Simmons-fitted curves. ........................................ 59
6.15 (V-I)- Curves for a sample at different temperatures including Simmons-fitted curves. ........................................ 60

7.1 Pulsed Laser Deposition Setup ........................................... 66
7.2 Pulsed Laser Deposition Setup ........................................... 66
7.3 Laser Optics ......................................................... 67
7.4 X-Ray Diffractometry ..................................................... 67
7.5 SQUID - Magnetometer ..................................................... 68
7.6 Wafer Prober ............................................................ 68
7.7 Optical Microscope ......................................................... 69
7.8 Photomasking Setup ......................................................... 69
7.9 Optical Lithography Setup ................................................... 70
7.10 Ar-Ion Beam Etching ......................................................... 70
7.11 Au-Sputtering System ......................................................... 71
7.12 Al Bonder ............................................................... 71
Chapter 1

Introduction

The main objective of this work is to study the field of spin-dependent tunneling (SDT) in magnetic tunnel junctions (MTJ). Two ferromagnetic electrodes separated by a nanometer scale insulator which allows electrons to tunnel across form a spin dependent tunneling junction. In this work we start with the introduction of the spin dependent tunneling and discuss the main issues involved in it. After this, we give a general description of what actually goes into making a good magnetic tunnel junction. Various aspects of magnetic tunnel junctions and methods for their fabrication and electrical characterization are discussed. The chapter ends with an overview of the thesis.

1.1 Introduction

Conventional use of magnetic materials in thin films include structures that utilize their magnetic properties to store information (as in recording tapes, hard disk drives and magnetic bubble memories) or to obtain field sensors (as in magnetic recording and reading heads or other magnetic field sensors). These applications use their property of large-scale magnetization that arises from the collective behaviour of electron spins. Separate from this is the field of electronics, where it is the electrical charge of an electron and its conduction through materials that is the object of attention. The term "Electronics" comprises all effects on electric transport that depends on the charge of the electron. In conventional electronics, the spins of the conducting electrons are largely ignored and both spin-up and spin-down electrons behave in an identical fashion. Thus, the term "Magnetoelectronics" has been defined to comprise all influences of the electron spin on electronic transport phenomenon.

1.1.1 Magnetoelectronics

The field of magnetoelectronics is a relatively new one. The term is used to describe a system in which the behaviour of the conducting electrons is also affected by their spins; i.e., electrons of different spins conduct differently. Such systems are typically based
CHAPTER 1. INTRODUCTION

on effects that arise from spin polarized transport, spin-depandant Coulomb-blockade, and different spin states in quantum wells and dots. Such systems were not feasible ten years ago and only recent advances in nanostructures have made them realisable. These include advances in fabrication and deposition techniques on the practical side and the developments in mesoscopic physics on the theoretical side. Examples of such systems include practically successful magnetoresistive devices such as AMR, GMR and TMR read heads and magnetic random-access memories (MRAMs), work combining magnetics with semiconductor, demonstrations of bipolar spin transistors, ferromagnetic hot-electron transistors, spin dependent resonant tunnelling transistors, even cellular automata and quantum computing structures. In this work, we shall explore magnetoelectronic devices where the electrons tunnel across a thin insulating barrier. To understand tunnel junction in general, we first describe what a tunnel junction really is.

1.1.2 Spin Dependent Tunnelling

Spin-dependent tunneling (SDT) is an imbalance in the electric current carried by spin-up and spin-down electrons tunneling from a ferromagnet through an insulating barrier. This phenomenon was discovered by Tedrow and Meservey in 1970 [1]. Using superconducting layers as detectors they measured the spin polarization of the tunneling current across an AlO$_x$ barrier originating from various magnetic electrodes.

In ferromagnetic materials the motion of an electron strongly depends on its spin orientation with respect to local magnetization. The origin of spin dependent tunneling can be explained by the fact that a ferromagnetic metal, such as Fe, Co or Ni, has a shift in the density of states (DOS) between spin-up and spin-down electrons to minimize the total energy of the system. Therefore, the number of electrons that can tunnel through the barrier and consequently the tunneling conductance depends on the spin. To define the spin polarization in a material, the total current is divided up in two currents, the majority spin current and the minority spin current. The majority (minority) spin electrons are the electrons whose spin is parallel (antiparallel) to the magnetization of the material and they are denoted by $\uparrow$($\downarrow$). The polarization is defined as the difference between the majority spin current, $I_\uparrow$, and minority spin current, $I_\downarrow$.

$$P \equiv \frac{I_\uparrow - I_\downarrow}{I_\uparrow + I_\downarrow}$$

1.1.3 Magnetic Tunnel Junction

A magnetic tunnel junction (MTJ) consists of two layers of magnetic materials separated by an ultrathin layer of insulator with a thickness of about 1-3 nm. The insulating layer is so thin that electrons can tunnel through the barrier if a bias voltage is applied between the two magnetic electrodes. In MTJs the resistance is dependent on the relative
orientation of the magnetization of the two ferromagnets. The easiest explanation is to compare two cases. In the first case, both electrodes are magnetized in parallel. The majority spin (minority spin) electrons will tunnel into the majority spin (minority spin) available states. If both electrodes are made up of same ferromagnetic metal, the density of states are the same which determines the conductivity of the junction. In the second case, both electrodes have antiparallel orientation of the magnetization, due to which the majority spin electrons must tunnel into the minority spin available states and the minority spin electrons must tunnel into the majority spin available states. The density of states in this configuration are not equal on both sides of the barrier, and thus decrease the conductance. Magnetic tunnel junctions are the basis of the new Magnetic Random Access Memory (MRAM) chips.

Figure 1.1: Sketch of the energy bands in ferromagnetic materials. Spin-up and spin-down electrons have different densities of states at the Fermi energy.

Figure 1.2: Tunneling through a trilayer MTJ system: The antiparallel resistance $R_{\uparrow\downarrow}$ is higher than the parallel resistance $R_{\uparrow\uparrow}$.
1.1.4 Tunneling Magnetoresistance

Tunneling Magnetoresistance is the change in the tunneling current in magnetic tunnel junctions when the relative magnetizations of the two ferromagnetic layers change their alignment. TMR can be interpreted in terms of Julliere’s model [2], which is based on two assumptions. First, it is assumed that the spin of electrons is conserved in the tunnelling process. It follows, then, that tunnelling of spin-up and spin-down electrons are two independent processes, so the conductance occurs in the two independent spin channels. According to this assumption, electrons originating from one spin state of the first ferromagnetic film are accepted by unfilled states of the same spin of the second film. If the two ferromagnetic films are magnetized parallel, the minority spins tunnel to the minority states and the majority spins tunnel to the majority states. If, however, the two films are magnetized antiparallel, the minority spins tunnel to the majority states and majority spins tunnel to the minority states. Second, it is assumed that the conductance for a particular spin orientation is proportional to the product of the effective density of states of the two ferromagnetic electrodes. According to these two assumptions, the tunneling current for the parallel and antiparallel alignments can be written as Eq. (1.1).

The expression for tunneling magnetoresistance (TMR) can be written as follows:

\[
TMR = \frac{R_{AP} - R_P}{R_P} = \frac{2P_1P_2}{1 + P_1P_2}
\]

(1.2)

![Figure 1.3: Tunneling phenomenon of majority and minority spins in parallel and antiparallel alignment. Resistance is lower in case of parallel alignment.](image-url)
1.2 Half Metallic Materials

The concept of half metallic ferromagnets was introduced by de Groot et al. [3], on the basis of band structure calculations in NiMnSb and PtMnSb semi-Heusler phases. A half-metallic material or semi-metal is characterized by the fact that one spin channel is metallic, while the other spin channel has a gap at the Fermi level. Hence, these materials exhibit 100% spin polarization of the conducting electrons. By simple counting of states, the total magnetic moment per unit cell must be an integer. Half metals are not common as all are compounds of more than one element and most are either oxides or Heusler alloys. The most commonly used half metals today are mixed valence manganites, double perovskites and magnetite etc. Half metallic ferromagnets may be applied in magnetoresistive devices. Such materials hold out the possibility for use in the data storage and semi-conductor industries as pure spin sources in spintronic devices. These materials exhibit colossal magnetoresistance which can be usefully exploited in magnetoresistive devices.

