Spin-dependent transport across anti-phase boundaries in magnetite films

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Chapter 3

Experimental methods

3.1 Introduction

The study and application of ultrathin films has developed over the last decades due to the improvement of ultra high vacuum technology. With accurate growth methods like molecular beam epitaxy (MBE), thin films can be grown with a very precise control over the thickness and stoichiometry. Furthermore, analytical techniques like electron microscopy can obtain a high resolution of the microstructure. Combining controlled growth of thin films with microstructural analysis and electrical conduction enables one to study the electrical properties in relation to the microstructure.

In this chapter we give a detailed description of the thin film growth method and the techniques used to analyse the films. The chapter is divided into four main sections. The experimental technique to grow the thin films (molecular beam epitaxy) and the techniques used in situ to analyse the structural quality and purity of the films are discussed in §3.2. Mössbauer spectroscopy, which is performed outside the vacuum system, will be treated in §3.3. §3.4 is devoted to transmission electron microscopy (TEM) and the electrical conduction- and magneto-resistance experiments are presented in §3.5.

3.2 Thin film growth: molecular beam epitaxy (MBE)

All the Fe$_3$O$_4$ films described in this thesis have been prepared by molecular beam epitaxy (MBE). In MBE a molecular beam of a metal species is created by heating the material, which then evaporates and condensates on a substrate. When the as-deposited film is single crystalline one speaks of MBE [74]. To grow metal oxides with this method, both a metal flux and a
flux of an oxidizing agent (for instance oxygen, ozone or NO$_2$) are employed simultaneously. A low background pressure prevents that the substrate and the growing film get contaminated within the time necessary to deposit the film and perform the characterisation experiments.

3.2.1 The ultra high vacuum setup

The ultra high vacuum setup consists of three separate chambers, as shown in Fig. 3.1: one for preparing clean substrates (the preparation chamber), one for growing the samples (the evaporation chamber) and one for analysing the substrate and samples (the analysis chamber). The samples can be transported from one chamber to the other via a transport system which is enclosed in the middle chamber (the preparation chamber).

The substrates are mounted on a stainless steel holder and first introduced into the preparation chamber. This chamber is equipped with an annealing oven which can reach $>1000$ °C. By heating the substrates, contaminants like water and hydrocarbons evaporate of the surface. When the substrate is an oxide, the substrate might become deficient in oxygen when annealing is done in vacuum. For that reason, O$_2$ can be introduced into the preparation chamber through a leak valve during the annealing. The chamber also has an Ar sputtering facility. After cleaning, the substrates can either be trans-
3.2. Thin film growth: molecular beam epitaxy (MBE)

Figure 3.2: Schematic drawing of the evaporation chamber. The chamber is pumped via a Ti sublimation pump and a liquid nitrogen cooled oil diffusion pump. There are Knudsen cells, a water cooled quartz crystal balance (not drawn), a mass spectrometer, a gas inlet and a high energy electron source. The chamber also contains a cryopanel, which is cooled with liquid nitrogen. The manipulator has 5 degrees of freedom and can be cooled or heated between 100 and 870 K.

Deposition of the films takes place in the evaporation chamber. A schematic drawing of the evaporation chamber is shown in Fig. 3.2. This chamber has
a background pressure of approximately $10^{-10}$ mbar which is obtained by a combination of a Ti sublimation pump and an oil diffusion pump with an efficient liquid nitrogen trap. The chamber itself contains a cryopanel which can also be cooled with liquid nitrogen. The composition of the residual gases can with checked be a quadrupole mass spectrometer.

The clean substrate is put on the manipulator which has five degrees of freedom (x, y and z movement, rotation around the substrate normal and a rotation in the plane of the substrate). The manipulator can both be cooled with liquid nitrogen or heated, in this way temperatures between 100 and 870 K can be reached. Metal is evaporated from an effusion cell, also called 'Knudsen' cell. It contains an alumina crucible filled with metal, which is heated up by a tungsten filament. The opening of the crucible is covered with a shutter. The flux of metal is measured with a water cooled quartz crystal balance. Oxygen, or other oxidizing agents, can be admitted via a gas delivery system which consists of a small buffer volume. The gas is let into the buffer volume via a leak valve. The flux of particles at the substrate depends on the buffer pressure, the dimensions of the tube and the distance of the tube opening to the substrate. At a distance of 10 cm between the tube opening and the substrate, the flux of particles arriving at the substrate surface is [35]: $F_{\text{gas particles}} = 1.9 \cdot 10^{20} P_{\text{buf}}$, with the buffer pressure in Torr. This is derived assuming the flux of particles arriving at the substrate is mainly due to the particle flow coming directly from the tube and particles from the background can be ignored [35]. The buffer pressure is measured with a baratron. The output of the baratron is in volts. This can be converted into Torr via the following relationship: $1 \text{mV} = 10^{-2} \text{mTorr}$. The evaporation chamber is furthermore equipped with an high energy electron source to perform reflection high energy electron diffraction (RHEED).

