Magnetic nanostructures: an experimental study of structural, magnetic and transport properties

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Magnetic Nanostructures

an experimental study of structural, magnetic and transport properties

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1. General introduction

This chapter gives a brief general introduction to the main research topics discussed in this thesis. The first section describes the research field of magnetic nanostructures and some possible applications. In the second and third section interlayer exchange coupling, giant and tunneling magnetoresistance are briefly explained.

1.1 Magnetic nanostructures

The name “magnetic nanostructures” is used in this thesis to summarize all the magnetic structures of which one, two, or three dimensions are reduced to a nanometer length scale, such as layers, wires, and dots. It was already recognized in the 1950s from theoretical considerations that reduced dimensions and the presence of interfaces should alter the magnetic properties of these structures, such as magnetic anisotropy and domain structure, for example, which could be useful for applications. However, at that time it was not possible to produce high quality nanostructures yet because of lack of technology, especially high vacuum deposition systems, and therefore successful verification of most of these predictions was far out of reach.

It was not until the first part of the 1980s that deposition techniques had improved, under the influence of the strong expansion of the semiconductor research and industry, to an extent that controlled deposition of ultrathin magnetic layers of high structural quality became possible. This opened a whole new field of research dedicated to the physics of magnetic nanostructures. The discovery in 1985 of an easy axis of magnetization perpendicular to the plane in thin Co / Pt multilayers [1], caused by a large interface anisotropy, may be considered as a first major breakthrough. More exciting discoveries were soon to follow. In 1986 Grünberg et al. [2] observed that two Fe layers separated by a thin Cr layer showed spontaneous antiparallel alignment of their magnetic moments, so-called antiferromagnetic interlayer exchange coupling. Directly after this discovery of the interlayer exchange coupling it was shown that a large change in resistance can occur when the antiparallel alignment is changed to parallel with an externally applied field [3, 4]: the Giant MagnetoResistance (GMR) effect. The most recent major advance is probably the successful fabrication of large Tunneling MagnetoResistance (TMR) structures in 1995 by Moodera et al. [5]. TMR is observed for a current flowing from one ferromagnetic layer across an insulating barrier to another ferromagnetic layer in a so-called tunnel junction.

Magnetic nanostructures have a number of potential applications, of which some are being commercialized already. Applications can be found in, for example, recording media, magnetoresistive sensors, read heads, and magnetic random access memory. Thin films with an orientation of the domains perpendicular to the film plane can be used as magnetic recording medium. The information density can be increased substantially, because a perpendicular orientation of the magnetization allows for smaller domain and bit sizes, due to more favorable magnetostatic interactions. Furthermore, the Kerr rotation (see section 2.2.3) of the polarization of light that is
reflected from the medium is larger for a perpendicular orientation of the magnetization, compared to in-plane magnetization. This can be used in high density magneto-optical recording, in which the magnetic information is read with a polarized laser.

Magnetoresistive sensors can be used to sense the position or speed of a ferrous body which is magnetized by a permanent magnet or the earth’s magnetic field. Important applications of magnetoresistive sensors can be found in automotive industry, in which magnetic sensing becomes a crucial function in, for example, cam- and crankshaft position sensing used for ignition timing and engine misfiring detection, in brushless electrical motors (used in fuel pumps, windshield wipers, etc.), and in wheel speed sensing (used for anti-lock breaking systems). Some important advantages of magnetoresistive sensors are their high sensitivity, their resistivity against contamination, in contrast to optical sensors, and the fact that the sensor can also determine the position at rest, in contrast to inductive sensors. Magnetoresistive sensors can also be used to sense fields from a current generated by a coil on a chip.

An other important class of applications of magnetoresistive materials are magnetic read heads for hard disk or tape recording. Because the output of GMR and TMR materials is larger than of traditionally used inductive or anistropic magnetoresistance materials, it will be possible to read out smaller bits, necessary to fulfil the demand for more storage capacity. Todays highest areal density hard disks use a spin-valve GMR sensor.

![Nanostructures](image)

**Fig. 1.1:** Cross section views of the nanostructures investigated in this thesis. (a) Layered structures of nonmagnetic (NM) and magnetic (M) layers. (b) Magnetic wires grown by electrodeposition in the pores of anodic alumina. (c) Granular films of magnetic clusters (M) separated by a nonmagnetic insulating matrix (I).

A new class of applications still in development are memory chips based on GMR or TMR materials, so-called Magnetic Random Access Memory (MRAM). The most promising design consists of an array of magnetic tunnel junctions, in which each individual tunnel junction is one bit which can be switched between high (antiparallel magnetizations) and low (parallel magnetizations), representing “0” and “1” (or vice versa). The advantage over classical semiconductor RAM is that MRAM is fast with low-power consumption and is non-volatile: the state of the memory is maintained when the power is removed (important for example in laptop applications).
1.2. Interlayer exchange coupling

This thesis

In chapter 3 to 10 of this thesis a number of studies is presented on several magnetic nanostructures, divided into magnetic layered structures, wires and clusters, as illustrated in Fig. 1.1. The aim of the research is not directly focused on the potential applications of these systems, although sometimes closely related, but rather on the understanding of the physics involved. Because the subjects of the chapters cover a rather broad class of systems and physical phenomena, each chapter is introduced and motivated separately. Nevertheless, the majority of the research can be categorized in two main research themes: interlayer exchange coupling and magnetoresistance, which will be briefly introduced in the next two sections.

In this thesis we will focus strongly on the relation between the physical effects and the structural properties of the systems studied, for the study of which a rather large number of experimental techniques have been employed. These are separately introduced in chapter 2.

1.2 Interlayer exchange coupling

In 1986 it was observed that two magnetic layers separated by a nonmagnetic spacer layer could display a spontaneous antiparallel alignment of the magnetizations at zero field (see Fig. 1.2). The discovery of this so-called antiferromagnetic interlayer exchange coupling, first for the rare-earth transition metal multilayers Dy / Y [6] and Gd / Y [7], and the 3d transition metal layers Fe / Cr [2], was considered as a major breakthrough in magnetic thin film research, because until then only ferromagnetic coupling was observed [8, 9], despite of much effort. The problem to observe antiferromagnetic coupling is the spacer layer, which has to be only 1 - 20 monolayers thick and free of direct ferromagnetic bridges (pinholes). This was a major technological challenge, met in the second half of the eighties, when deposition techniques, like sputtering and molecular beam epitaxy, had evolved and improved to an extent that it made possible the production these high quality layers. Soon after its discovery it was shown that the coupling oscillates between ferromagnetic and antiferromagnetic as function of the spacer layer thickness $t$ and it strength decays as $1/t^2$ [10]. Furthermore, almost any nonmagnetic 3d, 4d, and 5d transition metal spacer layer mediates interlayer coupling [11].

A common way to investigate interlayer exchange coupling is by analyzing the magnetization hysteresis curve of the stack of layers. As an example, in Fig. 1.2 schematically a magnetization loop is shown of an antiferromagnetically coupled magnetic/nonmagnetic/magnetic trilayer (for example Fe / Cr / Fe). At zero field (a) the macroscopic magnetizations of the two magnetic layers are aligned antiparallel due to the antiferromagnetic coupling. When an external positive (b) or negative (c) field is applied (in the plane of the layers), the antiferromagnetic interaction can be overcome and the two magnetic moments align both gradually towards the direction of the applied field, as shown in Fig 1.2. We note that this represents the most simple case, in which the anisotropy of the magnetic layers is small compared to the interlayer coupling. When anisotropy is important, jumps (flips) of the magnetic moments are observed towards saturation, rather than gradual changes. The saturation field (or flip field) is a measure for the coupling strength, usually described phenomenologically by the energy expression

$$E = -J_1 \cos \theta,$$

with $\theta$ the angle between the moments of the interacting layers and $J_1$ the bilinear coupling
strength, positive for ferromagnetic coupling and negative for antiferromagnetic coupling. Higher order terms like biquadratic coupling, varying with $\cos^2 \theta$ and favoring a $90^\circ$ alignment of the magnetic moments, are also observed (see for example chapter 4).

When the interlayer coupling is ferromagnetic, its strength cannot be deduced from the magnetization curve in this way, because both magnetic moments will always be aligned along the field direction. In that case a more complicated spin-engineered multilayer structure is used, in which one of the magnetic layers is exchange biased or antiferromagnetically coupled to a third magnetic layer [12, 13].

The origin of the interlayer coupling can be found in the reflection and transmission of the electron wavefunctions at the potential steps at the interfaces and outer boundaries of the layers. These potential steps induce oscillations in the electron density, in analogy with the well-known RKKY interaction [14–16]. Because spin-up and spin-down bands in ferromagnets are shifted with respect to each other, the potential steps will in general be different for spin-up and spin-down electrons. As a result also an oscillating spin density is induced in the spacer layer. The magnetic layers will tend to align along the induced spin density and hence align parallel or antiparallel to each other as function of the spacer layer thickness. A complete electron-optics theory was developed by Bruno [17], taking into account the complete potential landscape of the stack of layers. It turns out that almost all features of the oscillating interlayer coupling can be understood in this way, such as the oscillation period(s), the phase, the spacer thickness dependence, and the crystal orientation dependence. Furthermore, not only oscillations can be observed as function of the spacer layer thickness, but also as function of the magnetic [18] and even the cap layer.

![Schematic plot of the magnetization curve of an antiferromagnetically coupled magnetic/nonmagnetic/magnetic trilayer with the field applied in the plane of the layers. (a) At zero field the magnetic moments are aligned antiparallel. When (b) a positive or (c) a negative field is applied the antiferromagnetic interaction will be overcome and both magnetic moments will align along the field direction.](image-url)
thickness [19]. A complete experimental and theoretical overview of interlayer exchange coupling can be found in Ref. [20].

This thesis: chapter 3, 4, and 5

Oscillatory magnetic interlayer coupling in metallic thin film structures has been studied extensively in the last years and can be understood quite well within the Bruno electron optics model [20]. However, not only oscillatory behavior is found. For example, monotonically decreasing ferromagnetic coupling across Pt and Pd interlayers has been found as well [21]. For Fe / Cr multilayers the coupling does not oscillate around zero for thin spacers, but around an antiferromagnetic bias. The origin of this bias, however, is still unclear [22]. Recently a strong antiferromagnetic coupling was found for Fe / Si based layers, decreasing exponentially with spacer layer thickness [23, 24]. It was argued that in the spacer layer iron-silicide with the CsCl structure is formed, which displays a peak in the density of states near the Fermi-level, mediating an exponentially decaying interlayer coupling [25].

The structure and interlayer coupling of antiferromagnetically coupled Fe / Si based layers are studied in chapter 3. It is directly shown with Mössbauer spectroscopy that in the spacer layer iron-silicide with the CsCl structure is formed, supporting the proposed explanations for the antiferromagnetic coupling. In chapter 4 the temperature and thickness dependence of the interlayer coupling in Fe / Si based layers is evaluated. It is shown that the strong biquadratic coupling observed in Fe / Si is caused by so-called “loose spins” in the spacer layer.

When the dimensions of the nanostructures are reduced, magnetostatic interactions between, for example, wires or dots may become very important and dominate the magnetization behavior. In this respect, chapter 5 discusses the magnetization behavior of arrays of Co nanowires grown by electrodeposition in the pores of anodic alumina. It is shown that the wires are magnetically coupled via direct magnetostatic dipole-dipole interactions, which can be directly measured with nuclear magnetic resonance. The magnetization direction is determined by a competition of demagnetizing fields and dipole-dipole fields and can be tuned parallel or perpendicular to the wires by changing the length of the wires.

1.3 Magnetoresistance

Giant magnetoresistance

Soon after the discovery of the interlayer exchange coupling in Fe / Cr, huge magnetoresistances were found in this system by Baibich et al. [3] and Binasch et al. [4]. Resistance changes up to 50 % were observed when the relative orientation of the antiferromagnetically coupled metallic layers in this system was changed from antiparallel to parallel by applying a magnetic field. Today's record values amount to 220 % at 1.5 K for Fe / Cr [26]. This change in resistance is much larger than can be expected for “normal” magnetoresistance, caused by Lorentz forces, or for the anisotropic magnetoresistance effect, caused by spin-orbit interactions. Therefore, this effect became known as Giant MagnetoResistance (GMR). Further research showed that GMR is not restricted to Fe / Cr, but appears in many combinations of transition metal elements [10]. Moreover, the effect is not only observed in antiferromagnetically coupled layers, but also in systems where an antiparallel alignment is achieved by other means, such as exchange biasing of one magnetic
layer to an antiferromagnet [12]. Giant magnetoresistance is not limited to layered systems alone. Also magnetic clusters in a nonmagnetic matrix or combinations of layers and clusters will display a GMR effect.

![Diagram of current-in-plane GMR effect](image)

**Fig. 1.3:** Schematic drawing of the current-in-plane GMR effect in two magnetic layers separated by a nonmagnetic spacer layer with (a) parallel and (b) antiparallel magnetizations. The electrical transport in the layers can be divided in two spin-channels, illustrated as two electrons with different spin direction moving from the left to the right in the layers. Electrons with their spin opposite to the local magnetization direction experience more resistance than electrons with their spin parallel to the magnetization. In case of parallel magnetizations one current channel acts as a shunting current.

The origin of the effect lies in the spin-dependent transmission of conduction electrons between the magnetic layers through the nonmagnetic spacer, which depends on the relative orientation of the moments of the magnetic layers. This is depicted schematically in Fig. 1.3 for two magnetic layers separated by a nonmagnetic spacer. Such a trilayer is often referred to as a spin-valve. In the so-called two-current model the electrical current in the stack of layers is divided into two currents resulting from spin-up and spin-down electrons. These two types of electrons have different scattering probabilities at the interfaces and in the bulk of the layers, due to a spin-dependent potential landscape and differences in the density of states at the Fermi-level. In general an electron will have a higher scattering probability when its spin direction is opposite to the local magnetization direction. When both magnetic layers have parallel moments, see Fig. 1.3.a, the spin-down electrons will have a higher scattering probability than the spin-up electrons. This spin-up channel acts as a shunting current, which lowers the resistiviy of the complete stack of layers considerably as compared to the situation when the moments are antiparallel, shown schematically in Fig. 1.3.b. In this case both the spin-up and spin-down electrons will have a high scattering probability in one magnetic layer and a low scattering probability in the other. The relative change in resistance, the GMR-ratio, is usually defined as

\[
\text{GMR-ratio} = \frac{R_{\text{AP}} - R_{\text{P}}}{R_{\text{P}}},
\]  

(1.2)
with $R_{AP}$ and $R_P$ the resistance of the stack of layers with antiparallel (AP) and parallel (P) state of the magnetizations, respectively.

**Tunneling magnetoresistance**

Tunneling magnetoresistance can be observed for a current which flows from one ferromagnetic layer across an insulating barrier to another ferromagnetic layer in a so-called tunnel junction. Like for the GMR effect, a considerable change in resistance is observed when the relative orientation of the two magnetic layers changes from antiparallel to parallel. The first reports of a Tunneling MagnetoResistance (TMR) effect already date from 1975 [27]. It took, however, until 1995 before it was possible to produce tunnel junctions with reproducible properties and high TMR-ratios [5]. This was due to the fact that it is very difficult to make a closed insulating barrier layer of only a few monolayers thick. Nowadays this insulating barrier layer is usually Al$_2$O$_3$, produced by oxidation of a metallic Al layer.

![Schematic drawing of a tunnel junction](image)

**Fig. 1.4:** (a) Schematic drawing of a tunnel junction in which electrons tunnel from one magnetic electrode, $M_1$, to an other, $M_2$, across an insulating barrier. (b) Density of states of both electrodes and resulting tunneling current $I_P$ and $I_{AP}$ for parallel and antiparallel magnetizations, respectively.

The origin of the TMR effect lies in the spin-dependent tunneling probability of electrons from one magnetic electrode to the other across the insulating barrier. This is schematically explained in Fig. 1.4. The tunneling probability of electrons depends on the electron density of states of spin-up and spin-down electrons ($N_1$ and $N_2$) for both electrodes ($M_1$ and $M_2$). Figure 1.4.b shows schematically the spin-up and spin-down bands in case of parallel and antiparallel magnetizations. The Fermi-levels of the bottom and top electrodes are slightly shifted due to the application of a small voltage $V$, which gives rise to a net tunneling current from $M_1$ to $M_2$. It is assumed here that
the spin of the electrons is conserved during tunneling (which is not always true; see chapter 8). In case of parallel magnetizations the total current is then given by

\[ I_P = N_1 N_1 + N_2 N_2, \] (1.3)

the product of the density of states of both electrodes added for both spin directions. In case of antiparallel magnetizations the role of spin-up and spin-down is reversed in one electrode, which leads to the following expression for the total current:

\[ I_{AP} = N_1 N_2 + N_2 N_1. \] (1.4)

It is immediately clear from Eq. 1.3 and 1.4 that when \( N_1 \neq N_2 \), which is generally the case for magnetic materials, the current in the parallel case will be higher than the current in the antiparallel case. The TMR-ratio is usually defined as

\[ \text{TMR-ratio} = \frac{I_P - I_{AP}}{I_{AP}}. \] (1.5)

In the extreme case of a half-metallic ferromagnet, for which \( N_1 = 0 \) and hence \( I_{AP} = 0 \), this can even lead to an infinite TMR effect. Tunneling magnetoresistance is not only found in layered systems, but also in granular (cermet) films in which electrons can tunnel from one magnetic cluster to another through an insulating matrix (see chapter 8).

\[ \text{This thesis: chapter 6, 7, 8, 9, and 10} \]

In chapter 6 and 7 of this thesis GMR properties of several metallic spin-valve systems are discussed. Chapter 6 addresses whether the principal source of spin-dependent scattering is located in the bulk of the magnetic layers or at the interfaces between magnetic and nonmagnetic layers. Therefore, a new interface selective structure is presented, composed of a spin-valve on top of which a thick nonmagnetic back layer is deposited, as a straightforward experimental tool to measure the GMR induced by ultrathin magnetic layers. The interface selectivity of spin-dependent scattering is evidenced by calculations and illustrated in both Co / Cu / Co and Ni_{50}Fe_{20} / Cu / Ni_{50}Fe_{20} spin-valves by an almost constant GMR-ratio as function of the magnetic layer thickness down to extremely thin layers. The structure of these ultrathin ferromagnetic Co layers is studied with nuclear magnetic resonance. A detailed analysis of these measurements will be presented, which shows that the extremely short length scale associated with the onset of the GMR for the thinnest layers is caused by the formation of Co clusters.