1.3 Overview of Thesis

In this work, spin polarized tunneling characteristics of magnetite (Fe$_3$O$_4$), has been investigated using various techniques and measurement methods. The epitaxial thin film growth of Fe$_3$O$_4$ on MgO (001) single crystal wafers using ultrahigh vacuum pulsed laser deposition system has been optimized by testing different values for critical growth parameters including deposition temperature, laser optics and buffer layer thickness etc. The epitaxy was controlled with the help of in situ Reflection High Energy Electron Diffraction (RHEED). The surface analysis has been made by Atomic force microscopy (AFM). The crystal properties and layer thicknesses has been investigated with High Resolution X-ray Diffraction (HRXRD) experiments. As the thickness of the barrier must be less than 2 nm, the choice of the barrier material becomes critical. Al$_2$O$_3$ is perhaps the best tunneling barrier in terms of reproducibility and reliability. Five different barrier thicknesses have been used to optimize the insulating layer thickness for maximum tunneling magnetoresistance effect. Al$_2$O$_3$ barriers with a thickness less than 1.4 nm have been grown by depositing Al and then oxidizing it in a single step for 30 minutes, whereas the barrier layer with a thickness more than 1.4 nm has been oxidized in two steps after depositing Al. Micrometer sized magnetic tunnel junctions of various sizes and shapes have been fabricated and tested under different temperatures and magnetic fields during magnetotransport measurements using a cryostat system. Tunneling magnetoresistance values of as high as 8% have been found at room temperature. At low temperatures even higher values up to 11% have been obtained. The results obtained during magnetotransport measurements are presented in chapter 6.
Chapter 2

Magnetite

Magnetite (Fe$_3$O$_4$), double perovskite manganites and chromium dioxide (CrO$_2$) have been identified as possible half metallic ferromagnets with complete spin polarization at the Fermi level. Materials with complete spin polarization are ideal candidates for electrodes of a magnetic tunnel junction since they maximize the junction magnetoresistance. Magnetite, Fe$_3$O$_4$, is the oldest magnetic material known to man. It is abundantly found in nature (especially in rocks) and was first discovered by man in Greece around 2000 BC. It was found in the region called Magnesia, from which the names magnetite and magnetism were derived. Magnetite is magnetic at room temperature, in fact it is ferrimagnetic with a very high Curie temperature of 858 K. Not only is it magnetic at room temperature, magnetite is also conducting and band calculations predict the conduction electrons to be fully spin polarized making it a very interesting candidate for magnetic recording and spin-valve applications [15].

2.1 Chemical properties

Magnetite, Fe$_3$O$_4$, is one of the several important oxides of iron. The lattice structure is made up of a close-packed almost-fcc lattice of oxygen atoms. The interstitial sites are occupied by Fe$^{2+}$ and Fe$^{3+}$ in an ordering that leads to an inverse spinel crystal structure. The tetrahedral A sites are occupied by Fe$^{3+}$ ions and the octahedral B sites are half Fe$^{2+}$ and half Fe$^{3+}$ ions, thus leading to the formula Fe$_3$O$_4$. Magnetite is a rather poor conductor of electricity with a room temperature resistivity, $\rho$, of $3 - 6 \times 10^5$ $\Omega$m. Magnetite undergoes the well-known Verwey metal-insulator transition at around $T_V=120$ K [9], below which due to charge ordering it becomes an insulator. There is an energy gap of 0.79 eV in the majority spin states, thus making Fe$_3$O$_4$ a half-metal. The arrangement of spins in the Fe$^{2+}$ and Fe$^{3+}$ ions make it a ferrimagnet.
2.2 Crystal Structure and Magnetism

Magnetite is a member of the spinel group, space group [Fd3m], whose formal chemical formula can be written as \( \text{Fe}^{3+}_A[\text{Fe}^{2+},\text{Fe}^{3+}]_B\text{O}_4^- \), where \( A \) and \( B \) refer to the interstitial, i.e., tetrahedral and octahedral sites, respectively. This simple ionic picture implies that magnetite is a mixed-valent compound. The \( A \) sublattice is occupied only by \( \text{Fe}^{3+} \) cations in a ferromagnetic arrangement, while the \( B \) sublattice is occupied by both \( \text{Fe}^{2+} \) (\( B_1 \)-site) and \( \text{Fe}^{3+} \) (\( B_2 \)-site) cations, also in a ferromagnetic manner which, however, is antiferromagnetically aligned to the ferromagnetic order on the \( A \) sublattice. The oxygen atoms occupy the face-centered-cubic (fcc) close-packed sites. This arrangement causes a transfer of electrons between the different irons in a structured path or vector. This electric vector generates the magnetic field. The lattice constants of the elementary cubic unit cell amount to \( a = b = c = 0.8396 \text{ nm} \) which consist of 8 magnetite formula units.

![Figure 2.1](E:UserSulemanpicsMagnetit_ok_2.ps)

Figure 2.1: The inverse spinel structure of \( \text{Fe}_3\text{O}_4 \), consisting of an fcc oxygen lattice and \( \text{Fe}^{3+} \) ions filling 1/8 of the tetrahedral sites and equal amounts of \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) ions filling half of the octahedral sites.
2.3 Transport Properties

The electron transport in Fe$_3$O$_4$ is predicted to be fully spin-polarized such that it is half metallic. This, combined with the fact that the Curie temperature $T_C$ is very high, makes Fe$_3$O$_4$ a very interesting candidate for magnetic tunnel junction applications. The A-site Fe ions are stable trivalent, while the B-site Fe ions are of mixed valency with the ratio Fe$^{2+}$:Fe$^{3+}$=1:1. Here, the Fe$^{2+}$ and Fe$^{3+}$ ions have $t_{2g}^3e_{g}^{2}(S=2)$ and $t_{2g}^3e_{g}^{2}(S=5/2)$ configurations, respectively. The electrical conduction and the Verwey transition occur on the B-site sublattice.

In Fe$_3$O$_4$, the conduction is supposed to be due to hopping of minority spin electrons between octahedral Fe sites (Fe$^{2+}$ and Fe$^{3+}$) of the Fe$_3$O$_4$ inverse spinal structure. This results in high conductivity and an average charge of Fe$^{2.5+}$ at B-site sublattice. The five $d$-electrons of Fe$^{3+}$ are aligned parallel forming a filled sub shell. The additional spin-down electron of Fe$^{2+}$ can easily hop to a neighboring Fe$^{3+}$ site if their spins are parallel. This shows that only spin-down electrons can easily move in the magnetically ordered state resulting in spin polarized electron transport. The electron conduction is restricted to B-sites. B-site spins are oriented ferromagnetically to each other whereas mutually coupled anti-ferromagnetically to the A-site spins. Below $T_C$=858 K, Fe$_3$O$_4$ is ferrimagnetic i.e., the spins of the A and B sublattices are antiparallel, resulting in a net magnetization of $\sim$4$\mu_B$ per unit formula. When considering the charge ordering, transport, and optical properties of Fe$_3$O$_4$, only the $d^5$ (Fe$^{3+}$) and $d^6$ (Fe$^{2+}$) configurations are relevant because the on-site $d$-$d$ Coulomb interaction is sufficiently large ($U \sim 5$ eV) to prevent double occupancy of the B site by the extra electrons. Because the spins are fully polarized below $T_C$=858 K, the extra electrons at the B site enter the $t_{2g}$ level which is separated from the occupied $t_{2g}$ level by a gap of around 3.5 eV. Therefore a "spinless" Fermion model with intersite Coulomb interaction [11] has often been employed.

![Figure 2.2: Electronic configuration of Fe [(Ar)3d$^6$4s$^2$].](image-url)
\[ H = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j + \frac{1}{2} \sum_{i \neq j} U_{ij} n_i n_j \]  \hspace{1cm} (2.1)

Where \( t \) is a constant, \( c_i^\dagger \) and \( c_j \) are the electron creation and annihilation operators, \( U_{ij} \) is the Coulomb repulsion and \( n_i \) is the electron occupation number. \( U_{ij} (\ll U) \) is the nearest-neighbor (\( \equiv U_1 \)) or next-nearest-neighbor [\( \equiv U_2 (\ll U_1) \)] Coulomb energy. The first term describes the nearest-neighbor (nn) hopping and the second term the Coulomb repulsion.

At the Verwey transition, multiple ordering occurs. If \( U_2=0 \) below \( T_V \), \( U_1 \) determines only short-range order of the Anderson type [10], and a large number of configurations are degenerate in the ground state [13]. If \( U_2>0 \), this degeneracy is lifted and the Verwey order is stabilized. A finite transfer \( t \) or contributions from electron-lattice coupling, which arises from the different sizes of Fe\(^{2+}\) and Fe\(^{3+}\) ions, can stabilize other structures. Below \( T_V \), if \( t \) is negligibly small, a gap of \( 2(U_1+U_2) \) is opened between the occupied and empty \( B \) sites whereas above \( T_V \) the short range order partially destructs which creates new states in the middle of the gap partially filled by electrons [13]. Using this model, the electrical conductivity has been calculated [13], which shows an excellent fit to the experimental data (with \( t=0 \) and \( U_1=0.11 \) eV). In short the so-called order parameter, or charge difference on alternate sites, depends on the ratio of Coulomb repulsion \( U \) and the bandwith \( w \) i.e., different types of orders are obtained for different values of \( U/w \). Above \( T_V \) (\( U/w \) is small) only a metallic structure occurs whereas at the Verwey transition multiple ordering occurs which shows the existence of more than one non-zero order parameters. Below \( T_V \), as \( U/w \) increases, only a single order parameter structure exists.