### 3.2.2 In-situ analysis

The most important in-situ analysis tools for the crystal structure and thickness of the film are reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED). For both techniques an electron beam is incident on the sample. For LEED the electron energy is between 50 en 800 eV, resulting in a small wave vector $\mathbf{k}$ (which is of the same order of magnitude as a reciprocal lattice vector of inorganic crystals). For RHEED the energy is several keV and the electrons thus have a large wave vector. The other difference is the angle of incidence. For LEED the electrons come in perpendicular and for RHEED the incoming angle is grazing. The resulting Ewald constructions are shown in Fig. 3.3. From the diffraction pattern the symmetry of the sample can be determined and qualitative information can be obtained from the intensity of the background. MgO
Figure 3.3: Ewald sphere construction for a) LEED, where the electron energy and wave vector \( k \) are small and the incoming electrons make an angle of 90° with the surface and b) RHEED, where the electron energy and wave vector are large and the incoming angle is grazing.

has a cubic unit cell with face centred symmetry. Only diffraction spots or streaks are visible when \( h + k = 2n \). Because the lattice constant of \( \text{Fe}_3\text{O}_4 \) is about twice as large as the one for \( \text{MgO} \), the (400) planes of \( \text{Fe}_3\text{O}_4 \) have the same spacing as the (200) planes of \( \text{MgO} \) and their corresponding reflections will overlap in RHEED and LEED.

The thickness of the films was determined \textit{in situ} from RHEED intensity oscillations. These oscillations are obtained by recording the intensity of the specular spot. Oscillations in the intensity occur in case of layer-by-layer growth and the period of the oscillations corresponds to the formation of one monolayer. They result from the fact that the intensity of the specular spot of the clean substrate is maximum. When deposition starts, islands are formed on the surface resulting in an increase of the roughness and a corresponding decrease in intensity. After completion of one monolayer the surface is again smooth and the intensity increases. For \( \text{Fe}_3\text{O}_4 \) one monolayer corresponds to a quarter of the unit cell (see section 2.2) which is 0.21 nm. When the oscillation period is known, the thickness of the film can be calculated accurately from the deposition time.

### 3.2.3 Deposition of \( \text{Fe}_3\text{O}_4 \) thin films

The substrates (both cleaved and polished \( \text{MgO} \) and \( \text{MgAl}_2\text{O}_4 \)) have been annealed at a temperature of 650 °C (measured with a pyrometer) in an oxygen pressure of \( 10^{-6} \) mbar. Annealing was done during the night. This procedure results in clean, flat substrates for both the cleaved and the pol-
After annealing, the substrates were transported to the analysis chamber, where they were checked for purity with XPS and for crystalline quality with LEED. In the meantime, the iron in the Knudsen cell was heated up to temperatures between 1270 and 1300 °C such that the iron flux was 1.25 Å/min, which corresponds to $1.8 \cdot 10^{17}$ Fe particles m$^{-2}$ s$^{-1}$ [35]. The substrates were then transported to the evaporation chamber. During evaporation the cryopanel was filled with liquid nitrogen to maintain a low background pressure. Oxygen was let in the evaporation chamber at a background pressure of roughly $10^{-6}$ mbar and the baratron signal was 1V. At this signal, the buffer pressure is 10 mTorr and the flux of oxygen particles at the substrate $1.9 \cdot 10^{18}$ (m$^{-2}$s$^{-1}$). This flux of oxygen particles is

* The AFM images of the polished MgO substrates have been obtained by D.M. Borsa and J. Kerssemakers.
3.3 Ex-situ analysis: conversion electron Mössbauer spectroscopy (CEMS)

Figure 3.5: RHEED patterns of a) clean MgO (100) substrate and b) a 100 nm thick Fe$_3$O$_4$ film, which shows a surface reconstruction. Both patterns were recorded with the electron beam along the [100] direction and an electron energy of 15 keV.