Chapter 7 addresses the importance of the outer boundaries in a trilayer GMR spin-valve structure. Usually electrons are scattered diffusively at these boundaries, limiting the maximal attainable GMR-ratio. Specularly reflecting boundaries, however, mimic an infinite superlattice with much higher GMR-ratios. The possibility of electron reflectivity is experimentally investigated for an insulating NiO layer that is used to exchange bias a metallic spin-valve. For this purpose Ni_{50}Fe_{20} / Cu / Ni_{50}Fe_{20} and Ni_{50}Fe_{16}Co_{18} / Cu / Co_{50}Fe_{10} spin-valves are grown and subsequently covered by insulating NiO or by metallic FeMn. In all cases the giant magnetoresistance of the NiO spin-valves is systematically larger. The increased giant magnetoresistance ratios, compared to the FeMn exchange biased spin-valves, can be qualitatively understood on the
1.3. Magnetoresistance

basis of a semi-classical calculation, in which partial specular reflectivity at the NiO interface is included.

In chapter 8 TMR properties of reactively sputtered FeHfO and FeHfSiO thin granular films are studied. Maximum magnetoresistance ratios at room temperature of 2.0 % and 3.2 % are observed for films with compositions Fe$_{17}$Hf$_{10}$O$_{43}$ and Fe$_{40}$Hf$_{6}$Si$_{6}$O$_{48}$, respectively. The magnetoresistance shows a decrease with temperature, which cannot be explained by spin-dependent tunneling only. It is proposed that spin-flip scattering in the amorphous FeHf(Si)O matrix causes this decrease as a function of temperature.

In chapter 9 a structural study is presented of Co / oxidized-Al / Ni$_{60}$Fe$_{20}$ thin films, presently receiving much attention for their tunneling magnetoresistive properties. $^{59}$Co nuclear magnetic resonance shows that the Co layers are not single crystalline but consist of a mixture of fcc and hcp Co. The oxidation of Al is the most crucial step in the fabrication of these layers. Our measurements of the spin-spin relaxation time show that Co becomes oxidized, when the Al spacer layer is exposed to oxygen too long. This formation of CoO leads to a decrease of the tunneling magnetoresistance. First results are presented of $^{27}$Al NMR measurements, showing two distinct lines for Al and AlO$_x$.

Magnetite (Fe$_3$O$_4$) is a half-metallic ferromagnet and therefore of technological importance for all-oxide tunnel junctions with possibly an infinite tunneling magnetoresistance. Recently, there were a number of studies addressing the magnetization behavior of thin films of Fe$_3$O$_4$ / MgO, but not all of these studies were in agreement with each other and some contradictory observations were reported. In chapter 10 we have investigated the magnetic behavior and structure of Fe$_3$O$_4$ / MgO multilayers with Mössbauer spectroscopy, magnetization measurements, and scanning tunneling microscopy. Here, it is shown that a detailed structural knowledge of the layers is indispensable in understanding the magnetization behavior of the films and the contradictory results reported in the literature.
2. Experimental techniques

For the fabrication of the layers, wires, and granular films studied in this thesis three techniques were used: magnetron sputtering, molecular beam epitaxy, and electrodeposition. These techniques will be explained briefly in the first sections of this chapter. In the sections thereafter several methods to characterize our nanostructures are described. Nuclear magnetic resonance and Mössbauer spectroscopy are treated in more detail than the other techniques, because they are less common in the field of magnetic nanostructures, although extremely valuable.

2.1 Sample preparation

2.1.1 Sputtering

During sputtering deposition a material is removed and ejected from a target material as a result of bombardment by energetic particles. The target material is allowed to condense on a substrate, forming the thin film. The bombarding particles are usually Ar ions to avoid chemical reactions at the target and the substrate.

The sputtered layers discussed in this thesis were grown at Philips Research Laboratories in Eindhoven by DC and RF magnetron sputtering. In magnetron sputtering the Ar plasma, generated by a large DC or RF voltage between the target material and a nearby metallic plate, is confined near the target by a static magnetic field. The background pressure in the sputtering apparatus used was of the order of $10^{-7}$ mbar and the Ar pressure during deposition was of the order of $10^{-3}$ mbar. Growth rates of typically 1 to 2 Å/s were achieved.

The main advantages of sputtering are that it is a fairly easy technique to produce large quantities of layers within a short time (important for industrial applications), and that it is possible to deposit almost any material or alloy. The quality of the sputtered layers in terms of roughness, grain size, and stoichiometry depends on a number of variables, such as deposition rate, Ar pressure, background pressure, deposition temperature, etc., which have to be optimized.

2.1.2 Molecular beam epitaxy

In a Molecular Beam Epitaxy (MBE) system a material evaporates thermally (Knudsen cell) or by means of a beam of electrons (e-gun) from a source and condenses on a substrate, forming the thin film. The MBE grown layers discussed in this thesis were deposited with a VG Semicron V80M at the Eindhoven University of Technology. This MBE apparatus is equipped with 3 e-gun evaporators for high vapor pressure materials such as Fe, Co, and Ni, and 4 large Knudsen cells (40cc) for lower vapor pressure materials such as Cu, Si and Au. Two small Knudsen cells (2cc) were specially designed to deposit $^{57}$Fe and $^{56}$Fe, expensive materials, only available in small
amounts. The thickness of the layers is controlled by calibrated quartz crystal monitors. During deposition the substrate can be heated and rotated. By removing a shutter at constant speed during growth, wedge shaped layers can be produced with typical slopes of 1 - 5 Å/mm. After deposition the layers can be transported in-situ to special chambers for LEED, XPS, AES, and STM analysis (see section 2.2.5).

Oxidic layers were grown with a UHV Balzers UMS 630 multichamber MBE system at Philips Research Laboratories. This system is equipped with 3 e-gun evaporators (Fe, Co, Ni) and 3 Knudsen cells. A small 2cc Knudsen cell is used for the deposition of $^{57}$Fe. Atomic fluxes are controlled by a cross-beam quadrupole mass-spectrometer system. Oxidation of the layers is achieved by supplying oxygen through a ring-shaped doser located close to the substrate. In-situ Reflection High Energy Electron Diffraction (RHEED) can be used to monitor the growth during deposition.

### 2.1.3 Electrodeposition

In contrast to sputtering and MBE, electrodeposition is a low cost and simple technique to fabricate magnetic multilayers and nanowires. Electrodeposition, also called electroplating, is already in use for a long time for various applications, such as protective coatings and permalloy thin-film recording heads [28].

![Electrodeposition cell](image)

**Fig. 2.1: Schematic cross section view of the electrodeposition cell used for fabrication of the Co wires. The cell has a diameter and a height of about 4.5 cm.**

The deposition of metals takes place at ambient temperatures and pressures in an electrochemical cell containing the metal ions in an aqueous solution, as shown in Fig. 2.1. By applying a voltage between the substrate (work electrode/cathode) and the counter electrode (anode) the metal ions are reduced to metal and in this way deposited on the substrate. For the electrodeposition of Co ions as reported in this thesis the chemical reaction reads

\[
Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}. \tag{2.1}
\]
The deposition potential is carefully monitored by the reference electrode (Hg/Hg$_2$Cl$_2$) and layer thicknesses are determined by real-time integration of the total charge deposited.

If more than one type of metal ions is present in the solution, it is possible to deposit alloys and multilayers by choosing appropriate deposition potentials and metal ion concentrations. It was first demonstrated by Alper et al. [29] in 1993 that magnetic multilayers exhibiting giant magnetoresistance effects can be produced not only by sputtering and MBE but also by electrodeposition. A major advantage of electroplating is that deposition is not restricted to layers but by choosing appropriate templates it is, for example, possible to produce wires, as first demonstrated by Whitney et al. [30]. A review about electrodeposition of magnetoresistive films and wires can be found in Ref. [31]. In this thesis electrodeposition is used to fabricate large arrays of Co wires in the pores of anodic alumina (see chapter 5).

2.2 Measurement techniques

2.2.1 Nuclear magnetic resonance

Basic principles

When a magnetic field is applied to a nucleus which possesses a spin $I$, the ground state is split up into $2I + 1$ levels by the Zeeman interaction. The energy difference between adjacent energy levels is $\gamma \hbar B_0$, with $\gamma$ the gyromagnetic ratio of the nucleus and $B_0$ the total magnetic field at the nucleus site. We neglect electric quadrupole interaction, because for the Co layers and wires discussed in this thesis it is too weak to yield any visible effects. In a NMR experiment dipolar transitions are induced between consecutive energy levels by applying a radio-frequency field (RF field) $B_1$ perpendicular to $B_0$. Experimentally, this RF field can be applied with a copper coil wrapped around the material. Resonance is only achieved when the frequency of the RF field matches the energy difference between the energy levels, which directly leads to the resonance condition [32]

$$\omega_L = \gamma B_0,$$

where $\omega_L$ is the Larmor precession frequency of the nuclear spin. This resonance condition can be experimentally fulfilled by recording a spectrum as function of frequency or field.

In practice, a large number of nuclei $N$ (per unit volume) is involved. The field $B_0$ gives rise to a Curie-law nuclear magnetization

$$M = N \frac{\gamma^2 \hbar^2 I(I + 1)}{3k_B T} B_0,$$

with $k_B$ the Boltzmann constant and $T$ the temperature. Because the resonance signals are measured inductively (see next section) the intensity reads

$$I = M \omega_L = N \frac{\gamma^2 \hbar^2 I(I + 1) \omega_L^2}{3k_B T},$$

which shows that the magnitude of the resonance signal is proportional to the number of nuclei under investigation and the square of the Larmor frequency, and inversely proportional to the temperature.
Pulsed NMR

Experimentally, the relaxation of the nuclear magnetization back to thermodynamic equilibrium $M_0$ along $B_0$ (assumed parallel to $z$) can usually be described by $dM_z/dt = -(M_z - M_0)/T_1$, with $T_1$ the longitudinal relaxation time or spin-lattice relaxation time. Furthermore, interaction between the nuclear spins causes the transverse components of $\vec{M}$ to decay in time according to $dM_x/dt = -M_x/T_2$ and $dM_y/dt = -M_y/T_2$, with $T_2$ the transverse relaxation time or spin-spin relaxation time. In 1946 Felix Bloch proposed a set of equations, describing the motion of an ensemble of spins in a magnetic field, by combining the above mentioned experimental observations with the precession of an ensemble of spins $d\vec{M}/dt = \gamma(\vec{M} \times \vec{B}_0)$ in a magnetic field $\vec{B}_0$, along $z$, yielding:

\[
\begin{align*}
\frac{d}{dt} M_x &= -\frac{M_x}{T_2} + \gamma(\vec{M} \times \vec{B}_0)_x, \\
\frac{d}{dt} M_y &= -\frac{M_y}{T_2} + \gamma(\vec{M} \times \vec{B}_0)_y, \\
\frac{d}{dt} M_z &= -\frac{M_z - M_0}{T_1}.
\end{align*}
\]

These Bloch equations, which proved to give a correct description of the motion of the nuclear magnetization both in a static field and a RF field, led to the development of pulsed RF field techniques in NMR, of which some of the basic principles will be outlined below.

![Fig. 2.2: Schematic drawing of the motion of the nuclear magnetization in the rotating frame as a consequence of a 90° and 180° pulse series; the Hahn sequence.](image-url)
When a RF field $2\vec{B}_1 \cos \omega_L t$ is applied perpendicular to $\vec{B}_0$, the Bloch equations yield

$$\frac{d}{dt}\vec{M} = \gamma \vec{M} \times (\vec{B}_0 + 2\vec{B}_1 \cos \omega_L t),$$

(2.6)

in which relaxation effects have been neglected for the moment. This equation describes a complicated motion of precession around $\vec{B}_0$ and $2\vec{B}_1 \cos \omega_L t$, which can be visualized in a coordinate frame which rotates at the Larmor frequency $\omega_L$ around the $z$-axis. In this rotating frame Eq. 2.6 changes to

$$\frac{d}{dt}\vec{M} = \vec{M} \times [(\gamma \vec{B}_0 - \vec{\omega}_L) + \gamma \vec{B}_1] = \vec{M} \times \gamma \vec{B}_1,$$

(2.7)

that is a precession around $\vec{B}_1$. In the derivation of Eq. 2.7, $2\vec{B}_1 \cos \omega_L t$ is split up in two components, one with double frequency $2\omega_L$, which fast precession can be neglected [32], and one with zero frequency. When the RF field is only applied for a short period of time, $\vec{M}$ will rotate only over a small angle $\alpha = \gamma \tau_p \vec{B}_1$, with $\tau_p$ the duration of the RF pulse. In the following it is shown that by applying a well-defined set of pulses the nuclear magnetization can be controlled and manipulated in such a way that it produces so-called echo signals.

In a standard Hahn sequence experiment, shown in Fig. 2.2, two RF pulses are applied, one that rotates the nuclear magnetization over an angle of $90^\circ$ in the rotating coordinate frame, followed

![Fig. 2.3: Schematic representation of the envelopes of the RF signals for (a) the Hahn sequence, (b) the CPMG sequence and (c) the presaturation sequence. For the presaturation sequence is it assumed that $t \gg 2\tau$ so that the influence of spin-spin relaxation can be neglected.](image-url)
after a short period of time $\tau$ by a second pulse that rotates the nuclear magnetization by 180°. Because of field inhomogeneities and the finite length of the pulses, not all the excited spins have exactly the same Larmor frequency. This means that in the rotating frame the individual spins start to dephase (Fig. 2.2.c), which experimentally can be observed as a free induction decay (FID). Subsequently, this dephasing is reversed by the 180° pulse, which makes the individual spins rephase again after a period $\tau$. In the laboratory frame $\vec{M}$ rotates at a frequency $\omega_L$, and hence this rephasing can be observed as an induction signal in the RF coil, the so-called spin-echo. Figure 2.3.a shows a schematic representation of the envelopes of the RF signals during a Hahn sequence.

Two other pulse sequences are used in this thesis to measure spin-spin and spin-lattice relaxation times. These special pulse sequences are schematically depicted in Fig. 2.3.b and 2.3.c. The first pulse sequence is the Carr-Purcell-Meiboom-Gill (CPMG) sequence. It starts with a regular Hahn sequence, after which a series of 180° RF pulses are applied (32 in our experiments). Each 180° pulse generates a new spin-echo signal with progressively decreasing intensity, because the rephasing process is disturbed by spin-spin interactions. From the intensity of the echo signals ($\propto \exp(-t/T_2)$) the spin-spin relaxation time can be calculated.

The second alternative pulse sequence is the presaturation sequence. This sequence starts with a large number (about 40) of RF pulses of more or less random duration, the comb, which randomly distributes the nuclear magnetization. Next, the nuclear magnetization starts to increase again with a characteristic time $T_1$ towards equilibrium in $z$ direction, because of the static field $\vec{B}_0$ along $z$. After a certain delay time $t$ a Hahn sequence is applied which induces an echo signal. The intensity of this echo depends on the delay time $t$ and is proportional to $1 - \exp(-t/T_1)$. This procedure is repeated for different delay times, from which the spin-lattice relaxation time can be determined.

**NMR in magnetically ordered materials**

For paramagnetic and diamagnetic materials the applied magnetic field largely determines the resonance frequency (see Eq. 2.2). Small line shifts occur because of a small polarization of the unpaired electron spins (Knight shift) or because of a small influence of the field on the orbital motion of the filled shells (chemical shift) [33, 34]. On the other hand, in magnetically ordered materials, such as Co and Fe, the spontaneous magnetization leads to large magnetic hyperfine interactions at the nucleus site. The total static field experienced by these nuclei can be expressed as

$$\vec{B}_{\text{tot}} = \vec{B}_{\text{appl}} + \vec{B}_{\text{dip}} + \vec{B}_{\text{hf}},$$

(2.8)

Here $\vec{B}_{\text{appl}}$ is the externally applied field, $\vec{B}_{\text{dip}}$ the dipolar field, and $\vec{B}_{\text{hf}}$ the hyperfine field. The dipolar field resulting from all the electronic moments in the sample can be classically expressed in a demagnetization field, arising from the shape of the sample, a Lorentz cavity field $\frac{4\pi}{3}\mu_0 M_s$, and the field arising from the moments inside the Lorentz cavity except for the moment of the nucleus under consideration. The hyperfine field can be written as

$$\vec{B}_{\text{hf}} = \vec{B}_{\text{fc}} + \vec{B}_{\text{hf dip}} + \vec{B}_{\text{orb}},$$

(2.9)

with $\vec{B}_{\text{fc}}$ the Fermi contact interaction field, $\vec{B}_{\text{hf dip}}$ the dipolar field from all the other nuclear spins, and $\vec{B}_{\text{orb}}$ resulting from orbital moments. The Fermi contact interaction is the largest contribution
to the hyperfine field for Co and Fe; it arises from the spin-polarization of mainly s-electrons within the nucleus volume.

The magnitude of $\vec{B}_{hf}$ depends on the magnetic moment of the atom itself and on the number and the magnetic moments of neighboring atoms. The influence of neighboring atoms is usually limited to atoms in the first neighboring shell, making NMR, besides Mössbauer spectroscopy (see next section), a technique which provides the most local magnetic information about atoms possible. Unfortunately, it is very difficult to calculate the actual magnitude of the hyperfine field; usually too high values are obtained [35–38]. Therefore, in a real experimental situation, identification of resonance lines is done via standards and reference materials. In general, the resonance field distribution of the materials under investigation in this thesis (Co and Fe) depends on the following main features.

![NMR spectrum of Cu(111) + 35 Å Co + 30 Å Cu at 1.5 K showing three well resolved resonance lines. The resonance peaks at 215 and 225 MHz result from Co in fcc and hcp stacking, respectively. The satellite peak at 167 MHz corresponds to Co atoms with 3 Cu nearest neighbors, indicating that the Co / Cu interfaces are almost perfect in this layer [39].](image)

In the first place, the hyperfine field depends on the local crystallographic structure, such as bcc, fcc, and hcp (see, for example, chapter 5, 6, and 9). Secondly, strain in the lattice leads to a shift of the hyperfine field distribution, which offers the possibility to measure the strain in a magnetic layer on a local scale. Replacement of an atom in the nearest neighboring shell leads to a discrete shift of the hyperfine field, which offers the possibility to investigate interface roughness.
and topology of buried interfaces in a multilayer on an atomic scale. Finally, the resonance field distribution does not only give structural information, but also provides information on stray fields (dipole fields, demagnetization fields), which can be very important for small nanostructures (see chapter 5).