Figure 2.3: Electronic configuration of Fe\(^{2+}\) [(Ar)3d\(^6\)] and Fe\(^{3+}\) [(Ar)3d\(^5\)]. In Fe\(^{2+}\) the two 4s electrons are omitted, whereas in Fe\(^{3+}\) one more spin down electron is missing from 3d.
2.4 Band Structure and Spin Polarization

In order to explain the electronic structure of Fe$_3$O$_4$ in the ferrimagnetic state, first-principles calculations were performed [4], using the Local Spin Density Approximation (LSDA) method and to explain the insulating state of Fe$_3$O$_4$, (LDA+U) calculations were performed [6]. According to the LSDA calculation (Fig. 2.4), the spin down bands from the $A$-site Fe are fully occupied while the spin up bands are fully empty, respectively (corresponding to the high-spin Fe$^{3+}$ ion), and the Fermi level is located within the $t_{2g\downarrow}$ band of the $B$-site Fe, resulting in the metallic state. In the LDA+U calculations, two sublattices for the $B$ sites ($B1$ and $B2$ corresponding to the Fe$^{3+}$ and Fe$^{2+}$ sites, respectively), were assumed in a Verwey-type charge ordering, and the resulting DOS is shown in Fig 2.4. While the local DOS of the $B1$ sublattice is similar to that of the $A$ site (with the spin directions interchanged), the down-spin $t_{2g}$ band of the $B2$ sublattice is split into a nondegenerate occupied band and a twofold degenerate unoccupied band due to the on-site $U$, as in Mott insulators. Thus a small gap of 0.34 eV is opened between the $B2$-site $t_{2g\downarrow}$ band below $E_F$ and the $B1$-site $t_{2g\uparrow}$ band above $E_F$. Although the large on-site Coulomb interaction is a necessary condition for opening the gap in Fe$_3$O$_4$, the magnitude of the gap is determined by the smaller intersite $d$-$d$ Coulomb interaction. The intersite Coulomb energy was estimated using the constrained LDA method to be 0.18 eV, which is an order of magnitude smaller than the bare pointcharge value. This reduction is due to $p$-$d$ covalency and dielectric polarization of the constituent ions. The experimental evidence for the half-metallic ferromagnetic state of magnetite (Fe$_3$O$_4$) by means of spin- and angle-resolved vacuum ultraviolet (VUV, $h\nu=21.2$ eV) photoemission spectroscopy has been studied [17]. Room temperature negative spin polarization of -(80±5)% at $E_F$ is found for epitaxial Fe$_3$O$_4$(111). The spin-resolved photoemission spectra together with the total emission intensity and the spin polarization as a function of binding energy for the first series of oxide films are presented in figs. 2.5(a) and 2.5(b), respectively, for different oxygen exposures $x(L)$. Figs 2.5(a) and 2.5(c) show the spin polarized photoemission spectra [spin down (down triangle) spin up (up triangle)] and photoemission intensity (circle). Figs 2.5(b) and 2.5(d) show the spin polarization as a function of binding energy.
Figure 2.4: Density of states of Fe$_3$O$_4$ in the ferrimagnetic state, (a) calculated using the LDA, (b) calculated using the LDA+U, from [6].
Figure 2.5: Photoemission spectra from 5 nm magnetite film at room temperature. (a), (c) Spin polarized photoemission spectra and photoemission intensity and (b), (d) spin polarization as function of binding energy, from [17].
Chapter 3

Experimental Methods

In this chapter we will discuss the experimental methods used for the preparation of multilayer structure, the measurement of the magnetotransport properties of the sample. These include the Ultra High Vacuum (UHV) Pulsed Laser Deposition system, Reflection High Energy Electron Diffraction (RHEED), Atomic Force Microscopy (AFM), Electron Beam Evaporation (EVAP). The prepared samples were characterised by High Resolution X-Ray Diffraction (HRXRD) and Superconducting Quantum Interference Device (SQUID) Magnetometry. The micrometer sized tunnel junctions were fabricated by using Optical Lithography in combination with Ar - Ion Beam Etching. After that the electrical transport properties of small tunnel turrets were measured in the cryostat system at different magnetic field and temperatures.

3.1 UHV-Pulsed Laser Deposition System

The Ultra High Vacuum system, with which ultrathin films were produced, consists of a main chamber with sample transfer arm, at which PLD, EVAP, AFM and sample loading chamber are attached. The whole system is equipped with different pre-pumps and turbo pumps to keep the pressure inside in the range of $10^{-9}$ mbar. A focused laser beam is directed at the target surface to induce material ablation. We used a 248 nm KrF excimer laser with an energy density at the target of 2-5 J/cm$^2$ per shot, and a pulse repetition rate of 2-10Hz, depending upon the deposited material. A planar target is rotated in the focal plane of the laser beam to achieve a stationary ablation rate. The carousel with the target can rotate at a speed up to 600 rpm with a positioning accuracy of 0.36°. Target is placed in a stainless steel vacuum chamber and fixed on a copper target holder. The PLD-chamber is evacuated down to $10^{-8}$ mbar with the aid of a turbomolecular pump. During laser irradiation of the target (e.g. TiN), the chamber is filled with a gas (in our case Ar) at pressures typically between $10^{-3}$ and 1 mbar. A planar substrate located at a typical separation from the target is held stationary. For particular film growth regimes the temperature of the substrate may be selected between room temperature and typically
1000 °C. A process gas supply is provided for the inlet of selected gases to produce desired chemical reactions during film growth. The evaporated materials consist of highly excited and ionized atoms. This ablated material is transferred through the plasma plume onto the heated substrate surface. The conventional experimental setup for PLD method is presented in fig 3.1.

3.1.1 Heating Laser

An infrared laser heating system to heat substrates in a thin film deposition system to temperatures above 1200 °C has several advantages with respect to thin film epitaxy. First, inside the vacuum chamber of the deposition system the substrate is heated directly by the infrared laser positioned outside the vacuum system. Therefore, the substrate heating is more efficient than in the case of a radiation heater positioned inside the vacuum chamber. In particular, the use of a radiation heater results in parts with temperatures well above the substrate temperature inside the vacuum system. A high-power diode laser is used for substrate heating. The beam with a wavelength of 950 nm and a maximum power of 100 W is fed through a glass fiber which directly irradiates the backside of the substrate.
3.1.2 Temperature Measurement by Pyrometer

The non-contact temperature measurement (pyrometry) is an optical measurement based on the property of all materials to send out electromagnetic (infrared) radiation. The infrared thermometer (pyrometer) uses this radiation to determine the temperature. The pyrometer is focussed at a certain spot of the substrate and determines the temperature of this spot. The IMPAC IGA 120-TV installed with the PLD chamber has been used to determine the temperature of sample before and during the deposition process.

3.1.3 Laser Ablation Process

The process is often envisioned as a sequence of steps, starting with the laser radiation interacting with the solid target, absorption of energy and localized heating of the surface, and subsequent material evaporation. The properties and composition of the resulting ablation plume may evolve, both as a result of collisions between particles in the plume and through plume-laser radiation interactions. Finally the plume impinges on the substrate to be coated; incident material may be accommodated, rebound back into the gas phase, or induce surface modification (via sputtering, compaction, sub-implantation, etc.). Such a separation has conceptual appeal but, inevitably, is somewhat over-simplistic. Furthermore, the laser-target interactions will be sensitively dependent both on the nature and condition of the target material, and on the laser pulse parameters (wavelength, intensity, fluence, pulse duration, etc.). Subsequent laser-plume interactions will also be dependent on the properties of the laser radiation, while the evolution and propagation of the plume will also be sensitive to collisions and thus to the quality of the vacuum under which the ablation is conducted and/or the presence of any background gas. Obviously, the ultimate composition and velocity distribution (or distributions, in the case of a multi-component ablation plume) of the ejected material is likely to be reflected in the detailed characteristics of any deposited film.

3.2 RHEED

The most useful way of monitoring growth modes during thin film deposition is reflection high-energy electron diffraction (RHEED). RHEED works by firing a narrow electron beam at the sample surface at grazing incidence, typically at an angle of 1 or 2 degrees. The reflected and diffracted beams are observed on a phosphor screen with a camera. The electron beam energy is 10 to 30 keV, beam current is around 10 to 50 $\mu$A.

For growth mode monitoring, we look at the intensity of the specular reflection. The intensity of the reflected beam is proportional to the surface smoothness. The more rough the surface is, the less intense will be the reflected beam. Smooth surfaces give a high reflected intensity, rough surfaces don’t reflect well and the intensity is lower.
3.3 AFM

Attached to the UHV-System is another chamber containing a setup for Atomic Force and Scanning Tunneling Microscopy (AFM/STM) designed by Omicron. AFM operates by measuring attractive or repulsive forces between a tip and the sample (Binnig et al., 1986). In its repulsive "contact" mode, the instrument lightly touches a tip at the end of a leaf spring or "cantilever" to the sample. As a raster-scan drags the tip over the sample, some sort of detection apparatus measures the vertical deflection of the cantilever, which indicates the local sample height. Thus, in contact mode the AFM measures hard-sphere repulsion forces between the tip and sample. In noncontact mode, the AFM derives topographic images from measurements of attractive forces; the tip does not touch the sample (Albrecht et al., 1991). The direct connection of an AFM chamber with the UHV-system allows the transfer of samples from other growth chambers without leaving the ultra high vacuum.