Thus more than sufficient to oxidise all the Fe to Fe$_3$O$_4$. Iron was deposited at a substrate temperature of 250 °C. During deposition, RHEED intensity oscillations were recorded. The energy of the electrons was usually 15 keV (the maximum energy is 35 keV). From the RHEED oscillations, the thickness of the film was determined. After growth of the film, the composition was checked with XPS and the crystal structure with RHEED and LEED. RHEED images of the substrate and the epitaxial film are shown in Fig. 3.5a and b respectively. The lines are sharp and Kikuchi lines are visible, indicating a flat surface and a good crystalline quality. However, the RHEED pattern of the Fe$_3$O$_4$ film does not show the bulk terminated spinel pattern. All primitive reflections are visible, indicating a surface reconstruction. This reconstruction has been the subject of intensive study and we refer to the following references for more details: [35, 66, 67, 75, 76]. The lines are very sharp and the intensity of the background is low, from which we conclude that the structural quality of the films is very good. This is supported by the presence of the Kikuchi lines (that are still visible for very thick films) and the RHEED oscillations. The stoichiometry of the films was determined by Mössbauer spectroscopy, which is the subject of the following paragraph.

3.3 Ex-situ analysis: conversion electron Mössbauer spectroscopy (CEMS)

The stoichiometry of the Fe$_3$O$_4$ films was checked using Mössbauer spectroscopy [77]. With this technique, the sample is irradiated with γ-radiation from a $^{57}$Co nucleus. This radiation is absorbed by the $^{57}$Fe nuclei in the
sample. The nucleus is excited and when it falls back into the ground state it can either emit a photon or an electron. If the latter is detected the technique is called conversion electron Mössbauer spectroscopy (CEMS). The energy difference between the excited nuclear state and the ground state depends on the local electron density and on the presence of a local internal magnetic field.

A unit cell of Fe$_3$O$_4$ contains 8 Fe$^{3+}$ ions at the tetrahedral sites and 16 Fe$^{2.5+}$ ions on the octahedral sites (see §2.2). Because of this difference in electron density, the CEMS spectrum has two components, one from the Fe$^{3+}$ ions on the A sites and one from Fe$^{2.5+}$ ions on the B sites. The two components are both split into sextets originating from the hyperfine interaction between the nuclear magnetic dipole moment and the local internal magnetic field resulting from the electron spins (the magnetic coupling of the electron spins is ferrimagnetic).

The Fe$^{2+}$ ions at the B sites can be oxidised to Fe$^{3+}$, resulting in the formation of vacancies, located mainly on the octahedral sites [35]. Each vacancy can be viewed as a minus 2.5 charge. Consequently, 5 Fe$^{3+}$ ions will be localised around the vacancy [78, 35, 79]. These Fe$^{3+}$ ions will then no longer participate in the conduction process and instead of contributing to the Fe$^{2.5+}$ component, they will contribute to the Fe$^{3+}$ component. This changes the stoichiometry to Fe$_{3-\delta}$O$_4$, which can be written as [78, 79]:

$$\text{Fe}_4^{3+} \text{Fe}_2^{3+} \text{Fe}_y^{2.5+} = \text{Fe}_3^{3+} \text{Fe}_x^{2.5+} \text{O}_4$$

from which we obtain

$$1 + x + y = 3 - \delta.$$ 

We then obtain for $\beta$:

$$\frac{\text{Fe}^{2.5+}}{\text{Fe}^{3+}} = \frac{2 - 6\delta}{1 + 5\delta}$$

(3.1)

The average orientation of the magnetic moments can also be obtained from the CEMS spectra. For the thin layers considered her, the intensities of the six lines are related as $3 : x : 1 : 1 : x : 3$ and the value of $x$ depends on the orientation of the magnetic field with respect to the incoming $\gamma$-rays ($\theta$): $x = 4\sin^2\theta(1 + \cos^2\theta)$. When the magnetisation is in the film plane, $\theta$ equals 90° and $x$ is zero. For perpendicular magnetisation ($\theta = 0$) we obtain $x = 4$.

All CEMS experiments have been performed in an acetone filled gas detector operating at room temperature in zero field. In order to make an energy scan of the nuclear level differences, the source was moving with respect to the sample, which remained fixed within the detector. The velocity scale was calibrated using an $\alpha$-Fe foil.

The films were near stoichiometric, with very low values for $\delta$ ($\delta \approx 0.002$). The value for $x$ was about 2, such that the intensity ratio was $3 : 2 : 1 : 1 : 2 : 3$. This corresponds either to a random magnetisation or to an angle of 54.7°. This means that the magnetisation was not completely in the plane
of the film as would be expected from the shape anisotropy. This is further discussed in chapter 8. For very thin films, below 5 nm, the spectra become superparamagnetic and the stoichiometry and magnetisation direction could not be determined (see also chapter 8).