As an example we show in Fig. 2.4 a NMR spectrum of 35 Å Co + 30 Å Cu grown on a Cu(111) single crystal. The spectrum consists of three well resolved resonance lines, corresponding to hcp Co (225 MHz), fcc Co (215 MHz) and the Co / Cu interfaces (167 MHz), respectively. The fcc resonance line is shifted with respect to the bulk values (217 MHz), which indicates that the Co is strained due to the lattice mismatch between Co and Cu. The satellite peak at 167 MHz corresponds to Co atoms with 3 Cu nearest neighbors indicating that the Co / Cu interfaces are almost perfect in this layer [39].

**Enhancement factor**

The RF field $B_{\text{eff}}$ experienced by the nuclei in ferromagnetic materials is substantially larger than the applied RF field $B_1$, because it is enhanced by oscillations of the hyperfine field. These oscillations are caused by oscillating electronic moments induced by the RF field (transmitting enhancement). The enhancement factor, defined as

$$\eta = \frac{B_{\text{eff}}}{B_1},$$

(2.10)

can be determined from the optimum rotation angle of the nuclear magnetization, i.e. the rotation angle that induces the maximum spin-echo signal in a Hahn sequence experiment. The rotation

![Fig. 2.5: Data points (open squares) and fit with a Gaussian (solid curve) of the spin-echo intensity as function of the RF field strength $B_1$, from which the optimum field strength and $\eta$ can be determined.](image)
angle of the nuclear spins with enhancement is

\[ \alpha = \gamma B_{\text{eff}} \tau_p = \gamma \eta B_1 \tau_p, \]  
(2.11)

with \( \tau_p \) the duration of the pulse. Pulse duration \( \tau_p \), gyromagnetic ratio \( \gamma \), and \( \alpha = \frac{1}{2} \pi \) are known parameters and \( \eta \) is now determined by repeating the Hahn sequence for different \( B_1 \) (typically in the range between \( 0.5 \times 10^{-3} \) and \( 25 \times 10^{-3} \) T), as shown in Fig. 2.5. A maximum in the spin-echo intensity occurs for the RF field strength where \( \alpha = \frac{1}{2} \pi \).

On its turn the observed spin-echo signal arises not only from the nuclear precession, but also from the oscillating electronic moment induced by the nuclear precession (receiving enhancement). Consequently, the intensity of the spin-echo signal is enhanced by the same factor \( \eta \) and reads

\[ I \propto \eta \omega_L^2 N/T, \]  
(2.12)

with \( N \) the number of nuclei that resonate at the Larmor frequency \( \omega_L \). The NMR spectrum has to be corrected for \( \omega_L^2 \) and a complicated frequency dependence of \( \eta \) to relate the signal intensity to the number of nuclei in resonance at a given temperature.

For completeness it should be noted that generally the influence of spin-spin relaxation and spin-lattice relaxation leads to a reduced echo intensity. However, pulse and delay times were chosen sufficiently short to neglect the influence of spin-spin relaxation. The time between two successive Hahn sequences was always chosen long enough to neglect the influence of spin-lattice relaxation.

The magnitude of the enhancement in zero field can range between 10 and 10 000 and is determined by the local electronic moment stiffness related to anisotropy fields, coercivity fields, exchange biasing fields, and interlayer coupling fields. In an externally applied field \( \eta \) reduces to the more simple expression [40]

\[ \eta = \frac{B_{\text{hf}}}{B_{\text{appl}} + B_{\text{ani}}} - 1, \]  
(2.13)

with \( B_{\text{appl}} \) the externally applied field. Here, \( B_{\text{ani}} \) is directly related to anisotropy, coercivity and exchange coupling fields.

The NMR spectrometer

All NMR spectra presented in this thesis are recorded with a home-built pulsed NMR spectrometer, shown schematically in Fig. 2.6. A synthesizer generates a continuous RF signal between 25 and 500 MHz, which is transformed by a gate unit to pulses of the desired length (of the order of 0.2 to 2 \( \mu \)s). The pulses are amplified to the desired RF field strength \( B_1 \) and directed via an electronic switch to the RF coil which is wrapped around the sample. The sample is placed in a cryostat in the bore of a superconducting magnet in which fields up to 6 T and temperatures down to 1.5 K can be reached. The electronic switch redirects the echo signal from the sample, which is detected by the same coil used to apply the RF field, via an amplifier to a mixer unit, where the signal is transformed to an intermediate frequency of 40 or 70 MHz. After amplification the echo signal is demodulated into a P (phase) and Q (quadrature) signal with 90° phase difference. The P and Q signal are recorded and Fourier transformed by a computer to determine the intensity of the echo signal.
Because of a characteristic impedance of 50 $\Omega$ of the equipment the RF coil is part of a fully tuned and matched LC-circuit with two variable capacitors, as shown in Fig. 2.6. At every frequency the computer controlled capacitors $C_1$ and $C_2$ are automatically adjusted to give the LC-circuit the correct impedance of 50 $\Omega$.

### 2.2.2 Mössbauer spectroscopy

#### Basic principles

The majority of decaying radioactive nuclei produce so-called daughter nuclei in an excited state. These excited daughter nuclei subsequently de-excite by emitting $\gamma$-ray photons. It was already recognized in the beginning of this century [41] that it should be possible to use these $\gamma$-rays to excite other nuclei of the same isotope; so-called resonant nuclear absorption of $\gamma$-rays. Because the $\gamma$-rays have an extremely well-defined energy, defined by the Heisenberg uncertainty principle ($\Delta E \approx 6.78 \times 10^{-9}$ eV for $^{57}$Fe), this would open the possibility to study the very weak hyperfine interactions between the nucleus and its surroundings, experimentally inaccessible in those days.

However, it was soon realized that because of energy and momentum conservation the nucleus experiences a recoil, which reduces the energy $E_\gamma$ of the emitted $\gamma$-ray by [42]

$$E_R = \frac{E_\gamma^2}{2Mc^2}, \quad (2.14)$$

with $M$ the mass of the nucleus and $c$ the velocity of light. In the same way, the energy necessary to excite a nucleus is $E_\gamma + E_R$. This recoil energy can be considerably larger than the natural line width, which makes resonant absorption impossible, as illustrated in Fig. 2.7. Moreover,
thermal motion of the nuclei broadens the line width of the $\gamma$-rays. At first glance this may seem favourable, because some overlap between emission and absorption is regained. However, the broadening is much too large to study the nuclear energy levels in any detail. It was Rudolf Mössbauer who discovered in 1958 that for some nuclear transitions the negative effects of recoil and thermal broadening are absent [43], which makes nuclear resonant absorption for these nuclei possible. The origin of this effect lies in the fact that the nuclei are not isolated in space but fixed in a crystal lattice, where the recoil energy can be comparable in magnitude to the lattice vibrational phonon energies. When the energy of the photon is low enough, there is a considerable probability (recoilless fraction) that the recoil energy cannot be transferred to an allowed phonon excitation and, consequently, the photon energy is not affected by recoil or thermal broadening.

![Diagram](image)

Fig. 2.7: Schematic illustration of (a) decay of an excited nucleus by emission of a $\gamma$-ray photon and (b) excitation by absorption. The energy of the emitted photon is $2E_R$ smaller than that required for excitation, due to recoil of the nucleus, which makes resonant emission and absorption impossible.

There are over 83 different isotopes for which this Mössbauer effect has been observed, but only a few of these are useful and practical in terms of radioactive decay time and recoilless fraction [42]. For this thesis the 14.41 keV Mössbauer transition in $^{57}$Fe is used, the daughter nucleus of $^{57}$Co with a radioactive decay time of 270 days.

**CEMS spectrometer**

Figure 2.8 schematically shows the experimental setup of the home-built Mössbauer spectrometer used in this thesis. The absorber, the material under investigation, is irradiated with 14.4 keV $\gamma$-ray photons from a 50 mCi $^{57}$Co source in a Rh host. Because the absorbing nuclei may have their energy degeneracy lifted by hyperfine interactions, the energy of the $\gamma$-rays emitted by the source
has to be matched to the energy levels of the absorbing nuclei. This is done by moving the source periodically at a certain velocity, inducing a Doppler energy shift of the $\gamma$-rays. The splitting of the nuclear energy levels usually lies within the range of -16 to 16 mm/s ($1 \text{ mm/s} \approx 4.808 \times 10^{-8} \text{ eV}$). A Mössbauer spectrum represents the number of $\gamma$-rays absorbed as function of the velocity of the source.

![Schematic drawing of the CEMS setup. A $^{57}$CoRh source, which is Doppler modulated, irradiates the material under investigation, the absorber. The conversion electrons emitted by the absorber are detected by a He(90%)/CH$_4$(10%) gas-flow proportional counter.](image)

One way to measure the number of $\gamma$-ray photons is by placing a photon detector behind the absorber and count the transmitted photons, so-called Transmission Mössbauer Spectroscopy (TMS). However, when only a small amount of material is available or when the absorber is placed on a thick substrate, which prevents transmission of the $\gamma$-rays, a second method, called Conversion Electron Mössbauer Spectroscopy (CEMS), is preferred. When a nucleus in the absorber, that was excited resonantly, decays to its ground state it may do so by transferring its energy to one of the inner electrons. The most likely process, with about 81% probability, is the emission of a K-shell conversion electron with an energy of 7.3 keV. These conversion electrons can be counted with a simple gas-flow detector, as drawn schematically in Fig. 2.8. Resonant absorption of $\gamma$-rays will be detected as peaks rather than absorption dips.

**Study of hyperfine interactions with Mössbauer spectroscopy**

Because the emitted $\gamma$-ray photons have an extremely small energy linewidth, one of the major applications of Mössbauer spectroscopy is the study of the very small interactions between the nucleus and its surroundings, the hyperfine interactions. These hyperfine interactions provide us with local structural and magnetic information about the thin films and multilayers under investigation.
Three principal hyperfine interactions have to be considered, as shown in Fig. 2.9. First, Coulomb interactions between electronic charges and the nucleus, which are different in the ground state and the excited state, lead to a shift of the resonance line away from zero velocity. This shift is called the isomer shift and is usually denoted by \( \delta \). Secondly, an electric quadrupole interaction between the nuclear quadrupolar moment and the local electric field gradient tensor at the nucleus site, partially lifts the degeneracy of the excited state and leads to a two line resonance spectrum. The splitting of the two lines (doublet) is usually denoted by \( \Delta E \) or \( \Delta E \), the quadrupole splitting. Third, in analogy to section 2.2.1, a magnetic dipole interaction between the magnetic moment of the nucleus and the hyperfine field at the nucleus site leads to a Zeeman splitting of the ground and excited state, which gives the characteristic six-line spectrum (sextet) for Fe. The relative line intensities of the sextet are \( 3 : x : 1 : 1 : x : 3 \), in which \( x \) depends on the angle \( \theta \) between the incoming \( \gamma \)-ray photons and the hyperfine field, according to the relation \( x = 4\sin^2 \theta / (1 + \cos^2 \theta) \).

When both quadrupolar and magnetic interactions are present, the resulting behavior can be much more complex. Usually, however, the quadrupolar interaction can be treated as a small perturbation on the magnetic interaction (quadrupole shift). The isomer shift behaves additive to quadrupolar and magnetic interactions. Because the isomer shift of the source is not known a priori, it is common to report the isomer shift of the absorber with respect to an \( \alpha \)-Fe reference sample.

Fig. 2.9: Schematic energy levels of the source and the absorber and the influence of the three principal hyperfine interactions. At the bottom of the figure the corresponding CEMS spectra are shown.
2.2.3 Magnetization measurements

**SQUID**

Magnetization curves have been measured with a Quantum-Design MPMS-5S Superconducting QUantum Interference Device (SQUID) magnetometer, which uses superconducting coils to pick up the magnetic flux emerging from the sample under investigation. The absolute magnetic moment of the sample can be determined with a sensitivity (claimed by the manufacturer) of $10^{-10}$ Am$^2$. Measurements can be performed in fields up to 5 T and temperatures in the range between 1.7 and 400 K.

**MOKE**

To measure magnetization loops magneto-optically, a home-built MOKE magnetometer was available. The Magneto Optical Kerr Effect (MOKE) is the change of polarization of a polarized laser beam after reflecting from a magnetic material. This change in polarization can be a rotation of the polarization axis, the Kerr rotation, or a change from linear to elliptical polarization, the Kerr ellipticity. The measured change in polarization is proportional to the magnetization of the material. As the spot of the incident laser beam is very small (typically of the order of 0.1 mm), MOKE is a local technique, extremely suitable for measuring magnetization curves at different positions on, for instance, a wedge layer. However, no quantitative information about the magnitude of the magnetic moment of the material can be obtained and information is limited to the penetration depth of the laser beam.

In-plane and out-of-plane moments can be probed with MOKE by choosing different geometries. In the polar geometry the incident laser beam is almost perpendicular to the sample surface and the Kerr effect is proportional to the out-of-plane magnetic moment. In the longitudinal and transverse geometries the incident laser beam makes an angle of about $45^\circ$ with the film plane. In this case, the in-plane magnetic moment can be measured longitudinal or transverse with respect to the incoming laser beam, depending on a longitudinal or a transverse polarization axis of the laser beam, respectively. The transverse Kerr effect is in general much smaller than the longitudinal Kerr effect.

Measurements can be performed between 5 and 300 K in fields up to 100 kA/m in a flow cryostat. In a separate room temperature setup the maximum fields amount to 800 kA/m in polar geometry and 300 kA/m in longitudinal geometry. More information about MOKE and its application in the study of magnetic thin films can be found in Refs. [20, 44].

2.2.4 Magnetoresistance measurements

All magnetoresistance and resistance measurements described in this thesis are performed with a home-built setup, using a standard four-point contact method with field and current in the plane of the layers. Fields up to 1.35 T can be applied and the temperature can be varied between 5 and 350 K using a helium-cooled flow cryostat. A detailed description of the magnetoresistance measurement apparatus can be found in Ref. [44].
2.2.5 Structural characterization techniques

**SEM/EPMA**

A Scanning Electron Microscope (SEM) at the chemistry department of the Eindhoven University of Technology is used to visualize the Co wires investigated in chapter 5. In a SEM a beam of electrons at acceleration voltages of a few kV is scanned across a surface. A detector is used to measure the intensity of the secondary, backscattered, and Auger electrons or the X-rays, which emerge from the sample after excitation by the incident beam. The intensity of the electrons is used to make an image of the surface. The intensity and energy distribution of the X-rays is used for element specific analysis of the material, so-called Electron Probe Micro Analysis (EPMA). EPMA is used in chapter 8 to determine the composition of the FeHf(Si)O films.

**AES**

The Auger Electron Spectroscopy (AES) experimental setup, connected to the VG V80M MBE apparatus, resembles the SEM, with the difference that the electrons are not used for imaging but for chemical identification. The Auger electrons are part of the secondary electron spectrum, emitted under electron bombardment, with a characteristic energy that allows elemental identification. Because of the low escape depth of Auger electrons with energies up to 2 keV, only electrons from the first few atomic layers will escape from the material, which makes AES a surface sensitive technique. Examples and details of AES can be found in, for example, Ref. [45].

**XRD/GIXA**

With X-Ray Diffraction (XRD) information about crystal orientation, lattice constants, layer thicknesses, and roughness can be obtained. The experiments described in this thesis were performed with a Philips PWD3710 X-ray diffractometer. The sample is exposed to X-rays emitted by a Cu source ($K_{\alpha 1} : \lambda = 1.54434 \text{ Å}$ and $K_{\alpha 2} : \lambda = 1.54050 \text{ Å}$) at an angle $\theta$, with respect to the normal to the layers, and reflected X-rays are detected at a scattering angle $2\theta$. Constructive interference occurs only at those angles where the well-known Bragg-rule is satisfied [46], which shows up as peaks in a $\theta$-2$\theta$ scan. The crystal orientation, lattice constants, layer thicknesses, and roughness can now be obtained by analyzing the interference peaks in the $\theta$-2$\theta$ scan. When the X-rays are focused under grazing incidence this technique is often denoted as Glancing Incidence X-ray Analysis (GIXA), which is particularly useful for thin film characterization. Detailed information about X-ray analysis of thin films and multilayers can be found in Ref. [47].

**LEED**

Low Energy Electron Diffraction (LEED) is a surface-sensitive diffraction technique. In this method an electron beam of variable energy (of the order of 0 - 1 keV) is produced by an electron-gun and hits the surface of a sample. Elastically scattered electrons are accelerated by a grid at positive voltage towards a fluorescent screen where the LEED diffraction pattern is formed. Diffusely inelastically scattered electrons are rejected by several other grids at adjustable voltages. Because the energy of the incident electrons is not high enough to penetrate deeply into the material, the LEED pattern is essentially a diffraction pattern from crystallographically ordered atoms
in the topmost layers. The OMICRON SPECTALEED (OMICRON Vacuumphysik GmbH) apparatus used for the study presented in this thesis is connected to the VG V80M MBE system, which allows for an analysis of the surface structure and the symmetry of the deposited layers during several stages of the growth.

It is also possible to monitor the intensities of particular LEED spots as a function of the electron energy, so-called LEED $I$-$V$. An exact analysis of such $I$-$V$ curves is extremely difficult, because of the strong interactions between the incident electrons and the atoms in the material. Nevertheless, one can predict in first order that constructive interference occurs whenever the Bragg-rule for the electrons is satisfied, similar to X-ray diffraction, from which the out-of-plane lattice constant at the surface can be determined. More information about LEED can be found in Ref. [48].

**STM**

A Scanning Tunneling Microscope (STM) is able to probe surface structures down to an atomic scale. The heart of the STM is a sharp needle (the tip), which is, controlled by piezo-electric crystals, brought to about 0.2 - 1 nm from a conducting surface under investigation. When a bias voltage is applied between the surface and the tip, a tunneling current can be observed. By scanning along the surface and monitoring the tunneling current as function of position (or by keeping the tunneling current constant by adjusting the distance from the surface), a topographic map of the surface structure can be obtained with atomic resolution. The STM images presented in this thesis were recorded with an OMICRON UHV STM 1 (OMICRON Vacuumphysik GmbH).
3. Direct observation of the formation of nonmagnetic c-Fe$_{1-x}$Si in epitaxial Fe / Si / Fe

Low energy electron diffraction, Auger electron spectroscopy and conversion electron Mössbauer spectroscopy have been applied to study antiferromagnetically exchange coupled epitaxial Fe / Si / Fe(100). It is shown that a bcc-like (100) structure is maintained throughout the layers after a recrystallization of the spacer layer by Fe / Si interdiffusion. For the first time direct experimental evidence is presented that c-Fe$_{1-x}$Si (0 ≤ x ≤ 0.5) is formed in the spacer layer, a nonmagnetic metallic metastable iron-silicide phase with a CsCl structure (B2), which supports explanations for the antiferromagnetic exchange coupling given recently.