3.4 Electron Beam Evaporation

The EVAP 4000-UHV Electron Beam Evaporation Source, a self-accelerated bent beam source was mainly used for the deposition of tunnel barriers (Al$_2$O$_3$) and counter electrodes (Co). An electron emitter (filament) held at a high negative potential, emits electrons in all directions. The cathode assembly together with the beam former and deflection plate, form a beam in a defined direction. This beam of electrons is then accelerated through the steep potential gradient formed between the cathode and anode assembly. The culminated beam of high energy electrons is injected into a transverse permanent magnetic field. The magnetic field deflects and focuses the beam through a 270 degree arc where the beam impacts the evaporant material. The impinging electrons's kinetic energy is transformed into thermal energy at the impact surface of the source charge, which is supported in a water-cooled copper crucible. This surface oriented heating, forms a liquid area in the source charge while the portion of the source charge in contact with the crucible remains solid. Because the heating process takes place at (or very near) the surface, subsurface boiling does not occur. This allows a consistent vapor emitting area to develop. The solidified "skull" of source charge material separates the molten material from the water-cooled crucible and eliminates contamination by reactive molten material. To achieve uniform evaporation of subliming materials, movement of the beam impact area (sweeping) over the source charge is required. Beam "sweeping" or "scanning" is accomplished by varying the current supplied to electro-magnetic coils. These coils provide a time variable deflection of the electron beam along two axes to yield a uniform temperature over a maximum area of the source charge.
3.5 HIGH RESOLUTION X-RAY DIFFRACTION

Table 3.1: The critical parameters i.e., density and z-ratio of different materials have to be set before starting EVAP.

<table>
<thead>
<tr>
<th>Material</th>
<th>density</th>
<th>z-ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold (Au)</td>
<td>19.3</td>
<td>0.381</td>
</tr>
<tr>
<td>Aluminium (Al)</td>
<td>2.7</td>
<td>1.080</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>8.9</td>
<td>0.331</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>8.9</td>
<td>0.343</td>
</tr>
</tbody>
</table>

3.5 High Resolution X-Ray Diffraction

HRXRD is used to determine sample properties like chemical composition, lattice spacings and mismatches, layer thicknesses as well as lattice defects and stacking faults. The variations of the properties can be routinely, easily, and automatically mapped accross the sample surface. Both x-ray reflectometry and high resolution x-ray diffraction experiments have been performed on the multilayer structures to determine the film thickness from 0.1 nm to 50 nm with an accuracy of 1%, the density with an accuracy of ± 0.03g/cm$^3$, the surface and interface roughness from 0 to 5 nm with an accuracy better than ±0.1 nm and other lattice parameters using D8 DISCOVER HRXRD by Bruker AXS.

Figure 3.2: Schematic diagram of X-Ray Diffraction.
3.6 SQUID

Superconducting Quantum Interference Devices are electronic circuits consisting of one or more weak links, often Josephson junctions, interrupting an otherwise superconducting loop. SQUID’s are extremely responsive to magnetic signals. The SQUID measurements have been performed using the Quantum Design Magnetic Property Measurement System (MPMS) which is an analytical instrument configured specifically to study the magnetic properties of small experimental samples over a broad range of temperatures and magnetic fields. The system consists of two major hardware components: (1) the MPMS dewar and probe assembly, and (2) the associated control system in the MPMS control console. Automatic control and data collection are provided by a computer and two independent subsystem controllers. Gas control and other auxiliary functions in the system are also automated.

Within the dewar, a cryogenic probe integrates a superconducting magnet with a SQUID detection system and a high-performance temperature control system. The system provides rapid precision measurements over a temperature range of 1.9 to 400 Kelvin and a field range of up to 7 Tesla.

3.7 Micropatterning

The deposition and characterization of mulilayer thin film stacks was followed by patterning of small TMR turrets (contacts) of different shapes and sizes. The following processes and techniques were used for micropatterning TMR turrets.

3.7.1 Optical Lithography

For optical lithography, an optical microscope based projection system is used. In the projection system the mask pattern is demagnified by a factor of 5 to 100. Therefore, cheap foil masks can be used. With the system microstructure with a lateral width down to 1\(\mu\)m can be fabricated.

3.7.2 Ar - Ion Beam Etching

Ion beam etching is a versatile etch process in which the substrate to be etched is placed in a vacuum chamber in front of the broad-beam ion source. Ions (typically argon) are generated inside the ion source. They are accelerated into a broad parallel beam, and to a defined energy, by the extraction grids on the front of the source. As the ion beam etches the surface, the substrate is tilted to an angle in the beam and continuously rotated in order to optimize the smoothness of the etch. If a pattern is being etched by the use of a photomask, the use of tilt and rotation allows the user to adjust the wall angles in the
3.8. MAGNETOTRANSPORT MEASUREMENTS

resulting etch pattern. If one uses an inert gas such as argon, the process is relatively slow, and the heat that is generated must be removed with care.

<table>
<thead>
<tr>
<th>Material</th>
<th>Etching Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite (Fe₃O₄)</td>
<td>11-15 nm/min</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>50-100 nm/min</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>15-16 nm/min</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>15-30 nm/min</td>
</tr>
</tbody>
</table>

Table 3.2: Etching rate measured for different materials for the current setup.

3.7.3 Au - Sputtering

For the top Gold contact layer, the sputtering method is used. The modular design of the MED020 coating system enables a wide range of coating applications. For very fine-grained sputter coated films we required high vacuum sputtering. Undesired residual gas components such as water vapor are virtually eliminated from the vacuum chamber by a high vacuum pump. The working pressure required for sputtering of approximately $10^{-2}$ mbar is then re-established in the chamber with the admission of argon gas. To start the sputtering process a high voltage is applied to the target (cathode). This produces a high voltage field between the target and the specimen table (anode). The free electrons in this field are forced into a spiral path by a magnet system where they collide with the argon atoms in the field. Each collision knocks out an electron of the outer shell of the argon atom, positively charging the otherwise neutral argon. This is a cascading process that causes a glow discharge (plasma) to ignite. The positively charged argon ions are now accelerated to the cathode (target) where they impinge, knocking off metal atoms as they hit. Collisions also occur between the metal atoms thus released and the other gas molecules in the vacuum chamber. This causes the metal atoms to scatter widely, forming a diffuse cloud. The metal atoms from this cloud impinge on the specimen from all directions and condense evenly on it. Thus even very fissured specimen surfaces are coated with an even, thin metal film.

The fine grained structure of the sputtered film is a function of the target material, the working distance, the gas pressure and the sputtering current as well as of the process duration.

3.8 Magnetotransport Measurements

Magnetotransport measurements have been performed in a high magnetic field laboratory with a 8/10 and 15/17 Tesla magnet system. The magnet systems are decoupled from the building to avoid noise due to vibrations of the building. A variety of sample holders
can be mounted allowing for e.g. sample rotation during the measurement. For standard sample holders the accessible temperature regime is $1.5 \, \text{K} < T < 300 \, \text{K}$. However, also $\text{3He}/\text{4He}$ dilution refrigerator units ($T > 20 \, \text{mK}$) or high temperature units ($T < 700 \, \text{K}$) can be mounted. All measurements are fully computer controlled by the use of the LabView software tool allowing for remote control and almost continuous measurements.
Chapter 4

Layer Manufacturing and Characterization

4.1 Theory

The properties of thin films are determined essentially by the growth conditions during their deposition. There are many factors, which can influence the growth processes and modify the real structure of the film. Although many details of the thin film deposition can be explained already sufficiently, a complete theory of the thin film growth mechanisms does not yet exist, so that the optimization of the deposition parameters is dominated mainly by empirical points of view and experience. The reason is the large array of factors responsible for the growth processes and the developing of film structure and the difficulty to measure and control them in situ during the film deposition. In general three steps are essential in the thin film deposition process: nucleation and coalescence, followed by different growth processes as special cases of crystal growth (columnar, polycrystalline, epitaxial).

Firstly, they are different interaction of arriving atoms from the target with the surface of the substrate like absorption at special sites, surface diffusion, desorption and creation of clusters (nuclei) by capture of adatoms. The creation rate of nuclei can be described by a set of differential equations as a function of the impact rate $q$, the desorption time $\tau_A$, the capture rate $\lambda_i$ and the decay rate of the clusters $\kappa_i$. Many approximations are essential to solve this system of differential equations resulting in a semi-empirical description of the nucleation process. The nucleation is finished by the coalescence of the nuclei followed by the growth of amorphous or polycrystalline films, if the nuclei have statistically distributed crystallographic orientation or by the growth of monocrystalline films, if the nuclei are epitaxially oriented by a monocrystalline substrate and a sufficient high substrate temperature. The schematic process is illustrated in fig 4.1.

Secondly, a phenomenological description of the film growth and structure as a function of the surface mobility of the adatoms depending on the substrate temperature and the
residual gas pressure was given by Thornton [18]. The so-called Thornton diagram is illustrated in fig 4.3.

![Figure 4.1: Schematic diagram of atomic processes in the nucleation of three-dimensional clusters of deposited film atoms on a substrate surface.](image)

![Figure 4.2: Nucleation of three-dimensional cluster and corresponding energies.](image)

Depending on the substrate temperature and gas pressure four zones of the developing film structure can be distinguished. Zone I is characterized by a porous structure caused by shadowing effects of the incoming atoms by the adatoms, which can be demonstrated by computer simulations. In the transition zone T the structure is characterized by densely packed fibrous grains developing to columnar grains in zone II. The columnar structure...
4.1. THEORY

Figure 4.3: Thornton Diagram, from [18].