3.4 Transmission electron microscopy (TEM)

With TEM one can obtain diffraction patterns and images of the sample, revealing microstructural defects such as dislocations, grain-, twin- and anti-phase boundaries. In order for the electrons to pass through the specimen, it has to be electron transparent. Therefore, the specimens or the regions to be analysed have to be sufficiently thin, which is typically of the order of hundreds of nanometers. The thickness at which a specimen is still electron transparent depends on the energy of the incident electrons and the density of the specimen.

The advantage of an electron microscope is that it has a much higher resolution than a light microscope. This is because the electrons have a high energy (typically between 100 and 300 keV) and a wavelength of about 4 pm which is much smaller than the wavelength of visible light (around 500 nm). Furthermore, electrons have a much stronger interaction with matter than either visible light or X-rays. More details about TEM can be found in references [80] and [81].

In the following, we will first describe the microscope itself. Next, diffraction and imaging will be explained. In the last paragraph, specimen preparation for Fe$_3$O$_4$ thin films will be discussed.

3.4.1 The electron microscope

The basic components of a TEM are a vacuum system, a high voltage source and a column that consists of an electron gun, a condenser lens and apertures, a specimen holder, an objective lens system and objective aperture, intermediate and projector lens systems, and an image recording facility. The TEM described in this section is a JEOL 2000FX microscope.

The vacuum is obtained by a combination of rotary, diffusion and ion sputtering pumps to maintain the column at a vacuum below $10^{-6}$ mbar.

The electron gun is a tungsten (W) hairpin filament. The electrons are accelerated by the high voltage source to an energy of 200 keV. The condenser lens system gathers and focusses the accelerated electrons from the gun and provides control over the brightness of the image.

After focussing, the electrons pass through the specimen which is held in a holder that enables the specimen to be tilted about two axes such that specific diffraction conditions can be obtained. The electrons then pass through
the objective lens, which is the key lens that determines the ultimate resolution of the instrument. Note that all lenses are electro-magnetic and are subject to aberrations.

When the electrons pass through the specimen, they can either be diffracted or scattered in the forward direction. An objective aperture is used to select those beams, thus selecting which electrons are used to make up the image (see §3.4.3).

Further magnification occurs in the intermediate and projector lens systems. The intermediate lens also determines whether a diffraction pattern or an image is formed, this will be explained in §3.4.2 and in §3.4.3. Finally, a selected area aperture can be used to select electrons from a certain region such that the diffraction pattern can be related to a specific area.

In order to keep the magnification constant, the instrument was used at similar conditions for all experiments. The accelerating voltage was in all cases 200 keV and the specimen height in the objective lens was kept constant at the eucentric height (eucentric for goniometer tilts). The current in the objective lens was kept constant.

### 3.4.2 Diffraction patterns

The electron beams that pass through the specimen are diffracted by the specimen. The diffracted beams then pass through the objective lens. Parallel beams are focussed in the back focal plane, producing the diffraction pattern, as shown in Fig. 3.6a.

The back focal plane of the objective lens is then the object plane of the intermediate lens, which further magnifies the diffraction pattern [81]. This process is repeated in the last step, where the back focal plane of the intermediate lens becomes the object plane of the projector lens.

### 3.4.3 Imaging

An image can be produced when the image plane of the objective plane becomes the object plane of the intermediate lens, as shown in Fig. 3.6b. Images can be obtained in several ways. Two frequently used modes are with the direct beam (bright field imaging) or with one of the diffracted beams (dark field imaging), see Fig. 3.7 a, b and c. The direct beam consists of electrons that have been scattered in the forward direction. When this beam is used to image the specimen, defects in the stacking of these planes (due to a dislocation or a boundary) will scatter this beam, and the defects will be visible as dark features. Also, precipitates are visible as dark features.