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3.1 Introduction

Since the discovery of strong antiferromagnetic (AF) interlayer coupling in Fe / Si multilayers [49], there have been a number of studies addressing the transformation of the Si spacer layer into iron-silicide and its relation to the observed interlayer coupling. It is now well established that a metallic iron-silicide formed by Fe / Si interdiffusion is responsible for the interlayer coupling [23, 24, 50–55]. The exact composition of the iron-silicides in the spacer layer is considered to be crucial to understand the exponential decay of the AF coupling with the interlayer thickness [23] in the framework of predictions by Shi et al. [25] or the electron-optics model [56]. In several studies [24, 50, 55] it is suggested that Fe and Si form an FeSi alloy spacer layer with a metastable CsCl structure (c-FeSi) and an Fe : Si ratio close to 1. Although it has been shown that c-FeSi can be stabilized epitaxially [57, 58], the spontaneous formation of c-FeSi in antiferromagnetically coupled Fe / Si based layers has not been directly observed up to now. In this chapter we present direct experimental evidence for the presence of c-Fe$_{1-x}$Si with 0 ≤ x ≤ 0.5 in the spacer layer of AF coupled Fe / Si / Fe by means of Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES) and Conversion Electron Mössbauer Spectroscopy (CEMS).

3.2 Experimental

Fe / Si / Fe layers were grown in a Molecular Beam Epitaxy (MBE) system (VG-Semicon V80M) with a base pressure of 2×10$^{-11}$ mbar. An e-gun source with feedback control of the flux was used for the deposition of natural Fe, whereas $^{56}$Fe, $^{57}$Fe and Si were evaporated from temperature stabilized Knudsen cells. All thicknesses were controlled by calibrated quartz crystal monitors. The layers were grown at room temperature on Ge(100) substrates, which were cleaned by several
Ar$^+$ sputter (700°C) and anneal (780°C) treatments until a sharp Ge(100)-(2×1) LEED pattern and no more C and O contaminations were observed. The LEED and AES measurements were performed in-situ during several stages of the Fe and Si growth utilizing wedge-shaped as well as homogeneous layers. The room temperature CEMS measurements were done ex-situ in a spectrometer with a $^{57}$CoRh source and a gas-flow detector.

3.3 Results and discussion

Figure 3.1 shows the LEED patterns at 171 eV and LEED I-V curves of the 00-spot during several stages of the growth of Ge(100) + 60 Å Fe + 12 Å Si + 45 Å Fe. The penetration depth of the electrons at this energy is typically 3 - 4 monolayers, which ensures that we mainly probe the surface layers. After deposition of the 60 Å Fe layer a (1×1) LEED pattern of a bcc-Fe(100) surface is observed with relatively sharp spots, indicating good single crystalline growth of the Fe on the Ge(100) substrate. The good crystallinity was further confirmed by Magneto-Optical Kerr Effect (MOKE) measurements which showed hard and easy axes of magnetization for fields applied along the [110] and [100] directions, respectively, as expected for single crystalline bcc-Fe. LEED patterns (b), (c), and (d) show that upon deposition of Si the spots become more and more faint and completely disappear between 8 and 9 Å. For 12 Å Si only a bright background is left, which means that Si grows, at least above 9 Å, in an amorphous or at least strongly disordered manner onto the Fe.

![LEED patterns and I-V curves](image)

Fig. 3.1: (left panel) LEED I-V curves of the 00-spot intensity (no background correction) and (right panel) LEED patterns at 171 eV of Ge(100) + (a) 60 Å Fe (b) 60 Å Fe + 6 Å Si (c) 60 Å Fe + 8.5 Å Si (d) 60 Å Fe + 12 Å Si (e) 60 Å Fe + 12 Å Si + 6 Å Fe (f) 60 Å Fe + 12 Å Si + 45 Å Fe.
When Fe is deposited on this disordered 12 Å Si layer, the sharp (1×1) LEED pattern with the spots at exactly the same position reappears again at a nominal layer thickness of about 5 Å Fe, as shown in pattern (e) and (f). This implicates that by diffusion of Fe into the spacer a recrystallization of the disordered Si has taken place into crystalline iron-silicide. If this would not be the case one would expect polycrystalline rather than single crystalline growth of the top Fe layer. This reappearance of the LEED pattern can be observed up to a 21 Å Si spacer but disappears for larger thicknesses, indicating a limited diffusion depth at room temperature. A Fe / Si-wedge / Fe trilayer prepared in this way shows strong antiferromagnetic interlayer exchange coupling, which strength varies exponentially with the nominal Si layer thickness (see chapter 4), in accordance with de Vries et al. [23] for layers grown at 200°C.

In the left panel of Fig. 3.1 the 00-spot intensity versus the electron energy is plotted corresponding to the LEED pattern at the right hand side, except for (d) in which no LEED spots were found. Upon deposition of Si the I-V curves become less structured, but regain better pronounced peaks after deposition of the top Fe layer. Additionally, from the positions of the main Bragg reflections, as indicated with dashed lines in Fig. 3.1, it can be concluded, that the perpendicular lattice constant remains constant at ≈ 1.43 Å close to bulk values for Fe (d_{100} = 1.4331 Å). Thus, a bcc-like (100) growth is maintained throughout the whole structure.

![Normalized Si 92 eV LVV (open squares) and Fe 47 eV MVV (solid circles) AES peak intensities versus the nominal Si and Fe layer thickness for the growth of (a) Si on 60 Å Fe and (b) Fe on 60 Å Fe + 12 Å Si, respectively. The solid lines in (a) are exponential fits to the data for t_{Si} ≥ 4 Å.](image)

**Fig. 3.2:** Normalized Si 92 eV LVV (open squares) and Fe 47 eV MVV (solid circles) AES peak intensities versus the nominal Si and Fe layer thickness for the growth of (a) Si on 60 Å Fe and (b) Fe on 60 Å Fe + 12 Å Si, respectively. The solid lines in (a) are exponential fits to the data for t_{Si} ≥ 4 Å.
To obtain more insight in the iron silicide formation process we followed the growth of a Si wedge on Fe and an Fe wedge on Si by AES. In Fig. 3.2.a the evolution of the Auger Si LVV (92 eV) and Fe MVV (47 eV) peak intensities are plotted as a function of the nominal Si thickness deposited on a single crystalline 60 Å Fe base layer. For a Si coverage of about 4 Å a change in the exponential decrease and increase is observed in Fe and Si intensities, respectively, a clear sign of interdiffusion between the bottom Fe and the top Si layer up to this thickness, in agreement with earlier observations by Gallego et al. [59]. For coverages above 4 Å the AES intensities can be described with exponentials (solid lines in the figure) with attenuation lengths in agreement with closed Si layer growth, excluding further intermixing.

In Fig. 3.2.b the evolution of the Si and Fe Auger intensities are presented for an Fe wedge deposited on 60 Å Fe + 12 Å Si. A jump and two adjacent plateaus in the Fe as well as in the Si AES intensities are observed between 3.5 and 6.5 Å nominal Fe thickness. The jump at an Fe thickness of about 5 Å is accompanied by the already mentioned reappearance of the (1×1) LEED pattern. Apparently, at this point a recrystallization of the spacer layer takes place. The plateaus can be understood assuming that an equilibrium is reached between Fe deposition on top of the spacer layer and Fe diffusion into the spacer layer. When the Si spacer is saturated with Fe above 6.5 Å, an exponential increase and decrease of Fe and Si AES intensities, respectively, is observed, indicating a closed layer growth of Fe. The Fe and Si intensity ratios at the plateaus $I_{Fe}/I_{Si} = 0.56$ and 0.83, calculated from the absolute intensities, indicate that Fe$_{1-x}$Si is formed with $x$ in the range from 0 to 0.5, according to Gallego et al. [59]. However, we have to realize that the interdiffusion of Fe with Si is a complex process and Fe or Si segregation at the surface and the observed recrystallization can seriously alter the AES intensity ratio. Therefore, a definite identification of the formed iron-silicide phases cannot be given from the AES intensities alone.

The high sensitivity of CEMS to the local atomic environment together with the well-known Mössbauer parameters for the relevant iron-silicides gives us the opportunity to identify the iron-silicides formed in our exchange coupled layers. Furthermore position sensitive identification of the iron-silicides can be obtained using a $^{57}$Fe probe layer which easily can be shifted through the multilayer stack.

The measurements were performed on separately grown samples with 6 Å $^{57}$Fe probe layers at various positions in an $^{56}$Fe matrix, guaranteeing that the Fe in the iron-silicide of the spacer layer can be clearly discriminated from the rest of the Fe, in contrast to earlier studies [24, 50, 60]. A first sample was designed to give information about the iron-silicide spacer layer only, with the following nominal composition: Ge(100) + 68 Å $^{56}$Fe + 3 × (16 Å Si + 6 Å $^{57}$Fe+ 19 Å $^{56}$Fe) + 30 Å Si, schematically sketched in the inset of Fig. 3.4. The relatively thick $^{56}$Fe buffer layer prevents that any iron-germanide formation distorts the CEMS data and three repetitions were chosen for sensitivity reasons. For a nominally 16 Å thick Si spacer layer, AES measurements established that 6 Å $^{57}$Fe will completely react with the Si, ensuring that the observed CEMS spectrum is only due to the nonmagnetic iron-silicide in the spacer responsible for the interlayer exchange coupling. We will refer to this sample as “reference” in the following. A second series was grown with the nominal composition: Ge(100) + 60 Å Fe + 3 × (10 Å Si + 31 Å Fe) + 30 Å Si, with the 6 Å $^{57}$Fe probe layers deposited 4 Å below, 2 Å below, at the bottom of, on top of, and 6 Å above the Si spacer, as schematically sketched in Fig. 3.5.

Figure 3.3 shows the MOKE hysteresis loops for the 16 Å thick spacer, and for one sample of the second series with 10 Å nominal spacer thickness. Both loops show evidence of AF coupling with clear plateaus and high saturation fields. The high remanence is mainly caused by the thick
3.3. Results and discussion

Fig. 3.3: Representative longitudinal Kerr hysteresis loops of the Fe / Si samples with $^{57}$Fe probe layers and nominal spacer layer thickness of (a) 10 Å Si and (b) 16 Å Si, respectively. The field is applied along the [100] directions of the samples (easy axis of the Fe layers).

Fe buffer layer. We want to emphasize that for all of the samples, for which the CEMS results will be presented in the following, AF coupling is present, a necessary condition because we want to investigate the iron-silicide responsible for the coupling.

The CEMS spectrum of the reference sample is presented in Fig. 3.4. The spectrum consists of one quadrupole splitted line, which can be fitted well with a distribution of quadrupole doublets. The fitting parameters, isomer shift ($\delta$) and quadrupole splitting ($\Delta$) in the maximum of the distribution are listed in Table 3.1. There are several possible iron-silicides reported in the literature [57, 58] which qualify for the observed apparently nonmagnetic iron-silicide.

The first one is $\varepsilon$-FeSi, a nonmagnetic small-gap semiconductor with a cubic symmetry (B20). The local Fe symmetry is however trigonal which results in a quadrupole splitted CEMS spectrum with $\delta = 0.26$ mm/s and $\Delta = 0.51$ mm/s close to what we observe [61]. However, the formation of an $\varepsilon$-FeSi spacer is impossible because our LEED results clearly show that an epitaxial relationship is maintained throughout the whole stack of layers, incompatible with the lattice parameters of $\varepsilon$-FeSi. Furthermore, no semiconducting properties of the spacer layer were found from the temperature dependence of the interlayer coupling; see chapter 4.

A second candidate is $\alpha$-FeSi$_2$, the metallic state of iron-disilicide with a tetragonal structure and with Mössbauer parameters $\delta = 0.23$ mm/s and $\Delta = 0.47$ mm/s for one doublet and $\delta = 0.26$ mm/s and $\Delta = 0.73$ mm/s for a second doublet [61]. Although the parameters of the first doublet match perfectly with our results, we do not observe a second maximum in the distribution
3. Direct observation of the formation of nonmagnetic c-Fe$_{1-x}$Si in epitaxial Fe/Si/Fe

Fig. 3.4: Room temperature CEMS spectrum of Ge(100) + 68 Å $^{56}$Fe + 3 × (16 Å Si + 6 Å $^{57}$Fe + 19 Å $^{56}$Fe) + 30 Å Si. $^{57}$Fe deposited directly onto the Si will diffuse completely into the spacer, ensuring that the spectrum is only caused by Fe in the formed iron-silicide spacer. The solid line is a fit with a distribution of quadrupole splitted doublets.

matching the second known doublet parameters. Furthermore, the perpendicular lattice constant is inconsistent with our LEED results.

The remaining candidate is nonmagnetic c-Fe$_{1-x}$Si, a metallic metastable phase with a CsCl structure (B2). Stoichometric c-FeSi has an isomer shift of $\delta = 0.26$ mm/s, but no quadrupole splitting due to its cubic symmetry [57, 58]. However, when Fe vacancies are introduced (c-Fe$_{1-x}$Si) a quadrupole splitting is observed consistent with our results. For example, Fig. 3.4 shows a remarkable resemblance with the slightly assymetric quadrupole splitted doublet of c-Fe$_{0.5}$Si as reported by Fanciulli et al. [57]. In their study the spectrum was fitted with three quadrupole splitted doubletts, associated to different Fe sites of which the doublet with the highest intensity has a quadrupole splitting of $\Delta = 0.47$ mm/s, in agreement with our data. Furthermore, we have to realize that also strain reduces the local cubic symmetry introducing an electric field gradient. Thus we might already expect a quadrupole splitting for stoichometric c-FeSi grown coherently on bcc-Fe. From the previous analysis we conclude that our spacer layer exists of, possibly strained, nonstoichometric silicon rich c-FeSi with a CsCl structure.

We note that $\gamma$-FeSi$_2$, metallic iron-disilicide with a CaF$_2$ structure, may be magnetically ordered with $B_{hf} = 2.64$ T at room temperature. Our spectrum, however, cannot be fitted assuming a magnetically splitted sextet. Nevertheless, a small fraction of $\gamma$-FeSi$_2$ inclusions in the spacer, which may create ferromagnetic bridges at lower temperatures, can lead to direct magnetic contact between bottom and top Fe layer (pin-holes) as observed before [62].
Additional information can be gained from the second series of samples in which the $^{57}$Fe probe layer is shifted through the stack from nominally 4 Å below to 6 Å above the spacer layer. Figure 3.5 shows the CEMS spectra for the different positions. It is clear from the raw data already that the $^{57}$Fe spectra far enough from the spacer are identical and consist of a magnetically splitted Fe sextet, whereas the other spectra are a mixture of magnetic Fe from the magnetic layers and the nonmagnetic c-Fe$_{1-x}$Si doublet from the spacer layer. All the spectra are fitted with a distribution of hyperfine fields and, if present, a distribution of quadrupole splittings for the nonmagnetic doublet. The relative intensity ratio of the sextets is $3 : 4 : 1 : 1 : 4 : 3$ for all spectra indicating an in-plane magnetization direction in agreement with our magnetization measurements. The resulting Mössbauer parameters in the maximum of the distributions are listed in Table 3.1.

Table 3.1: Isomer shift ($\delta$), quadrupole splitting ($\Delta$), hyperfine field ($B_{hf}$), and relative intensities ($I_d$ and $I_s$) of doublets and sextets, as obtained from fits to the experimental CEMS spectra. Isomer shifts are given relative to $^{57}$-Fe at room temperature.

<table>
<thead>
<tr>
<th>$^{57}$Fe position</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta$ (mm/s)</th>
<th>$I_d$ (%)</th>
<th>$\delta$ (mm/s)</th>
<th>$B_{hf}$ (T)</th>
<th>$I_s$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>0.24</td>
<td>0.47</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6 Å above</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.012</td>
<td>32.4</td>
<td>100</td>
</tr>
<tr>
<td>on top of Si</td>
<td>0.24</td>
<td>0.43</td>
<td>15</td>
<td>0.076</td>
<td>28.0</td>
<td>85</td>
</tr>
<tr>
<td>below Si</td>
<td>0.24</td>
<td>0.43</td>
<td>29</td>
<td>0.059</td>
<td>29.4</td>
<td>71</td>
</tr>
<tr>
<td>2 Å below Si</td>
<td>0.24</td>
<td>0.43</td>
<td>17</td>
<td>0.037</td>
<td>31.6</td>
<td>83</td>
</tr>
<tr>
<td>4 Å below Si</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.009</td>
<td>32.9</td>
<td>100</td>
</tr>
</tbody>
</table>

The hyperfine field of the magnetically splitted part of the spectrum can be related to magnetic iron-silicide alloys using previous work by Stearns [63]. The maximum of the hyperfine field ranges from 32.9 T, close to pure $\alpha$-Fe for the probe layer at 4 Å below the Si, to 28.0 T, which can be assigned to Fe$_{92}$Si$_{8}$ for the probe layer directly on top of the Si. For all positions there is a broad distribution in hyperfine fields, indicating that there is a composition gradient from pure Fe in the bulk of the magnetic layers towards c-Fe$_{1-x}$Si in the spacer layer. Furthermore, an asymmetric iron-silicide profile is observed in spectra (b) and (c). More Fe diffuses from the bottom than from the top into this 10 Å Si layer. It is clear that the Fe / Si and Si / Fe interface are inequivalent with respect to the iron-silicide formation, an observation earlier made by photoemission studies by Kläsges et al. [64].