Figure 4.4: Schematic illustration of thin film growth method, showing the change in RHEED information as the growth mode changes from "step-flow" to 2-D nucleation, from [18].
can be dissolved by increasing surface mobility with increasing temperature (zone III) or by ion bombardment.  

Thirdly, for high Tc superconductors, ferromagnetic perovskites and semiconductors, the properties of thin films do not only depend on their chemical composition but mainly on their crystallographic structure and the interesting unique properties of these thin film materials can be achieved only with high quality monocrystalline films or films prepared with epitaxial growth at sufficient high temperature on monocrystalline substrates with matched lattice constants. The preparation of epitaxial films with atomically flat surfaces and interfaces requires very pure UHV conditions and low deposition rates necessary for the forming of equilibrium surface states under the condition of limited mobility. The most important growth mode for the preparation of such films is the 2-dimensional layer-by-layer growth known as Frank van der Merwe mechanism. The necessary conditions for this growth mode is

$$\gamma_{fv} + \gamma_{fs} \leq \gamma_{sv}$$  \hspace{1cm} (4.1)

where $\gamma_{fv}$, $\gamma_{fs}$ and $\gamma_{sv}$ are the surface energies between film and vacuum, film and substrate and substrate to vacuum. Otherwise 3-dimensional growth of clusters takes place (Kossel-Stranski mechanism). The necessary conditions for this growth mode is

$$\gamma_{fv} + \gamma_{fs} > \gamma_{sv}$$  \hspace{1cm} (4.2)

Important for the layer-by-layer growth is further the surface roughness, especially the distance between step edges in relation to the surface mobility of adatoms. These growth modes can be observed and in situ controlled by RHEED. Because the grazing incidence of the focused electron beam the penetration depth is limited to a thin surface layer and thus the diffraction pattern provides information about the first monolayer, their lattice parameters, surface reconstruction and disorder effects.  

4.2 Substrate  

The choice of the substrate material underneath the thin film plays an important role in component applications. The substrate used in this work was MgO (001) in single crystal wafers, which are one side polished and cut into 5 mm×5mm pieces. MgO has the rock salt crystal structure as shown in fig 4.5 and belongs to the space group [Fm3m]. The lattice constant of MgO is 0.4203 nm. The lattice mismatch with Fe$_3$O$_4$ is only -0.3% and for this reason MgO has extensively been used as a substrate for the growth of Fe$_3$O$_4$ films. The other important properties of MgO are: Cubic a=0.4203 nm, Density: 3.58 g/cm$^3$, Melting Point: 2800 °C, Thermal Expansion: 8 x 10$^{-6}$ K$^{-1}$, Dielectric Constant: 8.1, Loss Tangent (10GHz): 9 x 10$^{-3}$
4.3 Buffer layer

Due to the lattice mismatch between MgO and Fe$_3$O$_4$, a buffer layer of TiN is included in between to get a high quality epitaxial Fe$_3$O$_4$ layers on the MgO(001) substrate. The lattice constant of Fe$_3$O$_4$ (a = 8.3987Å) is nearly twice that of MgO (a = 4.203Å) due to the specific arrangement of Fe atoms at the vacant interstitial tetrahedral (A) and octahedral (B) sites. During the direct growth of Fe$_3$O$_4$ on MgO, the islands nucleate randomly and when they coalesce they can be shifted or rotated with respect to each other, forming antiphase boundaries. At some of these boundaries the angle subtended by the cation-anion-cation interaction is 180° and hence the superexchange interaction between the cations mediated by oxygen is antiferromagnetic. This results in a picture where large islands having ferromagnetic ordering within the islands are connected by regions (APBs) having antiferromagnetic and frustrated exchange. As a consequence the film’s magnetization cannot be saturated even by applying a high magnetic field [20]. The buffer layer of ~30 nm thickness has been included to have highly conducting bottom connection.

4.4 Magnetite on MgO

Magnetite, Fe$_3$O$_4$, exhibiting a high Curie temperature ($T_c = 858$ K), is one of the most attractive materials among half-metallic ferromagnets for future spin-transport applications. Great attempts are undertaken to grow thin magnetite films to be suitable for preparation of high quality tunnel junctions and multilayered structures. In this work magnetite thin films have been grown on MgO (001) substrates with TiN as buffer layer and the growth modes have been optimized to achieve high quality Fe$_3$O$_4$ thin films. In the first step, to optimize the substrate temperature, the substrate has been heated to
different temperatures before starting ablation of Fe$_3$O$_4$ and using different characterization techniques it was found that the magnetite layer can be best grown on MgO (001) substrate at 320 °C. Later on in this work a substrate temperature of 320 °C has been used. In the second step different other parameters have been adjusted to get maximum quality of the deposited films like the laser optics, amount of process gas, position of target material and number of pulses for pre-ablation.

After the growth of the TiN buffer layer the substrate temperature is lowered to $T_S=320$ °C. An epitaxial magnetite film has been grown also in the same Ar atmosphere of $2.5 \times 10^{-3}$ mbar, at a pulse repetition rate of 2Hz. With these parameters, best RHEED intensity oscillations has been obtained indicating the layer-by-layer growth of Fe$_3$O$_4$. The RHEED patterns are shown in fig 4.6 and 4.7. During the Fe$_3$O$_4$ growth the RHEED pattern becomes more streaky without any indication of transmission spots which indicates the smoothing of the surface. The stripes in the RHEED pattern obtained for magnetite have only about half the spacing of the diffraction spots obtained for TiN. This is caused by the fact that the lattice constant of magnetite is about twice the one of TiN and MgO. From the total number of RHEED oscillations, the number of laser pulses per single oscillation and the film thickness determined from x-ray reflectometry, we find that four RHEED oscillations are obtained during the growth of a single unit cell thick layer. That is, the magnetite unit cell grows in four subunit-cell blocks as discussed in [28]. The substrate-target distance was optimized at 15cm for both magnetite and TiN targets.

4.5 Insulating Barrier

Al$_2$O$_3$ is used as insulating barrier in the Fe$_3$O$_4$/Al$_2$O$_3$/Co multilayer stack because of its high quality for large values of tunneling magnetoresistance. The electron beam evaporation system is used to grow Al$_2$O$_3$ layer with the thickness ranging from 1 to 2 nm. In this process first the Al layers have been deposited on the Fe$_3$O$_4$ and then oxidised for certain specific time. Different oxidation times have been used for different thicknesses of Al layer keeping in mind the fact that the unoxidized Al remaining after the oxidation process strongly affects the magnetoresistance ratio due to the decrease of spin polarization at the interface between Fe$_3$O$_4$/Al$_2$O$_3$ electrode [22]. The Al layer with thickness of 1.4 nm or below is oxidised in a single step whereas the Al layer with thicknesses above 1.4 nm have been oxidised in two steps to optimize the quality of insulating layer.

4.6 Counter Electrode

The negative spin polarization of the transition metal Cobalt (Co) makes it very interesting candidate to use as a counter electrode with Fe$_3$O$_4$ as bottom electrode in TMR thin film stack. The d-band for spin up ($\uparrow$) electrons are filled, but only partly filled for spin down ($\downarrow$) electrons. The electrical current should consist of only spin down ($\downarrow$) electrons
Figure 4.6: RHEED patterns obtained during Pulsed Laser Deposition of TiN and Fe$_3$O$_4$. 

(a) MgO at 600 °C before ablation  (b) After 800 Pulses of TiN

(c) Substrate at 320 °C with TiN  (d) After 250 Pulses of Fe$_3$O$_4$
Figure 4.7: RHEED patterns obtained during Pulsed Laser Deposition of TiN and Fe$_3$O$_4$. 

(a) After 500 Pulses of Fe$_3$O$_4$   
(b) After 750 Pulses of Fe$_3$O$_4$   
(c) After 1250 Pulses of Fe$_3$O$_4$   
(d) After 1800 Pulses of Fe$_3$O$_4$
as the available states in the 3-d band at the Fermi level are only available for spin down (↓) carriers. The e-beam evaporation (EVAP) mechanism is used to grow ∼40 nm thick Cobalt layers on top of Al₂O₃. The growth parameters has been varied and optimized by structural analysis of the surface.

4.7 Structural Analysis by HRXRD

The X-ray laboratory provides both powder and single crystal diffractometers. The first two-circle system is used for powder diffraction. In this system the samples can be heated in oxygen atmosphere up to 1600 °C. It is equipped with a Göbel mirror and an area detector to save measuring time. The second system is a high resolution four-circle diffractometer that can be used for reciprocal space mappings. It is equipped with a Göbel mirror and an asymmetric two-fold monochromator and allows for the texture analysis of thin film superlattices and single crystalline materials. In both systems, measurements can be carried out fully computer controlled.

Structural characterization of the deposited Fe₃O₄/TiN/MgO(001) films was carried out in the four-circle high-resolution x-ray diffractometer. In principle XRD measurements come down to measuring distances between lattice planes with plane x-ray waves (wavelength of a few tenths of a nm). When \(2a\) in fig 4.8 equals \(n\lambda\) the Bragg condition \((n\lambda = 2d \sin \theta)\) is satisfied and a peak will be measured.