The diffracted beams have been scattered by reflecting planes. Defects in the stacking of these planes can reduce the scattered intensity, thus becoming visible. When a diffracted beam specific to a precipitate is used in dark
Figure 3.6: Schematic drawing of the operation of an electron microscope. Either a diffraction pattern (figure a) or an image (figure b) can be viewed. The electrons from the source are focussed in the condenser lens to produce either a parallel or a convergent beam. The specimen is located close to the objective lens. Parallel rays will be focused in the back focal plane, giving rise to a diffraction pattern. A magnified image of the specimen will be produced in the image plane. The intermediate and projector lenses further magnify the image or diffraction pattern. To do so, the intermediate lens is either focussed on the image plane of the objective lens or on the back focal plane of the objective lens.
Figure 3.7: Ray diagram showing the two imaging modes bright field (a) and dark field (b) and (c). For bright field imaging an aperture is placed such that only the direct beam is used to form the image. For dark field imaging one of the diffracted beams is selected. The specimen can also be tilted such that the diffracted beam is on the optic axis. This is called centred dark field imaging, as in figure (c). The advantage over configuration (b) is that aberrations are minimal.
field imaging, the precipitate will appear as a bright feature. Images reveal the variation in intensity as the beam has passed through the specimen. Defects are only visible if the beam used for imaging is affected by the defect [82]. In case of dark-field imaging, a two beam condition is often achieved. In this condition, the direct beam and one diffracted beam contribute to the formation of the image. This means that only one set of crystal planes is at (or close to) the Bragg condition. A crystal defect can displace atoms from their original lattice sites by a shift vector \( \mathbf{R} \). This shift vector could for instance be the Burgers vector of a dislocation or the shift vector of an anti-phase boundary. The diffracted beam \( \mathbf{g} \) from a plane is expressed as \((hkl)\) and is perpendicular to the \((hkl)\) plane. When these planes, with their orientation perpendicular to \( \mathbf{g} \), are not displaced the defect will not be visible. A defect with shift vector \( \mathbf{R} \) is thus not visible when:

\[
2\pi \mathbf{R} \cdot \mathbf{g} = 0, 2n\pi \tag{3.2}
\]

The shift vectors of the possible APB in \( \text{Fe}_3\text{O}_4 \) are \( \frac{1}{4}(110) \) or \( \frac{1}{2}[100] \). Dark field images have been obtained with the spinel \( (220) \) type reflection. Inserting this for \( \mathbf{g} \) and the APB shift vectors for \( \mathbf{R} \) in Eqn. 3.2, we obtain that not all APB shifts are visible when using the \( (220) \) reflection. In this case, only the APBs with an out of plane shift component are visible, i.e. the \( \frac{1}{4}[011], \frac{1}{4}[01\overline{1}], \frac{1}{4}[101], \frac{1}{4}[10\overline{1}] \) shifts.

### 3.4.4 Specimen preparation

The \( \text{Fe}_3\text{O}_4 \) thin films are grown on cleaved or polished MgO substrates. The substrates have a thickness between 0.5 and 1 mm and are therefore not electron transparent. In order to make suitable TEM specimens the substrate has to be thinned down or the films have to be removed from the substrate. For the \( \text{Fe}_3\text{O}_4/\text{MgO} \) system, the \( \text{Fe}_3\text{O}_4 \) can be chemically removed from the MgO substrate [45]. The sample is placed in a 4 wt % ammonium sulfate \( ((\text{NH}_4)_2\text{SO}_4) \) solution at 70 °C. After several hours, the film floats off the substrate and can be picked up on a copper grid. It is rinsed in a distilled water/alcohol solution and then dried.

### 3.5 Electrical conduction and magneto-resistance measurements

Electrical conduction and magneto-resistance have been measured in a commercial Physical Property measurement system (PPMS) by Quantum Design. The PPMS consists of a liquid helium cooled cryostat which is pumped by a rotary pump (pressure \( \sim 1 \) mbar) in which the sample can be placed and the temperature can be varied between 1 and 340 K. The PPMS is equipped
with a superconducting magnet which can reach a maximum magnetic field of 7 Tesla. The orientation of the sample and the magnetic field can be varied, such that the field can have any orientation between parallel and perpendicular to the sample surface. This is achieved by rotating the sample on a special holder, the horizontal rotator.

After growing the Fe$_3$O$_4$ samples in the MBE system, the samples were taken out and four contacts were made on the sample by depositing 20 nm of Ti and 40 nm of Au in an electron gun evaporation system (by Varian). Both resistance and magneto-resistance measurements have been performed. Resistance measurements were done as a function of temperature in zero field. Magneto-resistance measurements have been performed at a fixed temperature by increasing the field to 5 Tesla, then back to -5 Tesla and then to zero field. All measurements have been performed using a four point geometry in the constant voltage mode, where the voltage is applied and the current is measured (along the [100] direction). The voltage was applied in 10 steps and in all cases linear I/V curves have been obtained, from which the resistance was calculated.