The same c-Fe$_{1-x}$Si doublet as for the reference sample is found in spectrum (b), (c) and (d), although the quadrupole splitting is slightly lower, which could be a sign of more stoichiometric c-FeSi. A thickness dependent strain effect, however, would result in an increased quadrupole splitting for thinner layers instead of the decrease observed [58]. The c-Fe$_{1-x}$Si doublet is found not only for the probe layer directly below and on top of the Si layer but also for 2 Å below, which confirms the AES results that Fe diffuses also from the bottom into the Si. From the total intensities of the doublets and sextets we estimate that between 3.0 and 3.3 Å $^{57}$Fe and about 8 Å Si contribute to the nonmagnetic doublet, which results in c-Fe$_{1-x}$Si with an average $x$ in the range between 0.30 and 0.36, using bulk mole volumes of Fe and Si.
Fig. 3.5: CEMS spectra of Ge(100) + 60 Å Fe + 3 ∗ (10 Å Si + 31 Å Fe) + 30 Å Si with a 6 Å 57Fe probe layer deposited at various positions in the multilayer stack as indicated in the figure. The solid lines are fits to the experimental spectra as explained in the text.
3.4 Conclusions

One might argue that the complex formation of c-Fe<sub>1-x</sub>_Si by diffusion of Fe into the Si spacer layer could strongly depend on the preparation methods and conditions, which might make a universal interpretation of the interlayer exchange coupling in Fe/Si based layers impossible. However, as was already shown before [23,24], the thickness dependence and strength of the coupling are generally the same for layers prepared with initially different FeSi spacer and magnetic layer compositions. Apparently, the interlayer exchange coupling does not depend crucially on the exact spacer layer composition, as long as a crystalline FeSi spacer is formed with the CsCl structure. This is confirmed by recent calculations by Moroni et al. [65], who have shown that the density of states near the Fermi-level for stoichiometric and defective c-FeSi are almost identical, including a sharp peak in the density of states about 0.2 eV above the Fermi-level. Within the framework of the Anderson sd-mixing model, this peak is believed to mediate the coupling in Fe/Si based layers.

3.4 Conclusions

In conclusion we have systematically studied iron-silicide formation in AF coupled Fe/Si/Fe(100) layers. With LEED and AES it was confirmed that a crystalline iron-silicide is formed in the spacer layer, which was identified as c-Fe<sub>1-x</sub>_Si from CEMS measurements. The formation of c-FeSi corroborates the conjectures on which recent explanations for the antiferromagnetic exchange coupling in Fe/Si based layers were based [23].
4. Origin of biquadratic exchange in Fe / Si / Fe

We have studied the temperature and thickness dependence of the interlayer exchange coupling in MBE-grown Fe / Si / Fe. In contrast to earlier studies, we have determined the biquadratic coupling strength, not disturbed by vertical and lateral variations in the coupling properties. The biquadratic coupling shows a strong temperature dependence, which can be understood by loose spins in the spacer layer.

The contents of this chapter will be submitted for publication (1999).

4.1 Introduction

Recently, an exceptional type of coupling was found in Fe / Si / Fe, strongly antiferromagnetic and varying exponentially with the spacer layer thickness [23]. This rather unique behavior of the coupling is mediated by c-Fe_{1-x}Si formed by Fe diffusion into the Si spacer layer (see chapter 3) and can be qualitatively understood in terms of the Bruno electron-optics model [56] with imaginary extremal Fermi-vectors, or by the Anderson sd-mixing model [25]. Apart from bilinear also biquadratic exchange coupling was observed in Fe / Si based thin films. A number of studies have addressed the origin of this biquadratic exchange by analyzing the temperature dependence of the coupling in Fe / Si multilayers [66–70]. However, as pointed out by Kohlhepp et al. [69, 71], a qualitative interpretation of the biquadratic coupling in Fe / Si multilayers is impossible due to lateral and vertical variations of the coupling properties. It was shown that the degree of antiferromagnetic coupling strength depends strongly on the position in the multilayer stack and these variations are able to mimic a strong biquadratic coupling and hide the true intrinsic biquadratic contributions. Consequently, the study of Fe / Si multilayers cannot give a decisive answer to the origin of the biquadratic coupling.

To circumvent these problems, we have measured the biquadratic exchange in well-defined MBE-grown Fe / Si / Fe trilayers. Because these layers contain only one spacer, there are no vertical variations in the coupling parameters depending on the position in the stack. Lateral variations were avoided as much as possible by analyzing the magnetization locally with the Magneto-Optical Kerr Effect (MOKE). After a brief experimental introduction, we will present the temperature and thickness dependence of the intrinsic bilinear and biquadratic coupling constants obtained in this way. It will be evidenced that biquadratic exchange in Fe / Si / Fe is due to magnetic impurities in the spacer layer which are weakly exchange coupled to the Fe layers, so-called loose spins.
4.2 Experimental

The Fe / Si / Fe layers were grown in a Molecular Beam Epitaxy (MBE) system (VG-Semicon V80M) with a base pressure of $2 \times 10^{-11}$ mbar at room temperature. An e-gun source with feedback control of the flux was used for the deposition of Fe, whereas Si was evaporated from a temperature stabilized Knudsen cell. The thicknesses were controlled by calibrated quartz crystal monitors. The layers were grown at room temperature on Ge(100) substrates, which were cleaned by several Ar$^+$ sputter (700°C) and anneal (780°C) treatments until a sharp Ge(100)-(2x1) LEED pattern was observed.

Previous studies have shown that in these Fe / Si / Fe trilayers the Si spacer transforms to metallic c-Fe$_{1-x}$Si by Fe and Si interdiffusion (see chapter 3). However, this only slightly alters the thickness of the spacer layer and therefore we will refer to the nominal Si spacer layer thickness in the following. The temperature dependence of the coupling was studied in six samples of the following composition: Ge(100)$+60 \AA$ Fe $+t_{Si}Si+45 \AA$ Fe $+30 \AA$ Si, with $t_{Si}=14$, 14.5, 15, 15.25, 16, and 16.25 Å. The spacer layer thickness dependence was measured in a wedge-shaped sample composed of: Ge(100)$+60 \AA$ Fe $+7-17 \AA$ Si-wedge $+45 \AA$ Fe $+30 \AA$ Si.

4.3 Results and discussion

Figure 4.1 shows three normalized MOKE hysteresis curves with the field applied in-plane along the [100] easy axis of magnetization, at 300, 200, and 100 K for a nominal Si thickness $t_{Si}=15.25 \AA$. These magnetization curves are representative for all the other loops. At 300 K the magnetization loop can be characterized by two switching fields, indicated with $H_1$ and $H_2$ in the figure (defined in the middle of the hysteresis). Going from high to low fields, $H_1$ corresponds to a reorientation of the magnetic moments of the two Fe layers from a parallel to a perpendicular alignment, and at $H_2$ the alignment of the magnetizations changes from perpendicular to antiparallel. The difference between $H_1$ and $H_2$ is a measure for the biquadratic coupling strength $J_2$, and the sum is characteristic for the bilinear coupling strength $J_1$. When the biquadratic coupling strength is larger than the bilinear coupling strength, as is the case in Fig. 4.1.b and 4.1.c for 200 and 100 K, only one step is observed in the magnetization loop. The perpendicular alignment of the moments of the Fe layers is then maintained down to zero field. In latter case $J_1$ and $J_2$ can only be evaluated from a fit of the experimental curve. We note that sometimes small steps in the magnetization loops are observed at low fields, as also can be seen in Fig. 4.1. Although, the exact origin of these steps is not known, we think that they are caused by higher order anisotropy terms or by an extra uniaxial anisotropy term, as was also observed by Anderson et al. [72], because the position of these steps is only slightly temperature dependent. It is also possible that a small misalignment of the easy axis with respect to the field is causing these extra steps.

The magnetization hysteresis curves can be fitted by considering the phenomenological expression for the areal energy density of the two magnetic layers

$$E = - \mu_0 M_s t_1 H \cos(\phi_1 - \phi_H) - \mu_0 M_s t_2 H \cos(\phi_2 - \phi_H) + Kt_1 \cos^2(\phi_1) \sin^2(\phi_1) + Kt_2 \cos^2(\phi_2) \sin^2(\phi_2) - J_1 \cos(\phi_1 - \phi_2) - J_2 \cos^2(\phi_1 - \phi_2),$$

(4.1)
4.3. Results and discussion

Fig. 4.1: MOKE hysteresis curves for $t_{Si} = 15.25$ Å with the field applied along the [100] easy axis in-plane at (a) 300, (b) 200, and (c) 100 K, and corresponding fits (right-hand side) of the experimental curves with Eq. 4.1.
with $M$, the saturation moment of layer 1 and 2 with thickness $t_1$ and $t_2$. Here $\phi_1$ and $\phi_2$ are the angles between the magnetization of layer 1 and 2 and the [100] easy axis, while $\phi_H$ is the angle between the field $H$ and the [100] axis. The cubic anisotropy constant $K$ is assumed equal for both films. $J_1$ is the bilinear coupling constant ($< 0$ for antiferromagnetic coupling) and $J_2$ is the biquadratic coupling constant ($< 0$ for 90° coupling). By an absolute minimalization of Eq. 4.1 as function of the applied field $H$, the magnetization loops can be reproduced in a satisfactory way by choosing the correct combination of $J_1$ and $J_2$, as is demonstrated in the right-hand side of Fig. 4.1. Uncertainties in the determination of the coupling constants when $J_2 > J_1$ are overcome by combining easy and hard axis loops. The anisotropy $K$, evaluated from the shape of easy and hard axis loops, decreases with increasing temperature from about $3.5 \times 10^4 \, J/m^3$ at 10 K to approximately $1.8 \times 10^4 \, J/m^3$ at 300 K. The temperature dependences of $J_1$ and $J_2$, resulting from the fits, are plotted in Fig. 4.2.a and 4.2.b, respectively, for the six different nominal Si thicknesses.

First we will focus on the temperature dependence of the bilinear coupling constant. $J_1$ is antiferromagnetic and decreases slowly with increasing temperature for all Si thicknesses. In a previous paper by de Vries et al. [23] it was shown that the origin of the exponential thickness dependence of $J_1$ can be understood within the Anderson sd-mixing model by Shi et al. [25] or within the framework of Bruno’s theory introducing the concept of an imaginary critical Fermi-vector [56]. However, in this work it was already pointed out that the temperature dependence of the coupling cannot be understood with the latter model, because this model predicts an increase of the coupling strength with increasing temperature, not in agreement with the temperature dependence of $J_1$ shown in Fig. 4.2.a.

On the other hand, a real critical Fermi-vector does predict a decrease of the bilinear coupling with temperature $T$, according to

$$J_1(T) = J_1(0) \frac{2\pi k_B T m_e / \hbar^2 k_F}{\sinh(2\pi k_B T m_e / \hbar^2 k_F)}, \quad (4.2)$$

with $t$ the thickness of the spacer layer, $m_e$ the electron mass and $k_F$ the extremal wave vector [56]. $J_1(T)$ can be fitted reasonably well with Eq. 4.2 as shown in Fig. 4.2.a with solid lines, yielding a $k_F$ of the order of 0.2 - 0.6 Å$^{-1}$. Unfortunately, the scatter in the data does not allow for a more accurate determination of $k_F$. Nevertheless, this $k_F$ is in crude agreement with predictions for the Fermi-surface of metallic Fe$_{0.5}$Si$_{0.5}$ in the CsCl structure [73].

Before we will focus on the temperature dependence of $J_2$, we will first present the thickness dependence of $J_1$ and $J_2$. Figure 4.3 shows the coupling constants as function of the nominal Si spacer layer thickness measured on the wedge-shaped sample. We have only plotted $J_1$ and $J_2$ for $t_{Si}$ between 12.8 and 16.25 Å, when $J_1$ and $J_2$ could be separated unambiguously. Remarkably, both $J_1$ and $J_2$ decrease exponentially with the Si spacer layer thickness with approximately the same decay length. This suggests that $J_1$ and $J_2$ are intimately related and probably both find their origin in the same mechanism, exponentially decreasing with the spacer thickness. It seems that in the data of Fig. 4.3 on top of the exponentially decaying $J_1$ and $J_2$ a small oscillation is visible with a period of about 1.8 Å. Although this oscillation needs further experimental confirmation, it is noteworthy that the observed period is close to the oscillation period predicted from the temperature dependence of $J_1$ in Fig. 4.2.a. Because we want to focus on the origin of $J_2$ in this work, details concerning these oscillations will be published elsewhere.

The biquadratic coupling $J_2$, shown in Fig. 4.2.b, is much stronger temperature dependent than $J_1$. There are a number of possible mechanism for this biquadratic coupling. First of all,
4.3. Results and discussion

Fig. 4.2: Temperature dependence of (a) $J_1$ and (b) $J_2$ for six Si thicknesses as indicated in the figure. The solid lines are fits to the experimental data with Eq. 4.2, for $J_1$, and Eq. 4.6, for $J_2$, as explained in the text.
$J_2$ may be of intrinsic origin as was claimed recently [70]. We reject this possibility because the magnitude of an intrinsic second order term $J_2$ is generally orders of magnitude smaller than $J_1$, much smaller than observed experimentally [56]. Moreover, within the Bruno reflection model it is shown that the temperature variation of the intrinsic $J_2$ is only 2 times faster than $J_1$, which is clearly not the case here. Two other extrinsic mechanisms for biquadratic coupling are proposed by Slonczewski.

First, the fluctuation mechanism for biquadratic exchange [74] predicts a $J_2$ when spatial fluctuations of the interlayer thickness cause a competition between ferromagnetic and antiferromagnetic coupling for neighboring regions. The resulting frustration can lead to a perpendicular alignment of the magnetic moments, when the size of the thickness fluctuations is below the size of the domain walls. For Fe/Si, however, the bilinear coupling $J_1$ always favors an antiparallel alignment of the magnetic layers and therefore lateral thickness variations do not lead to a frustration of the coupling here. Furthermore, the fluctuation mechanism predicts a temperature dependence $J_2(T) \propto (J_1(T))^2$. As shown in Fig. 4.2, $J_1$ is only decreased by 20 - 30 % at 300 K compared to 10 K, while $J_2$ decreases by a factor 19, ruling out an interpretation in terms of the fluctuation model. We also note that magnetic dipole fields created by roughness can result in a biquadratic alignment of the moments [75]. The magnitude of this contribution is however small.

The second mechanism proposed by Slonczewski is biquadratic coupling mediated by paramagnetic ions in the spacer layer [76]. These so-called “loose spins” can couple to both ferromagnetic layers via an indirect exchange, which also is responsible for $J_1$. Indeed, it was shown in Fig. 4.3 that both $J_1$ and $J_2$ are exponentially decaying with spacer thickness, which suggested
4.3. Results and discussion

already a common origin. The total interaction potential \( U \) between loose spins and ferromagnetic layers is the vector sum of the interaction \( U_1 \) and \( U_2 \) of the loose-spins with ferromagnetic layer 1 and 2, respectively, and can be expressed as

\[
U(\theta) = (U_1^2 + U_2^2 + 2U_1U_2\cos(\theta))^{1/2},
\]

where \( \theta \) is the angle between the two moments. The free energy per loose spin is

\[
f(T, \theta) = -k_B T \ln \left( \frac{\sinh((1 + (2S)^{-1})U(\theta)/k_B T)}{\sinh(U(\theta)/2S k_B T)} \right),
\]

with \( S \) the atomic spin and \( T \) the temperature. The macroscopic free energy per unit spacer area \( F = c a^{-2} f \), with \( c \) the areal density of loose spins and \( a \) the nearest neighbor distance between atoms, can be phenomenologically expanded in

\[
F(\theta) = J_0 - J_1 \cos(\theta) - J_2 \cos^2(\theta) + \ldots,
\]

where

\[
J_2(T) = -\frac{1}{2} ca^{-2} [f(T, 0) + f(T, \pi) - 2 f(T, \pi/2)]
\]

is the loose spins contribution to the biquadratic coupling. Previously, this loose spin model has been successfully applied to explain the biquadratic coupling in Fe / Al / Fe, Fe / Au / Fe and Fe / Ag / Fe [76–79].

Unlike the other mechanisms for biquadratic coupling, the loose spins model predicts a strong temperature dependence of \( J_2 \). Indeed, the huge increase of \( J_2 \) shown in Fig. 4.2.b with decreasing temperature is a very strong indication for a loose spins origin. Figure 4.2.b is supplemented with fits of \( J_2(T) \) with the loose spins model (solid lines), assuming \( S = 1 \) and \( U = U_1 = U_2 \), which means that the loose spins are atoms near the midplane of the spacer or randomly distributed. The areal loose spins density \( c \) and \( U \) were adjusted for the fit. As can be seen in the figure, the loose spins model is in very good agreement with the experimental data. The density of loose spins following from the fits converged consistently to approximately 1 % for all thicknesses, and \( U/k_B = 343, 334, 292, 266, 222, \) and 199 K for \( t_{Si} = 14, 14.5, 15, 15.25, 16, \) and 16.25 Å, respectively. In another approach one can assume \( c = 2 \) and allow for \( U_1 \neq U_2 \), which describes the case of two loose spins layer near the ferromagnetic interfaces [76]. However, with these assumptions our data cannot be described, because this leads to a plateau in \( J_2 \) for lower temperatures, not observed experimentally.

The values of \( U/k_B \) between 199 and 343 K are high compared to the maximum bilinear coupling strength [23] of about \(-2 \text{ mJ/m}^2\) for \( t_{Si} = 6 \text{ Å} \) (\( U/k_B \approx 52 \text{ K} \)), although they compare well with values obtained for Fe / Al / Fe [76]. This is an indication that each loose spin may be composed of a cluster of Fe atoms, in which case \( U \) is also proportional to the number of Fe atoms in a cluster. On the other hand, the concentration of loose spins \( c \approx 1 \% \) seems quite low considering the fact that the spacer consist of c-Fe\(_{1-x}\)Si near to saturated with Fe, as was shown recently [39]. Apparently, not all Fe atoms in the spacer layer contribute to the biquadratic coupling, but only approximately 1 % of clustered Fe atoms.

Up to now, we have disregarded \( J_1 \) in the analysis with the loose spins model. The loose spins model, however, neglects the scattering effects of loose spins on the electron waves which mediate direct bilinear coupling between the two ferromagnetic layers and is therefore more suitable for
predicting the magnitude of $J_2$ rather than $J_1$. Although of higher order, $J_2$ may even dominate experimentally above $J_1$, which is the case in the present study for low temperatures, because scattering of the electron waves disrupts the wave coherence and lowers the magnitude of $J_1$.

4.4 Conclusions

In summary, we have studied bilinear and biquadratic coupling strengths in well-defined MBE-grown Fe/Si/Fe layers. In contrast to earlier studies we have determined the coupling parameters, not disturbed by vertical and lateral fluctuations of the coupling properties, as usually is the case for Fe/Si multilayers. The temperature dependence of the bilinear coupling is only weakly temperature dependent in agreement with Bruno’s electron reflection model. The biquadratic coupling can be understood in terms of Slonczewski’s loose spins mechanism.
5. Structure and magnetization of arrays of electrodeposited Co wires in anodic alumina

Arrays of Co nanowires in anodic porous alumina filters were produced by means of electrodeposition. The structure and magnetization behavior of the wires was investigated with Nuclear Magnetic Resonance (NMR) and magnetization measurements. NMR shows that the wires consist of a mixture of fcc and hcp texture with the (0001) axis of the hcp fraction oriented preferentially perpendicular to the wires. The magnetization direction is determined by a competition of demagnetizing fields and dipole-dipole fields and can be tuned parallel or perpendicular to the wires by changing the length of the wires.