Theta - 2theta scans give the possibility to see which planes are existing parallel to the reference plane (normally the film surface is taken as the reference plane). All layers have been grown in the (00ℓ) orientation of the substrate yielding only (00ℓ) peaks. To study the epitaxial growth of magnetite, \(θ-2θ\) scans have been performed for all samples. The figures below show the scans for one of these samples. Within the resolution of our X-ray diffraction system, no peaks of other chemical phases could be detected. Substrate peaks can be seen clearly. The magnetite peaks are also present besides these substrate peaks which can be visible when the area of interest is magnified by measuring the diffraction pattern in a small range.
From the samples containing individual TiN films grown for x-ray analysis previously [7], the following values of the c-axis parameter have been found: Fe$_3$O$_4$: $c=0.847$ nm and TiN: $c=0.420$ nm. The full width half maximum (FWHM) of the rocking curve of the magnetite (004) peak was about 0.033°. This value is more than 10 times smaller than the value measured for Fe$_3$O$_4$ films grown on Si(001) with TiN/MgO buffer system. This large difference can be attributed to the large lattice mismatch between Fe$_3$O$_4$ (as well as TiN/MgO buffer layer) and Si compared to Fe$_3$O$_4$ and MgO (lattice mismatch of Fe$_3$O$_4$: -2.4% on Si(001) for the 5-on-4 cube-on-cube growth mode and only -0.31% on MgO).

The underlying principle of X-ray reflectometry (XRR) is that the reflection of X-rays can be treated by the same Fresnel equations that describe visible light. As a result, X-rays exhibit total external reflection when they impinge on a sample below a critical incidence angle. This usually occurs at incidence angles of the order of several tenths of a degree. The exact value of the critical angle of total reflection is related to the film density. At incidence angles slightly above the critical angle of total reflection, some X-ray intensity penetrates into the film and part of that transmitted radiation is reflected at the interface between a film and substrate. The radiation reflected at the interface interferes with the radiation reflected from the surface. On changing the incidence angle, the two
4.7. STRUCTURAL ANALYSIS BY HRXRD

Figure 4.10: $\theta-2\theta$ scan of a sample with 30nm Fe$_3$O$_4$ layer on MgO(001). The (004)-Fe$_3$O$_4$ peak is present just besides the MgO(002).

Figure 4.11: $\theta-2\theta$ scan of a sample with 30nm Fe$_3$O$_4$ layer on MgO(001). The small figure shows the rocking curve for the (004)-Fe$_3$O$_4$ peak.
CHAPTER 4. LAYER MANUFACTURING AND CHARACTERIZATION

Figure 4.12: Rocking curve for the (004)-Fe$_3$O$_4$ peak. The FWHM is 0.0338°.

Contributions give rise to interference fringes whose spacing is characteristic of the film thickness. Over the years, the theory has been generalized to handle multilayer thin films and roughnesses. The technique does not rely on a material being crystalline, as X-ray diffraction does, and so can be used to characterize amorphous layers as well as crystalline layers. The X-ray reflectometry can be used to determine layer thicknesses, surface and interface roughnesses, layer densities etc. In the start of this work, many test samples have been prepared with a single magnetite layer on a MgO/TiN buffer system to perform XRD measurements. Different thin film parameters have been optimized during these test measurements e.g. film thickness, interface roughness etc. Later on all samples have been characterized with this method before starting patterning. During the process, first the X-ray reflectometry measurement is performed and afterwards using the software program Leptos, a non-linear curve fitting of the actual and simulated reflectometry graphs is done to acquire the values for the different parameters of the multilayer stack. Figure 4.13 shows the XRR curves for sample mtmr77 containing 30nm TiN, 20nm Fe$_3$O$_4$, 2nm Al$_2$O$_3$ and 40nm Cobalt. The figures from 4.14 to 4.16 show the graphs after fitting actual and simulated curves. The layer thicknesses shown are the values obtained after fitting actual and simulated curves.
Figure 4.13: X-ray reflectometry graph of a sample with a 30nm Fe₃O₄ layer.

Figure 4.14: Actual and simulated x-ray reflectometry curves.
CHAPTER 4. LAYER MANUFACTURING AND CHARACTERIZATION

Figure 4.15: Actual and simulated x-ray reflectometry curves.

Figure 4.16: Actual and simulated x-ray reflectometry curves.
Chapter 5

Magnetic Tunnel Junctions

In this chapter, the theory of electron tunneling through insulating barriers is presented. Also the methods used in this work for the preparation of micrometer sized tunnel junctions for TMR measurements will be discussed.

5.1 Theory

Relevant for a tunnel junction is the electron tunneling from one electrode to the other electrode as a function of the voltage applied on the junction. Though classically forbidden, from a quantum mechanical point of view there is a finite probability for an electron wave to cross a potential barrier.

Figure 5.1: Tunneling through an insulating barrier.
We consider a metal/insulator/metal structure with an applied bias voltage $V$. Due to the applied voltage, the Fermi level of one of the electrodes will shift by $eV$ with respect to the other (fig. 5.2). The tunneling current from the first electrode (I) to the second electrode (II) depends on the density of states at a given energy in the first electrode, $\varrho_I(E)$, the density of states at the same energy in the second electrode, $\varrho_{II}(E+eV)$, the probability of transmission through the barrier expressed as the square of a matrix element $|M|^2$, as well as the probabilities that the states in the first electrode are occupied and the states in the second electrode are empty. These probabilities can be expressed by the Fermi-Dirac function as $f(E)$ and $[1-f(E+eV)]$. The tunneling current from the first to the second electrode is then given by:

$$I_{I-II}(V) = \int_{-\infty}^{+\infty} \varrho_I(E)\varrho_{II}(E+eV)|M|^2f(E)[1-f(E+eV)]dE \quad (5.1)$$

and the total current can be expressed as $I_{I-II}-I_{II-I}$.

**Figure 5.2: General barrier in the insulating film between two metal electrodes.**

### 5.2 Simmons - Model

For a trapezoidal barrier of average height $\bar{\varphi}$, Simmons expressed the tunnel current density as a function of the barrier thickness, $d$, the average barrier height, $\bar{\varphi}$, and the bias voltage $V$ [24]. The calculated current density is shown in the following equation
5.3. PATTERNING OF TMR TURRETS

\[ J(V) = J_0[\bar{\psi} \exp(-A\sqrt{\bar{\psi}}) - (\bar{\psi} + eV) \exp[-A\sqrt{(\bar{\psi} + eV)}]] \]  (5.2)

where \( \triangle d = d_2 - d_1 \), and \( \bar{\psi} \) is the mean barrier height above Fermi level of the negatively biased electrode, given by

\[ \bar{\psi} = \frac{1}{\triangle d} \int_{d_1}^{d_2} \varphi(x) dx \]  (5.3)

and \( A \) is a constant given by

\[ A = \frac{4\pi \triangle d \sqrt{2m}}{h} \]  (5.4)

and

\[ J_0 = \frac{e}{2\pi h (\triangle d)^2} \]  (5.5)

where \( J \) is expressed in \( \frac{A}{m^2} \). Equation (5.3) has the advantage that it can be applied to any shape of potential barrier providing the mean barrier height is known, or, alternatively, if the current-voltage characteristic of a tunnel junction is known, the mean barrier height can be determined. Equation (5.3) can be interpreted as a current density \( J_0 \bar{\psi} \exp(-A\sqrt{\bar{\psi}}) \) flowing from electrode I to electrode II and a current density \( J_0(\bar{\psi} + eV) \exp[-A\sqrt{(\bar{\psi} + eV)}] \) flowing from electrode II to electrode I, resulting in a net current density \( J \).

It is straightforward to see that at very low voltages, the current density is linear in voltage whereas for larger voltages, the dependence becomes rapidly non-linear. Therefore, a non-linear (I-V) characteristic is a sign of a tunneling phenomenon in a metal/insulator/metal structure. Equation (5.3) is used to determine the barrier height and thickness by non-linear curve fitting of (V-I) curves obtained through magnetotransport measurements.

5.3 Patterning of TMR Turrets

In this work we intend to study the effect of shape, area and orientation of the tunnel junctions on the tunneling magnetoresistance and for this purpose different sized and shaped TMR turrets have been prepared through optical lithography and ion beam etching. In this section, the technologies and practice of making three dimensional structures and devices with dimensions in the order of micrometers will be discussed. The setup installed in the state of the art clean room helped us to develop very small TMR turrets in different shapes. The three step process of patterning TMR turrets involved optical lithography, Ar-ion beam etching, electron beam evaporation and Au sputtering techniques.

5.3.1 Optical Lithography

The lithography unit consists of a light source, a resist coated sample and an image control system, which regulates, which part of the sample is illuminated by the radiation. Lithography is the basic technique used to define an etch mask consisting of a photoresist pattern. By using optical lithography three times, we patterned small TMR turrets of
CHAPTER 5. MAGNETIC TUNNEL JUNCTIONS

Figure 5.3: TMR Multilayer Stack.