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5.1 Introduction

The fabrication and properties of arrays of tunable magnetic nanostructures is of interest not only from a fundamental, but also from a technological point of view, as recording technologies in the future will require higher bit densities to fulfill the unrelenting demand for more storage capacities. There are several approaches to fabricate large arrays of magnetic structures, for example by lithographic techniques such as electron beam lithography and ion beam lithography. The disadvantage of these techniques is that they are expensive and it is time consuming to write nanostructures on large scales, although recently optical interference techniques are being developed to circumvent this problem [80]. Another way to fabricate large scale periodic nanostructures is by electrodeposition of magnetic materials in the pores of nuclear track-etched polycarbonate membranes [81–85] or in the pores of self-ordered nanochannel material formed by anodization of Al in an acid solution [86–89], a low cost and fast technique to produce large arrays of identical magnetic entities with a very large aspect ratio (length divided by diameter), which is not possible with standard lithographic techniques. Wires in anodic alumina have the advantage above wires in polycarbonate membranes that they are completely parallel and exactly perpendicular to the membrane surface and, moreover, the wires are assumed to have a constant diameter throughout their entire length [90].

Specifically, here a study is presented of the structure and magnetization behavior of Co wires electrodeposited in commercially [91] available nanoporous alumina, with nominal pore diameters of 100 and 20 nm. Nuclear Magnetic Resonance (NMR) is used to determine the microstructure of the wires and it will be shown that the crystallographic structure of the Co wires consists of a mixture of fcc and hcp stacking. The crystallographic quality of the Co is comparable to sputtered or Molecular Beam Epitaxy (MBE) grown Co layers. The magnetic behavior, studied with direct
magnetization measurements and through the anisotropy of the resonance fields, is determined by a competition of self-demagnetization of the wires and dipolar interactions between the wires. It will be shown that dipolar interactions can lead to a preferential direction of the magnetization perpendicular to the wires, which can be tuned by changing their length.

5.2 Fabrication of the wires

As a starting material, commercially available \[91\] nanoporous alumina filters were used with a thickness of 60 μm and nominal pore diameters of 100 nm and 20 nm. Scanning Electron Microscopy (SEM) images of the surface of the filters suggest that the diameter of the pores is up to a factor 2 larger than the nominal diameter. However, we will refer in the rest of this chapter to the nominal pore diameter as the precise diameter of the pores is not crucial for our analysis. The nominal pore density is \(1\times10^{15}\) per m\(^2\) in both cases, which is confirmed by SEM images, yielding an average spacing between individual pores of approximately 320 nm. One side of the filters was covered with a few micrometer thick DC sputtered gold layer to obtain a conducting base layer at the bottom of the pores. The Co wires were then grown by electrodeposition of \(\text{Co}^{2+}\) ions from an electrolyte with the following composition: 400 g \(\text{CoSO}_4\cdot7\text{H}_2\text{O}\), 40 g \(\text{H}_3\text{BO}_3\) and 1 l \(\text{H}_2\text{O}\). Deposition is performed in an ertalyte cell with the nanopores facing upwards at a deposition potential of \(U_{\text{Co}} = -1.05\) V with respect to a saturated calomel reference electrode (SCE). The total thickness of the alumina filters is 60 μm. Deposition is stopped when the desired wire length is reached, which was determined from the total integrated charge passing between the

![Fig. 5.1: Cross section SEM picture of Co wires in 20 nm anodic alumina filter. The bright broad line at the bottom of the figure is the gold base layer.](image-url)
working electrode and the counter electrode. The length of the wires was separately checked after deposition with cross section SEM images and with a normal light microscope and is found to be uniform within 5%. The area of deposition is approximately 1 cm$^2$, which can easily be enlarged to fabricate larger arrays of wires. NMR measurements were performed with a phase coherent spin-echo spectrometer at $T = 4.2$ K in the frequency range between 195 and 235 MHz and fields up to 4.5 T. Magnetization measurements were done with a Quantum Design Superconducting QUantum Interference Device (SQUID).

In Fig. 5.1 a cross section SEM image is shown for Co wires grown in 20 nm anodic alumina. The bright broad line at the bottom of the figure is the Au base layer with a thickness of about 3 $\mu$m. As can be seen, the individual wires are very straight and parallel with a length of about 40 $\mu$m, which corresponds to an aspect ratio of about 2000. To obtain a cross section image the filter was broken which is probably the reason why some of the wires seem somewhat distorted and blurred in the picture. SEM images of the surface show that the array of pores is rather disordered and not hexagonally ordered as they were produced recently [92].

### 5.3 Characterization with NMR

Figure 5.2 shows zero-field and field-swept NMR spectra of our 100 and 20 nm Co wires. All spectra are recorded at 4.2 K and corrected for enhancement of the spin-echo signal because of oscillations of the electronic moment [93]. We have used NMR because it is a powerful technique [93–95] to probe the microstructure of Co. Furthermore, through the anisotropy of the resonance fields we can obtain valuable information on the magnetic behavior. Figure 5.2.a and 5.2.d show the zero applied field NMR spectra of the 100 and the 20 nm wires. In both spectra a clear peak can be distinguished at about 217 MHz which corresponds to fcc Co and contributes to about 40% of the total spectrum. To the right of this fcc peak a mixture of hcp Co and stacking faults (twinning, deformation, etc.) are visible. Co in hcp structure gives rise to a resonance frequency along the c-axis (hcp$_c$) at 220 MHz and perpendicular to the c-axis (hcp$_\perp$) at 228 MHz. On the left-hand side of the fcc peak the intensity does not drop to zero completely which might be caused by Co atoms at the interfaces with Al$_2$O$_3$ or by grain boundaries [95]. The zero-field spectra resemble NMR spectra of sputtered [95] and even MBE grown [94] Co layers, which indicates that the crystallographic quality of our Co wires can be compared to layers made with other fabrication techniques.

The resonance condition for NMR in this configuration is

$$f = \frac{\gamma}{2\pi} (B_{\text{hf}} - B_{\text{appl}} + B_{\text{surr}} + B_{\text{dem}}), \quad (5.1)$$

with $B_{\text{surr}}$ the field produced by the surrounding Co lines and $B_{\text{dem}}$ the self-demagnetizing field of the wires. In an in-plane magnetized uniform film the last two fields are not present. For long wires, however, $B_{\text{dem}}$ perpendicular to the wire axis is $\frac{1}{2}\mu_0 M_s$ ($\approx 0.9$ T), with $M_s$ the saturation magnetization of Co [96], and wire-wire interactions can lead to a sizeable $B_{\text{surr}}$. From Eq. 5.1 it is clear that we can measure $B_{\text{surr}}$ by recording a NMR spectrum as a function of an externally applied field and hence we can gain more insight in the magnitude of the wire-wire interactions. In Fig. 5.2.b, 5.2.c, 5.2.e and 5.2.f the NMR spectra at constant frequency of the 100 and 20 nm wires are shown as function of the field applied either perpendicular or parallel to the wires. The horizontal axes of the spectra are plotted in such a way that they scale with the frequency axes
Fig. 5.2: $^{59}$Co Nuclear Magnetic Resonance spectra of 100 and 20 nm wires. (a,d) Spin-echo intensity as function of frequency in zero field. (b,e) Spin-echo intensity as function of an applied field perpendicular to the wires. (c,f) Spin-echo intensity as function of an applied field parallel to the wires. The arrows indicate the shift of the spectra with respect to the zero-field spectra. The line positions of fcc Co and hcp Co are indicated with the dashed lines. Spectra (b) and (c) are recorded at a frequency of 200 MHz; (e) and (f) at 195 MHz.
of the zero-field spectra via Eq. 5.1, assuming \( B_{\text{surr}} + B_{\text{dem}} = 0 \). This means that the line shifts indicated with arrows in Fig. 5.2 are equal to \( B_{\text{surr}} + B_{\text{dem}} \). First we consider the spectrum of 100 nm Co wires with the applied field perpendicular to the wires (Fig. 5.2.b). With respect to the zero-field spectrum of Fig. 5.2.a the overall spectrum is shifted with about 0.3 T, which gives \( B_{\text{surr}} = -0.6 \) T using \( B_{\text{dem}} = 0.9 \) T. Figure 5.2.c shows the NMR spectrum with the applied field along the wire axes. The shift with respect to the zero-field spectrum is about 1.30 T, even higher than with the field perpendicular to the wires, and because \( B_{\text{dem}} = 0 \) along the wire axis this results in \( B_{\text{surr}} = 1.30 \) T. Apparently, for the 100 nm Co wires the surrounding field introduces and easy axis perpendicular to the wires, although a magnetization along the wire axes was expected from the magnitude of the self-demagnetizing field of the long wires. On the other hand, the 20 nm wires behave more isotropically with a small preference for the magnetization parallel to the wires. The overall shift of the spectrum is about 0.75 T when the applied field is perpendicular to the wires and only 0.43 T when the applied field is parallel to the wires, leading to \( B_{\text{surr}} = -0.15 \) T and \( B_{\text{surr}} = 0.43 \) T, respectively.

Before focusing further on this magnetization behavior for the different wire diameters, first the shape of the NMR spectra will be discussed in more detail. The NMR spectra with the field perpendicular to the wires in Fig. 5.2.b and 5.2.e consist of an fcc, a hcp, and a hcp \( \perp \) Co peak (and some stacking faults [94]). When the field is applied parallel to the wires, a dip in the spectra appears at the position of hcp, and, when the field is applied perpendicular to the wires, more intensity is found at the position of hcp \( \perp \), from which directly follows that the texture of the hcp Co fraction is mainly with the c-axis perpendicular to the wires. As a result, an extra anisotropy contribution of the magnetic anisotropy along the c-axis has to be taken into account. This also was observed in electrodeposited Co wires in polycarbonate membranes by Ounadjela et al. [83] and by Piraux et al. [97].

5.4 Magnetization behavior

Now we will discuss in more detail the magnetization behavior of the wires. Figure 5.3 shows the magnetization measurements for the 100 and 20 nm Co wires. The saturation fields are qualitatively in agreement with the shifts of the NMR spectra indicated with arrows in Fig. 5.2. The 100 nm Co wires are more easily saturated perpendicular to the wires than parallel to the wire axes, while the 20 nm wires behave more isotropically as saturation is reached at approximately the same value for the field parallel and perpendicular to the wires. From this we conclude that the magnetization behavior is mainly a result of a competition between demagnetization and dipole-dipole interactions.

The small differences in magnitude between the saturation fields observed in the magnetization measurements and the shifts of the NMR spectra are caused by the magnetocrystalline anisotropy of the hcp Co fraction, which does affect the shape of the magnetization curve in a way that it slightly favors a magnetization direction perpendicular to the wires, but does not add to the shift of the NMR spectra. Therefore, saturation for the 20 nm wires (see Fig. 5.3.d) with field parallel to the wires is reached at higher fields than for the field perpendicular to the wires, while the NMR spectra (see Fig. 5.2.e and 5.2.f) suggest a slight tendency for an easy axis of magnetization parallel to the wires. Because the crystalline anisotropy of hcp Co decreases at higher temperature [98] the saturation fields parallel to the wires decrease at higher temperatures.
5. Structure and magnetization of arrays of electrodeposited Co wires in anodic alumina

Fig. 5.3: Magnetization hysteresis curves of 100 nm wires (a,b) and 20 nm wires (c,d) at 300 and 10 K, with the applied field perpendicular (open circles) and parallel (solid squares) to the wires.

From a simple consideration we can understand that a competition of dipole-dipole interactions and demagnetization can lead to a preferential direction of magnetization perpendicular to the wires. The array of wires may be approximated by a 2-dimensional infinite array of magnetic dipoles located on a square grid. The total field acting on one wire is the total dipole sum produced by all the other wires and reads [99, 100]

$$B_z = 4.2 \frac{\mu_0}{4\pi} \cdot \frac{p}{d^3},$$  \hspace{1cm} (5.2)

when all the moments are aligned along the wires. Here, $p$ is the moment of one wire and $d$ the distance between the wires. When all the moments are aligned perpendicular to the wires the total field acting on one wire is the sum of the dipole fields and the self-demagnetizing field of the wire:

$$B_x = -2.1 \frac{\mu_0}{4\pi} \cdot \frac{p}{d^3} + B_{dem}. \hspace{1cm} (5.3)$$

The sign of $B_z$ and $B_x$ is chosen with reference to Eq. 5.1, that is opposite to the applied field. Depending on the magnitude of the moment $p$, which in our experiments can be chosen by changing the wire length or diameter, either $B_z$ or $B_x$ is smallest leading to an easy direction of magnetization parallel or perpendicular to the wires, respectively.

We realize that this model, based on a uniform magnetization reversal, is in principle too simple and does not describe detailed magnetization reversal processes in the wires. Including these would require extensive micromagnetical calculations, which are far beyond the scope of
Fig. 5.4: Magnetization hysteresis curves of 100 nm wires as a function of the wire length at 10 K, with the applied field perpendicular (open circles) and parallel (solid squares) to the wire axes.
this study. Nevertheless, as will be shown in the following, we can qualitatively describe the basic magnetization behavior with our simple magnetostatic model.

In accordance with the previous predictions, we have experimentally observed such a transition, as shown in Fig. 5.4. When the wire length is decreased from 40 µm to 0.5 µm a crossover takes place from a perpendicular easy direction of magnetization towards an easy direction parallel to the wires. This can be quantified by the effective anisotropy constant $K_{\text{eff}}$, derived from the magnetic anisotropy density, that is the area between the magnetization curves with field orientation parallel and perpendicular to the wire axes, which is presented in Fig. 5.5. The magnetostatic energy $E$ per unit volume is given by $E = -K_{\text{eff}} \times \cos^2 \theta$, with $\theta$ the angle between the wire axes and the magnetization direction. A change from easy axis of magnetization perpendicular ($K_{\text{eff}} < 0$) to parallel ($K_{\text{eff}} > 0$) occurs at a wire length of about 1 µm. Assuming a diameter of 100 nm and an average distance between the wires of 320 nm we have calculated the effective anisotropy constant as function of the wire length from Eq. 5.2 and 5.3, which also is shown in Fig. 5.5 (dashed line). The calculated change from perpendicular to parallel magnetization ($K_{\text{eff}} = 0$) at about 4 µm is in reasonable agreement with the measured change at 1 µm. Moreover, as mentioned before, we have some indications from SEM images that the actual diameter of the wires is up to a factor 2 larger than the nominal diameter, which would explain this difference of a factor 4. However, the calculated magnitude is much larger than the measured $K_{\text{eff}}$, especially for the longest wires, when clearly the assumption of a 2-dimensional array of magnetic dipoles does no longer hold. Also, we have to realize that the analysis of $K_{\text{eff}}$ is based on a uniform magnetization reversal without domain wall motion, curling or buckling of the magnetization in the wires, which leads to a smaller effective anisotropy than for purely magnetostatic interactions.

Furthermore, for the sample with the shortest wires we may have to consider the possibility that, due to inhomogeneities in the electrodeposition process, part of the pores are not filled. This also would lead to a decrease of the dipole interactions and could account for the sharp increase in $K_{\text{eff}}$. Although we cannot rule out these inhomogeneities completely, the NMR linewidths for

![Fig. 5.5: Effective anisotropy constant $K_{\text{eff}}$ as function of wire length; measured (open squares) and calculated (dashed line) from Eq. 5.2 and 5.3.](image-url)
these short wires are not significantly different from those observed in Fig. 5.2, as would be the case for inhomogeneous growth with a large spread in dipole fields.

5.5 Conclusions

In summary, we have produced large arrays of Co nanowires by electrodeposition in commercially available anodic alumina. We have seen that the magnetization behavior is determined by a competition of demagnetizing fields and dipole-dipole interactions and to a lesser extent by magnetocrystalline anisotropy. The easy direction of magnetization can be tuned either perpendicular or parallel to the wires by changing the length of the wires.
6. Giant magnetoresistance induced by ultrathin magnetic layers

In this chapter we introduce an interface selective structure, composed of a spin-valve on top of which a thick nonmagnetic back layer is deposited as a straightforward experimental tool to measure the GMR induced by ultrathin magnetic layers. The interface selectivity of spin-dependent scattering is evidenced by calculations and illustrated in both Co/Cu/Co and Ni$_{80}$Fe$_{20}$/Cu/Ni$_{80}$Fe$_{20}$ spin-valves by an almost constant GMR-ratio as function of the magnetic layer thickness. The temperature dependence of the extremely short length scale associated with the onset of the GMR for thin layers is discussed in relation to the structure of ultrathin ferromagnetic layers, obtained from nuclear magnetic resonance measurements.


6.1 Introduction

In Giant MagnetoResistance (GMR) studies, the interface contribution to Spin-Dependent Scattering (SDS) is believed to depend crucially on the electronic (and possibly also the structural) matching of a specific combination of 3d or 4d ferromagnetic and nonmagnetic materials. However, from an experimental point of view it is an extremely difficult task to separate straightforwardly the interfacial scattering processes from the spin-dependent bulk scattering processes, and so far this has been attempted only by Parkin [101] in ferromagnetic/nonmagnetic/ferromagnetic structures where a different ferromagnetic material is buried at the interfaces.

In this chapter we introduce an extremely simple spin-engineered structure in which the presence of spin-dependent interface scattering can be directly established without the need to add another (foreign) ferromagnetic element. The structure (see Fig. 6.1) consists of a ferromagnetic layer F, separated by a nonmagnetic spacer S from the ferromagnetic probe layer PR, on top of which a thick nonmagnetic back layer B is grown. The imbalance in current distribution induced at or in the ferromagnetic probe layer may penetrate into the back layer [102] over a distance of the order of the mean free path. As will be shown by a semi-classical calculation, this feature makes the structure selective for an interfacial mechanism for SDS at the interfaces with PR, resulting in a discontinuous behavior of the GMR effect in the limit of thin (interfacial) ferromagnetic layers PR where the contribution from the bulk can be safely neglected. Experimentally, we have observed this discontinuous behavior in the transport properties of Co/Cu and Ni$_{80}$Fe$_{20}$/Cu based structures. The discontinuity in GMR can be expressed by a typical length scale $\xi = 1 - 3 \text{ Å}$, which is similar to the observation of Parkin [101], and may be associated with the evolution
of spin-polarized quantum-well states as seen in photoemission studies on Cu(100) / Co / Cu wedges [103, 104]. However, from our data supplemented with structural information from Nuclear Magnetic Resonance (NMR), we will show that the behavior of $\xi$ with temperature is most likely related to the stabilization of clusters when the probe layer is extremely thin.

6.2 Interface selectivity

To illustrate the interface selectivity of the GMR-ratio in our spin-valve structure we start here with the Co / Cu / Co spin-valves. Figure 6.2.a shows the composition of these spin-valves, in which a Co / Ru bias system is used to obtain the required antiparallel alignment in the Co / Cu / Co part of the spin-valve (more details about this type of spin-valves can be found in Ref. [105]). A typical result of the GMR-ratio as a function of the probe layer thickness is shown in Fig. 6.3. It is evidently seen that the GMR-ratio is discontinuous since it persists down to almost monatomical ferromagnetic layer thickness. To have a quantitative measure for the discontinuity of the GMR effect at small $d_{PR}$ we have plotted a phenomenological exponential expression through the data, yielding a characteristic length $\xi$. The length scale is typically below 3 Å, which rules out the involvement of a bulk scattering length.

The interface selectivity of our structure, intuitively based on a discontinuity in the GMR for $d_{PR} \rightarrow 0$, can be substantiated by a semi-classical calculation of $\Delta G$, i.e., the difference in conductivity between the parallel and antiparallel state of the magnetization vectors. In a first order approximation we will neglect the integration over the various directions of the electron trajectories, which allows us to derive an analytical expression for $\Delta G$ as a function of the probe layer thickness. Interface spin-dependent scattering is modeled by an asymmetry in the transmission
Fig. 6.2: Schematic drawing of (a) spin-valves with $F = 25 \, \text{Å} \ Co$, $\text{PR} = \text{Co}$ and $B = \text{Cu}$ and (b) exchange biased spin-valves with $B = 200 \, \text{Å} \ Cu$ and $F = 20 \, \text{Å} \ Ni_80Fe_{20}$, $\text{PR} = Ni_80Fe_{20}$ or $F = 20 \, \text{Å} \ Co$, $\text{PR} = \text{Co}$.

probabilities of the electrons at the interfaces, $T^\uparrow \neq T^\downarrow$, and bulk spin-dependent scattering by different mean free paths for spin-up and spin-down electrons, $\lambda^\uparrow \neq \lambda^\downarrow$. The mean free path of the nonmagnetic back layer is $\lambda^*$. In the limit of infinite back layer thickness ($d_B \gg \lambda^*$) it follows that

\[
\Delta G_B = \frac{m^2 e^2 v_F^2}{6\pi^2 \hbar^3} e^{-d_S/\lambda^*} \times \left[ \lambda^\uparrow (1 - e^{-d_F/\lambda^\downarrow}) - \lambda^\downarrow (1 - e^{-d_F/\lambda^\uparrow}) \right] \\
\times \left[ (\lambda^\uparrow - \lambda^*) (1 - e^{-d_{\text{PR}}/\lambda^\downarrow}) - (\lambda^\downarrow - \lambda^*) (1 - e^{-d_{\text{PR}}/\lambda^\uparrow}) \right],
\]

(6.1)

and

\[
\Delta G_I = \frac{m^2 e^2 v_F^2}{6\pi^2 \hbar^3} \lambda^2 \times \left( (T^\uparrow - T^\downarrow)^2 e^{-d_S/\lambda^*} \times (1 - e^{-d_F/\lambda}) \right) \\
\times \left( 1 + [(T^\uparrow + T^\downarrow)\lambda^* / \lambda - 1] e^{-d_{\text{PR}}/\lambda} \right),
\]

(6.2)

for bulk and interface spin-dependent scattering, respectively (in case of interface spin-dependent scattering $\lambda = \lambda^\uparrow = \lambda^\downarrow$). When we focus on the behavior as a function of the probe layer thickness $d_{\text{PR}}$, we see that bulk spin-dependent scattering is characterized by a slow exponential
growth starting from zero, while an interfacial spin-dependent scattering mechanism always leads to a finite \( \Delta G \propto (T^{\uparrow} - T^{\downarrow})^2(T^{\uparrow} + T^{\downarrow}) \), and hence also to a finite GMR-ratio, in the limit of \( d_{pr} \to 0 \).

The prominent role of the back layer in the interface selectivity of our layered construction can be understood with the help of Fig. 6.1, which is supplemented with a semi-classical calculation [106] of the local \( G \) as a function of \( z \). The key feature is that \( \Delta G \) induced by a thin probe layer is not limited to the magnetic layers but extends to the nonmagnetic back layer too.\(^1\) In other words, while up and down electrons are usually scattered at the boundaries of the magnetic layers, the up electrons are now allowed to contribute to the conductivity over their full mean free path inside the nonmagnetic back layer.

![Diagram](image)

**Fig. 6.3:** GMR-ratio for the Co / Cu / Co spin-valves with \( B = 200 \text{ Å} \) Cu. The curves represent exponential behavior with a characteristic length \( \xi \).

In our experiments, as shown in Fig. 6.3, the predicted discontinuity is evidently observed. To facilitate the comparison with Eq. 6.1 and 6.2 more directly we have plotted \( \Delta G \) in Fig. 6.4 for several back layer thicknesses. Without back layer (solid symbols) \( \Delta G \) slowly increases due to diffuse scattering at the boundaries, which represents the common observation in spin-valves. When a back layer (open symbols) is grown on top, \( \Delta G \) is always finite at extremely small Co thickness (similar to the GMR-ratio), which according to the calculations directly refers to the existence of an interfacial mechanism for spin-dependent scattering. The magnitude of the step at small \( d_{pr} \) grows with increasing back layer thickness demonstrating the increased contribution of the local \( \Delta G \) in the nonmagnetic back layer. The behavior of \( \Delta G \) for larger probe layer thickness

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\(^1\) In this calculation we have chosen equal mean free paths \( \lambda = 100 \text{ Å} \) in all layers. Spin-dependent interface scattering is modeled via the spin-dependent transmission coefficients \( T^{\uparrow} = 1 \) and \( T^{\downarrow} = 0 \).
6.2. Interface selectivity

depends on several aspects, such as the thickness of the back layer compared to $\lambda$, and bulk contributions to the spin-dependent scattering, which we will not discuss here.

To illustrate that this structure may in principle be generally applied we also investigated spin-valves containing Ni$_{80}$Fe$_{20}$. Figure 6.5 presents a comparison of the GMR-ratio for the exchange biased spin-valves with $\text{PR} = \text{Co}$ and Ni$_{80}$Fe$_{20}$ (Fig. 6.2.b). From the data it becomes immediately clear that also in the case of Ni$_{80}$Fe$_{20}$ the GMR-ratio is preserved down to small ferromagnetic layer thickness. This is surprising because it was suggested [107] that (at least at room temperature) the presence of a compositionally intermixed and a magnetically dead region at the Ni$_{80}$Fe$_{20}$ / Cu interfaces are centers of spin-independent scattering, reducing the interface contribution to the spin-dependent scattering and thus favoring a dominant contribution from the bulk. From our data, however, it is evident that the presence of an interfacial nature of the spin-dependent scattering is certainly not limited to Co / Cu but also applies to Ni$_{80}$Fe$_{20}$ / Cu.

The extremely small characteristic length as introduced before, which represents experimentally the almost discontinuous behavior of the GMR effect is extremely small (less than 3 Å) and should therefore not be associated with a bulk scattering length. Moreover, a scattering length is expected to be reduced when the temperature is rising, which is opposite to our observation that $\xi$ increases with temperature as plotted in Fig. 6.6. The figure is supplemented with the $\xi$ as observed by Parkin [101] for thin Co layers at a Ni$_{80}$Fe$_{20}$ / Cu interface. It is surprising to see that the length scale deduced from both experiments are coinciding within the experimental errors, despite the different constructions used to extract the relevance of the interfaces for spin-dependent scattering. Apparently, in both experiments the interface of Co with Cu is the dominant source for the scattering asymmetry that is experienced in the adjacent nonmagnetic back layer or in a permalloy layer employed by Parkin. The main challenge now is to find out the origin behind

Fig. 6.4: $\Delta G$ of Co / Cu / Co spin-valves obtained at $T = 10$ K for several back layer thicknesses. The lines are guides to the eye.
the observed non-zero length scale $\xi$, which may be related to the electronic and/or structural nature of the interfacial layers. In photoemission experiments on Co / Cu wedges [104] a minimum barrier thickness of 0.6 - 2.2 Å was found to form spin-polarized quantum well states in a Cu layer confined by the Co potentials, which according to the authors indicates that GMR and the observed length scale $\xi$ may be intricately related to the evolution of electronic structure. On the other hand, it was speculated by Parkin that the structural growth mode of the interfacial layers may be related to $\xi$ as well.

Fig. 6.6: Characteristic length scale $\xi$ as a function of temperature, obtained from the GMR-ratio of the structures with $B = 200$ Å Cu (solid circles), supplemented with data of Parkin [101] for thin Co layers at Ni$_{80}$Fe$_{20}$ / Cu interfaces (open squares).
A first clue to unravel the behavior of the length scale $\xi$ is found in the magnetization reversal of the ferromagnetic probe layer. From the magnetoresistance curves we have determined a characteristic field at which the probe layer switches its magnetization direction, which is plotted in Fig. 6.7 as a function of temperature for the Co / Cu spin-valves with $d_{PR} = 3$ Å and $d_{PR} = 9$ Å. For the latter the switching field gradually increases as the temperature decreases, indicating ferromagnetic behavior. For the 3 Å Co layer, however, $H_{\text{switch}}$ suddenly increases below 70 K, which can be understood in terms of clusters which behave ferromagnetically below and superparamagnetically above a blocking temperature $T_B$ of about 70 K. This blocking temperature was confirmed by SQUID magnetization measurements, which show a clear difference between the magnetization loops at room temperature and at 10 K. Further proof for the existence of clusters in very thin Co layers we have obtained from NMR experiments on separately grown Co / Cu multilayers, sputtered under exactly the same conditions, which will be discussed in the next section.

![Fig. 6.7: Switch field of the Co probe layer PR as a function of temperature with $B = 200$ Å Cu and $d_{PR} = 3$ and 9 Å.](image)

6.3 Structure of thin Co layers

Further proof for the existence of clusters in very thin Co layers we have obtained from NMR experiments on separately grown Co / Cu multilayers, sputtered under exactly the same conditions. Because of the small amount of material involved no spin-echo signal could be observed in the spin-valves. Although it is not obvious that the outcome of the NMR investigation of these Co / Cu multilayers can be directly extrapolated to the spin-valves, we will see that the cluster formation observed in the multilayers is in agreement with the short length scale $\xi$ observed in the spin-valves.
The multilayers have the following composition: 200 Å Cu + 50 × (30 Å Cu + t Å Co) + 50 Å Cu, with t in the range between 5 and 15 Å. X-ray diffraction experiments yielded a (111) texture for the Co and the Cu, the same as for the spin-valves discussed in the previous sections. NMR experiments were performed at 1.5 K, with magnetic fields larger than the saturation field for Co, applied parallel to the plane of the films. The spectra were recorded at various fixed frequencies between 120 MHz and 200 MHz by sweeping the applied field.

In Fig. 6.8 the NMR spectra of the Co / Cu multilayers are shown for Co thicknesses in the range between 5 and 15 Å. The spectra consist of a peak located at $B_{hf} = 21.2$ T, which corresponds to strained fcc Co in the bulk of the layers [108]. No hcp Co contributions to the spectra are observed. The intensity at the left-hand side of the bulk peak corresponds to Co at the interfaces with Cu.

![Graph showing NMR spectra](image)

Fig. 6.8: NMR spectra of the Co / Cu multilayers at $T = 1.5$ K recorded at various fixed frequencies by sweeping the applied field. The spectra are normalized to the total amount of Co and corrected for enhancement.

In the following we will analyze the spectra with two methods. First we will divide the spectra into a bulk peak and the remaining interface contribution. This allows us to make a coarse estimate of the interface roughness. Next we use an interface model to obtain a detailed concentration profile of the Co and Cu layers.

### 6.3.1 Coarse analysis

A first step in the quantitative analysis is made by fitting the bulk peak of the spectra with a Gaussian, as is shown in Fig. 6.9 for the multilayer with a Co thickness of 10 Å. From the relative intensities of the bulk and interface area (shaded area), the amount of nuclei in the bulk and in the
interface areas of the multilayers can be estimated. For this Co thickness of 10 Å the interface area to bulk area ratio is 0.52 which means that about 52% of the Co atoms is surrounded by one or more Cu atoms. In Fig. 6.10 the bulk and interface intensities are plotted as a function of the Co layer thickness. For the Co thickness between 10 and 15 Å the interface signal remains approximately constant, whereas the number of Co atoms with bulk environment increases linearly.

Fig. 6.9: Spectrum of the Co / Cu multilayer with a Co thickness of 10 Å. The bulk peak is fitted with a Gaussian, which divides the spectrum in a bulk area and an interface area.

Apparently, when the nominal Co thickness is more than 10 Å a continuous layer is stabilized, leaving the interface structure almost unchanged. Extrapolation of the bulk intensity to zero (solid line) gives us a total amount of Co in the interface regions of about 5 Å, that is 2.5 Å per interface. When the Co thickness decreases below 10 Å, we observe that the interface intensity decreases more rapidly (dashed line). This resembles cluster formation as was observed in Co / Ag multilayers by van Alphen et al. [109], leading to a reduced interface area at small Co thickness. The interpretation in terms of clusters is corroborated by the fact that for a Co layer of 5 Å, which is somewhat more than 2 monolayers, there is still a significant bulk contribution to the NMR spectrum, what one would not expect in case of two continuous monolayers.

Although this analysis provides a fairly reasonable estimate of the interface roughness and we even could establish the disassociation of the Co layers into clusters below 10 Å, some remarks have to be made. In the first place, the assignment of the bulk peak as originating only from Co in the bulk of the layers is not completely correct. All Co with 12 Co nearest neighbors contribute to this peak, and hence also those which are located in the interface regions. Secondly, we have expressed the interface region in terms of Co thickness. The real interface thickness, however, depends on to what extend Co and Cu are mixed in this region and to what length scale this
admixtue spreads. A more sophisticated model is necessary to overcome these limitations in the analysis.

![Graph](image)

**Fig. 6.10:** Bulk and interface region intensity as a function of the Co thickness. The interception with zero of the extrapolation of the bulk intensity (solid line) for Co thicknesses between 10 and 15 Å results in an estimate of the interface roughness of about 2.5 Å per interface. The dashed line is a guide to the eye of the decreasing interface intensity.

### 6.3.2 Detailed interface model

For a more detailed analysis of our multilayers we will introduce a model multilayer as is shown in Fig. 6.11. Three regions can be identified with mono-atomic planes of pure Cu, pure Co or a mixture of Co and Cu and each atomic plane is characterized by a Co concentration $x_i$. From this model the multilayer satellite intensities can be deduced which are used to reconstruct the NMR spectra.

First we will assume that the Co and Cu in the mixed layers are randomly distributed in the plane of these layers, that is perpendicular to the cross section view of Fig. 6.11. The probability $\Phi$ of finding a Co atom, with $N$ Co nearest neighbors of $M$ total nearest neighbors is given by the binomial distribution

$$\Phi(N, M, x) = \frac{M!}{N!(M-N)!} x^N (1-x)^{M-N}, \quad (6.3)$$

with $x$ the Co concentration. Because our multilayers have a (111) texture, an atom in layer $i$ has 3 nearest neighbors in layer $i+1$ and layer $i-1$ and 6 nearest neighbors in layer $i$. Therefore the
probability of finding an atom in a specific layer \( i \) with \( N \) nearest neighbors becomes

\[
P_i(N) = \sum_{N} \Phi(n_{i-1}, 3, x_{i-1}) \times \Phi(n_i, 6, x_i) \times \Phi(n_{i+1}, 3, x_{i+1}),
\]

(6.4)

with the summation taken over all sets satisfying \( N = n_{i-1} + n_i + n_{i+1} \). The total number of Co atoms with \( N \) nearest neighbors can now be calculated by a summation over all atomic layers \( i \):

\[
P(N) = \sum_i x_i P_i(N).
\]

(6.5)

Fig. 6.11: Concentration profile (left) and cross section view of the Co / Cu multilayer (right)

Until now we have assumed that the Co and Cu in the plane of the layers are randomly distributed. However, as Co and Cu are non-miscible elements we expect Co and Cu rich patches in which Co and Cu are clustered together. We incorporate this in our model by introducing an atomic short-range order (ASRO) parameter \( \alpha [110, 111] \). In case of \( \alpha = 0 \), Co and Cu atoms are randomly distributed, while \( \alpha > 0 \) corresponds to segregation and \( \alpha < 0 \) corresponds to ordering. ASRO is taking into account by replacing \( x \) in Eq. 6.3 by \( p(x, \alpha) \), which we define as:

\[
p(x, \alpha) \equiv \frac{1 - \exp(-x\alpha)}{1 - \exp(-\alpha)}.
\]

(6.6)

The probability \( p(x, \alpha) \) varies linearly from \( p(0, \alpha) = 0 \) to \( p(1, \alpha) = 1 \) for \( \alpha = 0 \), but more progressively when \( \alpha > 0 \) (segregation) and more slowly when \( \alpha < 0 \) (ordering). Equation 6.6 deviates from the expression used in Ref. [110]:

\[
p_i(x_i, \alpha_i) \equiv x_i + \alpha_i(1 - x_i),
\]

(6.7)

with \( \alpha_i \) different for each atomic layer. We prefer Eq. 6.6 above 6.7 because with this expression only one \( \alpha \) is needed for all atomic planes. Furthermore, Eq. 6.6 does not lead to the unphysical situation that the probability for finding a Co atom \( p_i = 1 \) when \( x_i = 0 \) and \( \alpha_i = 1 \).

Figure 6.12 illustrates the effect of \( \alpha \), with the definition of Eq. 6.6, on the distribution of atoms in the layers. The left panel is a random distribution \( \alpha = 0 \) and the right panel shows the effect of \( \alpha = 1.5 \).
The appropriate concentration profile corresponding to the measured NMR spectrum is now calculated as follows. First the spectrum is fitted with a set of Gaussian distributed lines, corresponding to $P(12) = \text{bulk line}$, $P(11) = 1 \text{ Cu neighbor}$, $P(10) = 2 \text{ Cu neighbors}$, etc. Then the concentration profile is optimized so that measured and calculated bulk and satellite intensities are the same within 5%. The variables in this procedure are the concentration of Co in the atomic planes and the ASRO parameter $\alpha$. Some restrictions to the variables are made. Going from Cu to Co the concentration of Co starts with zero ($x_1 = 0$) and increases with every atomic plane ($x_i > x_{i-1}$).