Figure 5.4: Mask for Step 1.
5.3. PATTERNING OF TMR TURRETS

Figure 5.5: Masks for step 2.

different shapes and areas with gold contacts on the top for the measurement of magnetotransport properties. In the first step, the shadow mask shown in figure 5.4 has been used to prepare the main region of the structure for bonding connections as well as to hold small tunnel turrets inside the central bridge. Negative photoresist AZ5214E is used of the thickness of 1 $\mu$m on top of multilayer stack and then rotated on the spinner with a speed of 4000 rpm. To make the photoresist hard, it is placed on the hot plate for 1:10 min at the temperature of 107 °C. Negative photoresist is used to weaken the surface by the application of ultraviolet light. In this way the resist that is not exposed to light can be removed. In the second step different shapes of small structures shown in the figure 5.5 have been patterned inside the main bridge. The third and last step includes the mask shadowed for the top gold plating as contact region. The mask is shown in figure 5.6.

5.3.2 Ion Beam Etching

With the use of an Ar$^+$ ion beam, bulk material can be removed from the surface of a sample allowing the construction of small turrets via the multilayer stack. The ion beam is produced by leaking Ar gas into the ion gun source chamber and then getting ionized by electron bombardment. The resulting Ar$^+$ ions are then accelerated and focused onto the sample surface for etching. The Ar-ion beam etching technique is used to pattern small TMR turrets after photomasking and optical lithography. In the first step, with the main shadow mask (fig. 5.4), we etched through the whole multilayer stack down to the substrate. In the second step, with the second shadow mask (fig. 5.5), we etched through
to the TiN buffer layer. The following values of the parameters $E_{Ar} = 500$ eV, Cathode Current = 4.34 A, Discharge Voltage = 55 V, Discharge Current = 0.29 A, Beam Voltage = 500 V, Beam Current = 12 mA, Accelerated Voltage = 350 V, are used for ion beam etching.
5.3. PATTERNING OF TMR TURRETS

Figure 5.7: Patterned Sample.

Figure 5.8: Patterned Sample.
5.3.3 Au-Sputtering

In third and last step the patterned structures were then covered by a top gold contact layer providing electrical contact to the top layer of the turret. Two masks have been used in this step to get both connected and separated configurations on the top of each TMR turret. MED020 coating system has been used to grow ∼100nm thick Au layer on the top. The top layer also was used to provide bonding connections from the Cu strips glued separately on the special holder used for magnetotransport measurements. The figure 5.11 shows the sample containing four structures with bonding connections from outside Cu strips.

Figure 5.9: Patterned TMR turrets (a) elliptical with connected Au layer and (b) square with separated Au layer on top.
5.3. PATTERNING OF TMR TURRETS

Figure 5.10: Sample with Al bonding wires for electrical connection from outside.

Figure 5.11: Complete structure bonded on the copper sample holder ready for transport measurements.
Chapter 6

Transport Measurement

In this section, the results obtained by magnetotransport measurements across mesoscopic magnetic tunnel junctions is presented. By definition, the spin dependent tunneling between two ferromagnets in a magnetic tunnel junction, can result in a large tunnel magnetoresistance (TMR) at room temperature. The first observation of this effect was made by Julliere in 1975 [2]. However, since then, reliable room temperature TMR values were reported only in 1995 [27]. Over the past decades, this field attracted, and still does attract a lot of interest from a fundamental point of view and in view of possible applications in non-volatile Magnetic Random Access Memories (MRAMs) and next-generation magnetic field sensors.

There are two principal geometries of the TMR effect. In the first case current flows perpendicular to the layers (CPP) and in the other case current flows in plane of the layers (CIP). In this work, the CPP geometry has been considered for magnetotransport measurements. The CPP geometry is easier to treat theoretically but much more difficult to realize experimentally. This is because the transverse dimensions of typical multilayers are of the order of $\mu m^2$ whereas their thickness is only of the order of a few nanometers. It follows that the resistance of the multilayer in the CPP geometry is extremely low if a normal metal is used to separate the ferromagnetic layers and, therefore, very sophisticated experimental techniques are required to measure accurately the very small voltage drop across the sample. In trilayer system, the electric current flows in two channels, one corresponding to electrons with spin projection $\uparrow$ and the other to electrons with spin projection $\downarrow$. The $\uparrow$ and $\downarrow$ spin channels are independent (spin is conserved) the sample can be modeled as two resistors. Fig 6.1 shows the simple resistor model of the TMR effect in a trilayer system when the ferromagnets have same sign of spin polarization.

In the ferromagnetic configuration of the trilayer, electrons with $\uparrow$ spin have high tunneling current whereas the electrons with $\downarrow$ spin have low tunneling current. This is modeled by two small resistors in the $\uparrow$ spin channel and by two large resistors in the $\downarrow$ spin channel. In the antiferromagnetic configuration of the trilayer, both spin-up and spin-down electrons have low tunnelling current. In the first case, since the $\downarrow$ and $\uparrow$ spin channels are connected
in parallel, the total resistance of the trilayer in its ferromagnetic configuration is low as compared to the antiferromagnetic configuration.

![Figure 6.1: Tunneling current of spin up and down electrons through the multilayer stack both in parallel and antiparallel alignment.]

### 6.1 Magnetic Properties

The switching behavior in a soft-hard multilayer stack is schematically shown in fig 6.2. The solid line corresponds to the case where the ferromagnetic layers are switching independently, whereas the dashed line corresponds to the situation when a small ferromagnetic coupling is present. For an antiferromagnetic coupling, the hard layer will switch at a higher coercive field than without coupling. All the multilayers grown in this work are designed as a soft-hard system. Both the soft and hard layers have same easy axis of magnetization but different coercive fields as $H_1$ and $H_2$, respectively. In all the magnetic measurements, the magnetic field is applied parallel to the layer structure along the [001] crystalline direction of the MgO substrate. Schematic drawing of a stepped hysteresis loop is shown in fig 6.2.
Every sample is prepared in duplicate for parallel investigation of magnetic properties along with characterization and patterning. The samples used for measuring magnetic properties all have magnetite film thickness of \( \sim 20 \text{nm} \) but have different barrier thicknesses. The clear magnetite switching is found only in a sample with 1.4nm \( \text{Al}_2\text{O}_3 \) barrier. One reason could be the oxidation method as all other samples with higher barrier thicknesses are those in which the \( \text{Al}_2\text{O}_3 \) barrier is oxidised in two steps. The idea is that the one sample with 1.4nm barrier can have some coupling between the two ferromagnetic layers so that we get a clean switching of \( \text{Fe}_3\text{O}_4 \) layer as shown in fig 6.3. The other two samples shown in fig 6.5 and 6.4 do not show very clean switching of the magnetite layer.
Figure 6.3: M(H) for a sample with 1.4nm Al₂O₃ oxidised in one step, the thicknesses of Fe₃O₄ and Co layers are 20 nm and 40 nm respectively.
Figure 6.4: $M(H)$ for a sample with 1.8nm Al$_2$O$_3$ oxidised in two steps, the thicknesses of Fe$_3$O$_4$ and Co layers are 20 nm and 40 nm respectively.
Figure 6.5: \( M(H) \) for a sample with 1.6nm \( \text{Al}_2\text{O}_3 \) oxidised in two steps, the thicknesses of \( \text{Fe}_3\text{O}_4 \) and Co layers are 20 nm and 40 nm respectively.
6.2 R(H) - Measurement

The tunneling magnetoresistance (TMR) is determined by R(H)-measurements on the mesoscopic tunnel junctions of different shapes and with different thicknesses of the insulating barrier layer. A high magnetic field cryostat system with a 8/10 Tesla magnet was used to carry out transport measurements. The resistivity was measured with a four-probe method in a magnetic field of \(-0.3 \leq \mu_0 H \leq 0.3\) Tesla at temperatures ranging from 100 to 330 K. During the computer controlled measurement procedure, in the first step the magnetic field is always driven to the value of 2 Tesla to insure the parallel alignment of the magnetic domains in ferromagnetic electrodes. Then using high sweep rate, the magnetic field is driven down to 0.3 Tesla at which we start to measure the change in tunneling resistance. We used slow sweep rate to drive the magnetic field from 0.3 Tesla to -0.3 Tesla to avoid noise in the resistance signals. The measurements have been carried out sweeping the magnetic field in both positive and negative directions.

The tunneling magnetoresistance (TMR) of various tunnel junctions with different shapes, areas and also different barrier thicknesses are measured. The insulating barrier layer used in this work is Al$_2$O$_3$ because it was found to yield high values of the tunneling magnetoresistance (TMR) in contrast to very small TMR effect for MgO and SiO$_2$ and almost a zero TMR effect for SrTiO$_3$ and NdGaO$_3$ barriers [28]. The magnetite (Fe$_3$O$_4$) and cobalt (Co) layer thicknesses in all samples are 20 nm and 40 nm respectively.

![Figure 6.6: 8% TMR effect measured across the rectangular turret with dimensions of 37.5μm x 3μm at Room Temperature. The Al$_2$O$_3$ barrier thickness is 2nm.](image-url)
CHAPTER 6. TRANSPORT MEASUREMENT

Figure 6.7: Rectangular turret with dimensions of 37.5µm x 3µm (a) at 200 K, (b) at 225 K. The Al₂O₃ barrier thickness is 2nm for both turrets.

(a) 7.3% TMR
(b) 8.5% TMR

Figure 6.8: Square turret with dimensions of 10µm x 10µm (a) at 295 K and (b) at 360 K. The Al₂O₃ barrier thickness is 1.4nm in both turrets.

(a) 3.5% TMR
(b) 4% TMR
6.2. \( R(H) \) - Measurement

![Graph](image)

(a) 5.5% TMR  
(b) 6.3% TMR

Figure 6.9: Square turret with dimensions of 18\( \mu \)m x 18\( \mu \)m (a) at 295 K and (b) at 225 K. The Al\(_2\)O\(_3\) barrier thickness is 2nm.

![Graph](image)

(a) 7.7% TMR  
(b) 11% TMR

Figure 6.10: Elliptical turret with dimensions of 35\( \mu \)m x 15\( \mu \)m (a) at 295 K and with 2nm Al\(_2\)O\(_3\) barrier, (b) at 250 K and with 1.2 nm Al\(_2\)O\(_3\) barrier.
6.3  R(T) - Measurement

The change in resistance with temperature is measured for all samples with different barrier thicknesses and for each TMR turret during transport measurements. The magnetic field is set to the value of 0.5 Tesla before starting R(T) measurements to ensure that the ferromagnetic electrodes aligned their magnetization direction. As in this work only Al₂O₃ is used as insulating tunneling barrier, no major difference in the shapes of the curves has been found. Different shapes and barrier heights had slightly different turning points on the R(T) curves. The curves obtained for different samples and TMR contacts are shown in fig 6.12. High change in resistance with temperature has been found at low temperatures usually below 125 K, the Verwey transition temperature (Tᵥ) of Fe₃O₄. The comparison of the R(T) curves obtained for different shapes of the small tunnel turrets is presented in fig 6.11. The Fe₃O₄ layer thickness in all samples is 20 nm. From the results, it can be concluded that increase of R with decreasing T mainly results from increase of the electrode resistance. Tunneling resistance shows weak temperature dependence as expected.

![Figure 6.11: R(T) - curves for tunnel junctions of different sizes and shapes.](image-url)
Figure 6.12: \( R(T) \) - curves.
6.4 V(I) - Measurement

The (V-I) characteristics measured for mesoscopic tunnel junctions with different barrier thicknesses at various temperatures are shown in fig. 6.14 and 6.15. Each curve shows a clean non-linear behaviour, which could be taken as a sign of tunneling. Before starting (V-I) measurements, the magnetic field is set to 0.5 Tesla to ensure that the electrodes align their magnetization directions. The current is varied from -1 mA to 1 mA in small steps for each tunnel turret and the corresponding change in voltage has been measured. The measurements have been repeated for different temperatures to study the influence of temperature on the (V-I) characteristics.

Conventional Al$_2$O$_3$ barriers have breakdown voltages around 1.5 V or less so no higher voltages have been applied to the insulator barrier. It was found that at low temperature the (V-I) curves show more non-linear behaviour in comparison to the curves at high temperature. At room temperature the current nearly changes linearly with voltage. The curves shown in the figures 6.14 and 6.15 represent the relation between current density (J) and voltage (V). After performing a non-linear curve fitting using the Simmons model [24], the barrier height and thickness for different tunnel junctions have been obtained. The sample with 1.2 nm Al$_2$O$_3$ barrier has a barrier height of 0.07 eV, whereas the sample with barrier thickness of 2 nm has a barrier height of as much as 0.63 eV. Since in (I-V) characteristics, both the tunneling resistance and the series resistance of the junction electrodes are increased, the values derived for the barrier height and width have to be taken with great care. They only can give same trend.

![Graphs](image-url)

(a) (V-I) characteristics @ 150K  
(b) (V-I) characteristics @ 200K

Figure 6.13: (V-I)- Curves for a sample at different temperatures.

By performing non linear curve fitting of (V-I) characteristics, the values of barrier potential have been obtained. At low temperatures the Al$_2$O$_3$ barrier exhibits higher barrier potential as compared to low temperatures.
6.4. $V(I)$ - MEASUREMENT

Figure 6.14: (V-I)- Curves for a sample at different temperatures including Simmons-fitted curves.

(a) 1.4nm Al$_2$O$_3$ Barrier @ 150K

(b) 1.4nm Al$_2$O$_3$ Barrier @ 200K

(c) 1.4nm Al$_2$O$_3$ Barrier @ 200K

(d) 1.4nm Al$_2$O$_3$ Barrier @ 200K

(e) 1.4nm Al$_2$O$_3$ Barrier @ 295K

(f) 1.4nm Al$_2$O$_3$ Barrier @ 295K
Figure 6.15: (V-I)- Curves for a sample at different temperatures including Simmons-fitted curves.
6.5 Conclusions

The whole work has been devoted to study the study of spin polarized tunneling in magnetite/insulator/Co tunnel junctions. For the fabrication of such MTJ’s most deposition parameters have been optimized. The applicability of Al$_2$O$_3$ as insulating barrier has been extensively investigated. Cobalt is used as the top counter electrode to measure its effect on the overall change in magnetoresistance in comparison with Nickel studied already [28]. TMR values as high as 8% have been found in Fe$_3$O$_4$/Al$_2$O$_3$/Co multilayer system at room temperature. For certain shapes of tunnel junctions even higher (up to 11%) TMR values have been found at low temperatures. The TMR curves obtained during R(H)-measurements are shown in figures 6.6 to 6.10. For elliptical shaped turrets peak shaped R(H)-curves have been observed. One reason is supposed to be the lack of formation of magnetic domains in the elliptical electrodes [29]. The shape anisotropy of the ellipse favors magnetization parallel to the long axis of the ellipse. The other geometries (square and rectangular) of tunnel turrets show normal TMR shapes as predicted previously. Maximum TMR effect (8%) is obtained for a sample containing 20nm(Fe$_3$O$_4$)/2nm(Al$_2$O$_3$)/40nm(Co) stack.
Chapter 7

Appendix

In this section the list of samples prepared for magnetotransport measurements is presented including the growth parameters and various effects obtained. Also shown are the pictures of experimental setups used throughout this work.
<table>
<thead>
<tr>
<th>Date</th>
<th>Probe</th>
<th>Substrate</th>
<th>Pressure mBar/~Torr</th>
<th>Temp °C</th>
<th>Laser mJ</th>
<th>Pulses</th>
<th>Thickness</th>
<th>RHEED</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
<td>30/03/04</td>
<td>MTMR66</td>
<td>MgO(001)</td>
<td>M7-25</td>
<td>P320</td>
<td>450T2</td>
<td>3250P, 2Hz Fe3O4, 600P, 2Hz MgO</td>
<td>~40-50nm, 10-20nm</td>
<td>Needed more pulses (~13) per oscillation than expected. The laser window seems to be dirty.</td>
<td>Not a very good fit curve after X-ray reflectrometry was obtained.</td>
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<td>MgO(001)</td>
<td>M7-26</td>
<td>P300</td>
<td>450T2</td>
<td>2000P, 2Hz Fe3O4, 600P, 2Hz MgO</td>
<td>~50nm, 10-20nm</td>
<td>That’s it. After cleaning window, it needed only ~8 Pulses/oscillation.</td>
<td>Few droplets and dust particles found when checked under optical microscope.</td>
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<td>RT</td>
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<td>50nm Co, TF58.8, 1nm Al EVAP:30min Oxid 1nm Al EVAP:30min Oxid 25nm Co</td>
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<td>-</td>
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<tr>
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<td>MgO(001)</td>
<td>M7-28</td>
<td>P600</td>
<td>450T2</td>
<td>1600P, 2Hz TiN, 800P, 2Hz Fe3O4</td>
<td>~30nm</td>
<td>Stopped: The temp has gone up to 650 °C due to which TiN layer transformed to islands.</td>
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<td>MgO(001)</td>
<td>M7-30</td>
<td>P600</td>
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<td>~30nm, ~20nm, ~1.6nm, ~40nm</td>
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<td>MgO(001)</td>
<td>M7-20</td>
<td>P600</td>
<td>450T2</td>
<td>1600P, 2Hz TiN, 800P, 2Hz Fe3O4, 0.9nm Al EVAP:30min Oxid 0.9nm Al EVAP:30min Oxid 40nm Co</td>
<td>~30nm, ~20nm, ~1.8nm, ~40nm</td>
<td>Needed around 9.6 pulses per oscillation for magnetite growth. Not bad. 900P → 19.6nm Fe3O4</td>
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Needed around 13 pulses per oscillation for magnetic growth. Window again gets dirty. 1225P → 19.9nm Fe3O4

These samples have been made because both samples MTMR 71&72 were destroyed during cleaning processes.

Few dust particles on the surface.

Looking quite clean.
Figure 7.1: Pulsed Laser Deposition Setup

Figure 7.2: Pulsed Laser Deposition Setup
Figure 7.3: Laser Optics

Figure 7.4: X-Ray Diffractometry
Figure 7.5: SQUID - Magnetometer

Figure 7.6: Wafer Prober
Figure 7.7: Optical Microscope

Figure 7.8: Photomasking Setup
CHAPTER 7. APPENDIX

Figure 7.9: Optical Lithography Setup

Figure 7.10: Ar-Ion Beam Etching
Figure 7.11: Au-Sputtering System

Figure 7.12: Al Bonder
Bibliography


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