In Fig. 6.13 the fitted NMR spectra and corresponding concentration profiles are presented. The average distance between two satellite lines is 1.57 T, which is in good agreement with literature [112, 113]. All the multilayers have about 3 mixed planes per interface, as indicated in the concentration profiles in the figure, and for all Co layers there is at least one closed layer, except for the multilayer with a Co thickness of 5 Å. This demonstrates again that the thinnest Co layer is not continuous yet. Moreover, the ASRO parameter $\alpha$ for the 5 Å layer is significantly larger than for the other layers, from which can be concluded that this layer is not alloyed but consists of long patches of Co. From zero-field and field cooled magnetization as function of temperature a blocking temperature was found of about 300 K for 5 Å Co layer, which means that the long patches still behave ferromagnetically at room temperature. The blocking temperature decrease rapidly for thinner layers to about 75 K for 2 Å Co. At first glance it seems strange that the layer with Co thickness of 8 Å has 2 closed Co layers whereas for a Co thickness of 10 Å only 1 closed
Fig. 6.13: Fitted spectra (left side) and calculated concentration profiles (right side) for $t_{Co} = 5, 8, 10, 12$ and $15$ Å.
layer is observed. However, the magnitude of $\alpha$ is higher for 10 Å Co than for 8 Å Co, which means that effectively this layer consist of almost 3 continuous layers.

From the foregoing structural information obtained with NMR it is clear that in the interpretation of the discontinuity in the GMR-ratio we should incorporate the formation of the ferromagnetic layer via clusters for the thinnest probe layers in the Ångström regime. In that regime we are dealing with a spin-valve consisting of a ferromagnetic Co layer separated by Cu from a secondary layer Co that is not continuous yet. At higher temperatures, the disorder in the paramagnetic cluster system obviously suppresses the GMR-ratio, leading inevitably to an increase of $\xi$ as shown in Fig. 6.6. This is substantiated by the observation that the magnetoresistance at higher temperature becomes entirely reversible due to the absence of remanence (or coercivity), and is hard to saturate at higher magnetic fields. A completely analogous situation is encountered in hybrid structures including both layers and clusters [114], in which the crossover to superparamagnetic behavior is seen in a similar way. At sufficiently low temperatures, the ferromagnetic response of our system is guaranteed by the blocking process of the clusters, and therefore, the length scale $\xi$ becomes minimal and is no longer masked by the structural influence on the GMR. In this regime, the observed $\xi$ of only 1.3 Å may be intrinsically related to the spin-dependent scattering process at extremely thin ferromagnetic layers, although from the present data the role of the evolution of the electronic structure suggested in Ref. [104] cannot be explicitly evaluated.

### 6.4 Conclusions

In summary, we have introduced a Co / Cu / Co and Ni$_{50}$Fe$_{20}$ / Cu / Ni$_{50}$Fe$_{20}$ based spin-valve structure on top of which a thick nonmagnetic back layer is deposited as an experimental tool to measure the GMR induced by ultrathin magnetic layers. We have shown that the discontinuous behavior of the GMR-ratio as a function of the magnetic layer thickness is a fingerprint for a significant contribution of spin-dependent interface scattering to the GMR effect in these materials. The temperature dependence of the extremely short length scale associated with this discontinuity was related to the structure of these ultrathin ferromagnetic layers.
7. Specular reflection in spin-valves bounded by NiO

We have experimentally investigated the possibility of increased electron reflectivity induced by an insulating NiO layer that is used to exchange bias a metallic spin-valve. For this purpose Ni$_{80}$Fe$_{20}$ / Cu / Ni$_{80}$Fe$_{20}$ and Ni$_{60}$Fe$_{10}$Co$_{18}$ / Cu / Co$_{90}$Fe$_{10}$ spin-valves were grown and subsequently covered by insulating NiO or by metallic FeMn. In all cases the giant magnetoresistance of the NiO spin-valves is systematically larger upon a variation of the exchange biased ferromagnetic layer thickness, also after correcting the data for the conductivity of FeMn which we have determined from a separately grown series of samples with variable FeMn thickness. The increased giant magnetoresistance ratios can be qualitatively understood on the basis of a semi-classical calculation in which partial specular reflectivity at the NiO interface has been included.

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7.1 Introduction

In studies on the Giant MagnetoResistance (GMR) effect, it has been recognized that the electronic and structural nature of the interfaces are key elements in the understanding of the mechanism behind GMR [115]. In theoretical models these details of the “internal” interfaces are extremely relevant for the transport behavior and are usually described in terms of reflectivity, transmission and scattering at the nonmagnetic/magnetic interfaces. As far as the role of reflectivity of electron waves at interfaces is concerned, there still exists no straightforward experimental evidence and usually it is neglected in the analysis of data on GMR. Up to now, there are some indications that reflection of electron waves occurs at the outer boundaries of a metallic spin-valve structure, interfaced to one or two insulating layers. Due to the presence of the potential step at the insulating interface, the electrons are expected to be internally reflected, by which the Spin-Dependent Scattering (SDS) can be most effectively experienced since the mean free path of the electrons is no longer limited by the presence of outer boundary scattering. This in turn should necessarily lead to enhanced GMR-ratios since the trilayer now mimics an infinite multilayered system. Large GMR-ratios have been observed [116–120] in recent years when NiO was incorporated into a spin-valve structure. As an example, we show in Fig. 7.1 the GMR of a Co / Cu system bordered by two NiO layers. The GMR-effect of almost 15 % at room temperature and 23 % at low temperature is unusually large in comparison with the all-metal structures, such as the well-known spin-valves exchange biased to metallic FeMn [121]. Egelhoff et al. [117] were the first to find indications for the presence of specularity of electron waves in so-called symmetric spin-valves of the type Co / Cu / Co / Cu / Co confined within NiO. From the behavior of the GMR effect
with the thickness of the inner versus outer Co layer, it was suggested that reflectivity should be, at least partially, present.

What is lacking in the available experimental data is some clear unambiguous evidence for specular reflectivity, which is the actual motivation of the present study. To address the role of electron reflectivity induced by a metal/insulating interface in a straightforward way, we designed two identical spin-valve trilayers, one capped with insulating NiO and the other with metallic FeMn. To avoid any ambiguities, we have grown these structures under exactly equal conditions, immediately after each other in the same deposition run. Since these systems do only differ from each other by the introduction of one insulating layer instead of a metallic layer at one side of the sandwich, we could draw pertinent conclusions on the role of reflectivity at the insulating interface.

![GMR-ratio graph](image)

**Fig. 7.1:** GMR-ratio of the NiO based spin-valve 500 Å NiO / 20 Å Co / 20 Å Cu / \( t_{Co} \) Å Co / 12 Å Cu / 100 Å NiO at \( T = 300 \) K (solid circles) and \( T = 10 \) K (open circles). The lines are guides to the eye only.

The organization of this chapter is as follows. First we will analyze the impact of specularity on the GMR via semi-classical model calculations. We will concentrate on the magnitude of the GMR-ratio upon a variation of the magnetic layer thickness, from which the presence of specular reflection should be concluded in the experiments. Then the data of the GMR-ratio will be presented for NiO and FeMn based systems, using trilayers composed of \( \text{Ni}_{80}\text{Fe}_{20} \) (Permalloy, Py) / Cu / \( \text{Ni}_{80}\text{Fe}_{20} \) and \( \text{Ni}_{66}\text{Fe}_{16}\text{Co}_{18} \) / Cu / Co30Fe10. Finally, we will discuss the data in relation to the semi-classical prediction, from which evidence is provided for the presence of reflected electron waves at the NiO interface by comparison with FeMn based spin-valves.
7.2 Model calculations

In this section we will calculate the giant magnetoresistance with the semi-classical Boltzmann equation, adapted for magnetic multilayers by Camley and Barnas [106, 122] and further refined by others [123, 124]. At present, there seems to be no compelling reason to prefer a quantum-mechanical model above a semi-classical model, because the semi-classical description is suitable to describe experimental data satisfactorily [125]. In the Camley and Barnas model the current density \( J_x(z) \) in the plane of the layers at zero temperature (when spin-mixing is neglected) reads [106, 122]:

\[
J_x(z) = \frac{e^2 E_x m_e^2 v_F^2}{8 \pi^2 \hbar^3} \int_{\beta=0}^{\pi/2} \sum_{\pm, \uparrow, \downarrow} \lambda^{\uparrow\downarrow} [1 + F_{\pm}^{\uparrow\downarrow} \exp\left(\frac{\mp z}{\lambda^{\uparrow\downarrow} \cos \beta}\right)] \sin^3 \beta d\beta, \tag{7.1}
\]

with \( z \) normal to the film plane, \( E_x \) the electric field in the plane, \( m_e \) the mass of an electron, and \( e \) its charge. Also we have used the expression for the mean free path \( \lambda \equiv \tau \times v_F \), with \( v_F \) the Fermi-velocity (assumed constant in all layers), and \( \tau \) the relaxation time. Further a separation has been made between \( \uparrow \) (spin-up) and \( \downarrow \) (spin-down) electrons, and electrons moving in the + or \(- z\)-direction (\( \perp \) film plane). For each layer, this equation has to be solved numerically after the four coefficients \( F_{\pm}^{\uparrow\downarrow} \) are calculated from the boundary conditions at the interfaces. Here Camley and Barnas have simply introduced phenomenological fitting parameters, \( T \) for the probability of coherent transmission of electrons, \( R \) for the probability of specular reflection, and the remainder \( D = 1 - T - R \), for diffuse scattering.

An assumption that is frequently made in semi-classical calculations is to completely neglect specular reflection at the inner interfaces of the multilayer but also at the outer boundaries of the multilayer. To incorporate the presence of a large potential step induced by an insulator, we will allow for a nonzero reflectivity \( 0 \leq R \leq 1 \) at one or two (outer) interfaces of the metallic trilayer, with \( D \) determined by \( 1 - R \). We realize that, obviously, this represents a much too elementary treatment of electrons that are impinging on an insulating layer. The diffuse part of the scattering should e.g. depend on the angle of incidence on a rough surface, and was treated more elaborately by models introduced by Soffer [126] and many others. However, we like to emphasize that we do not pursue a quantitative description of the data since this would require a detailed fitting procedure which is far from obvious and does not necessarily yield a satisfactory description of experimental data [125, 127]. Instead, we would like to give insight in the qualitative impact of specularity of electrons on the current distribution and the corresponding GMR effect in spin-valves confined within insulating layers.

Additionally, we will analyze the role of current shunting through a metallic back layer, such as the FeMn in an exchange biased spin-valve, to be able to compare the intrinsic GMR-ratio of FeMn based materials with structures incorporating NiO, that carries no current. In the calculations the GMR-ratio is defined as \( (G_P - G_{AP})/G_{AP} \equiv \Delta G/G_{AP} \), with \( G_P \) and \( G_{AP} \) the sheet conductivity in parallel and antiparallel configuration of magnetization vectors, respectively.

7.2.1 Two reflecting interfaces

To start with, we define a model system \( I / t_{F1} F1 / S / t_{F2} F2 / I \) composed of 2 ferromagnetic layers \( F \) separated by the spacer material \( S \), of which the thickness is 25 Å in accordance with
Fig. 7.2: Calculated GMR-ratio as a function of the thickness of the ferromagnetic layer F1, F2 of the structure I / F1 F1 / 25 Å S / F2 F2 / I, for reflectivity R = 0, 0.5, 1 at the interfaces I / F1 and F2 / I; the mean free path is 100 Å throughout the structure; in (a) interface SDS with T≠ = 1 and T≠ = 0.2 is assumed, in (b) bulk SDS with λ≠ = 100 Å and λ≠ = 20 Å; (c) both SDS processes are active.
7.2. Model calculations

Fig. 7.3: Calculated GMR-ratio as a function of the thickness of the ferromagnetic layer F2 of the structure 80 Å F1 / 25 Å S / tF2 F2 / I, for reflectivity R = 0, 0.5, 1 at the interface F2 / I; at the outer boundary of F1 electrons are diffusively scattered; the mean free path is 100 Å throughout the structure; in (a) interface SDS with T ↑ / T ↓ = 1 and T ↓ / T ↑ = 0.2 is assumed, in (b) bulk SDS with λ↑ = 100 Å and λ↓ = 20 Å; (c) both SDS processes are active.

GMR effect now occurs roughly speaking at λ↓, since for thinner layers the scattering probability in the bulk of F (tF < λ↑ < λ↓) is significantly reduced. In fact the behavior shown in Fig. 7.2 exactly resembles the transformation from a trilayered to a multilayered structure, of which similar calculations have been reported by Dieny [129].

7.2.2 One reflecting interface

Now we will concentrate on a calculation closer to the experimental situation in section 7.3, in which there is only one insulating layer interfaced to a spin-valve sandwich. In Fig. 7.3 the results are shown for a system 80 Å F1 / 25 Å S / tF2 F2 / I, again for bulk and interface spin-dependent scattering and variable reflectivity R. What is observed in this case is analogous to Fig. 7.2 except for the fact that the enhancement of the GMR-ratio as well as the shift of tmax with R is smaller. This is simply because the reflectivity on one side does not allow the electrons to fully experience their mean free path but only partially. In fact for R = 1 the trilayer system is mirrored at the interface F2 / I, and can be regarded as 80 Å F1 / 25 Å S / 2tF2 F2 / 25 Å S / 80 Å F1. This shows that the outer boundaries, although still present, are located further away from F2 compared to R = 0, thereby increasing the GMR-ratio.

We like to note that the impact of reflectivity would have been much smaller when the insulating layer were at the bottom of the trilayer I / 80 Å F1 / 25 Å S / tF2 F2, see Fig. 7.4. In that case
7. Specular reflection in spin-valves bounded by NiO

Fig. 7.4: Calculated GMR-ratio as a function of the thickness of the ferromagnetic layer F2 of the structure I / 80 Å F1 / 25 Å S / t_{F2} F2, for reflectivity $R = 0, 0.5, 1$ at the interface I/F1; at the outer boundary of F2 electrons are diffusively scattered; the mean free path is 100 Å throughout the structure; in (a) interface SDS with $T^{+}/T^{-}/=1$ and $T^{+}/T^{-}/=0.2$ is assumed, in (b) bulk SDS with $\lambda^{+}/=100$ Å and $\lambda^{-}/=20$ Å; (c) both SDS processes are active.

the reflected electron waves may penetrate the second ferromagnetic layer only over a distance $t_F$ before they are scattered diffusively at the boundary. In the experiments that will be used to obtain clues on reflectivity, we have therefore intentionally varied the thickness of the ferromagnetic layer adjacent to NiO; see section 7.3.

7.2.3 Current shunting through metallic FeMn

In the experimental systems, we will compare the GMR-ratio of a system with insulator F1 / S / F2 / I with the system having no insulator on top, but instead an FeMn metallic layer that is exchange biasing F2 to induce the required antiparallel orientation with respect to F1. We will represent this system by F1 / S / F2 / B, with B the metallic back layer. The back layer of the spin-valve may hinder a meaningful comparison with F1 / S / F2 / I since it is able to carry part of the current by which the GMR-ratio will be suppressed or enhanced. Now we will try to find out how to correct for the conductivity of B, yielding the intrinsic GMR-ratio of the trilayer.

In Fig. 7.5 we have modeled the system 80 Å F1 / 25 Å S / t_{F2} F2 / 100 Å B with diffusive scattering at the outer boundaries, without any reflectivity. In accordance with the poor conductivity of FeMn we have chosen rather small mean free paths in B, viz. $\lambda_B = 10$ Å, and 20 Å, which will be confirmed later on experimentally, and $\lambda_B = 0$ to represent the intrinsic magnetoresistance of the trilayer. The calculation shows that, as expected, the GMR-ratio decays with increasing $\lambda_B$,
7.3 Experimental results

All structures were grown by magnetron sputtering in a multisource deposition apparatus with a base pressure better than $1 \times 10^{-8}$ Torr. Metal films were deposited by DC magnetron sputtering at 5 mTorr Ar, and NiO was deposited by RF sputtering from a ceramic target at 1 mTorr and is predominantly (111) oriented after growth, as shown by X-ray diffraction using Cu K$_\alpha$ in Fig. 7.6.
The entire stack of one series of samples is composed of Si(100) / 35 Å Ta / 80 Å Ni₈₀Fe₂₀ / 25 Å Cu / \(t_{\text{NiO}}\) Å Ni₈₀Fe₂₀, each time grown with a 400 Å NiO top layer in one sample and 100 Å FeMn in the next sample, immediately after each other. This ensures an identical structure below the top layer, which is seen in Fig. 7.6 by the (111) and (222) reflections of Cu and Ni₈₀Fe₂₀ in both the NiO and FeMn system. The FeMn samples are capped with 35 Å Ta to protect the structure from corrosion. The reason for interfacing the spin-valve only at one side to the NiO or FeMn is given by the fact that in this configuration we have full control of the growth in relation to the reproducibility of exchange biasing and GMR, which would not have been guaranteed for bottom spin-valves. Moreover, it has been shown by the calculations in section 7.2 that electron reflectivity should be equally evident when a spin-valve is capped with one instead of two insulating layers, provided that the ferromagnetic layer next to the insulator is varied in thickness.

Fig. 7.6: X-ray diffraction spectrum of Si(100) / 35 Å Ta / 80 Å Ni₈₀Fe₂₀ / 25 Å Cu / 40 Å Ni₈₀Fe₂₀ capped with 400 Å NiO (top) and 100 Å FeMn / 30 Å Ta (bottom); the origin of each reflection is indicated by the labels. For clarity the spectra are shifted along the y-axis.

In Fig. 7.7 we compare the room temperature GMR-ratio of a NiO and FeMn sample with \(t_{\text{NiO}}\) = 40 Å. It is seen that an antiparallel orientation of the magnetization is well obtained in both samples indicated by \(\uparrow\) in the figure, which is a necessary condition for a meaningful comparison of GMR in exchange biased spin-valves [121]. This antiparallel orientation is confirmed by the observation of a clear plateau in the magnetization as shown in Fig. 7.8 for \(t_{\text{NiO}}\) = 30 Å. Most important for the present investigation, it is observed in Fig. 7.7 that in these identical structures, apart from the cap layer(s), the GMR-ratio in the case of NiO is roughly a factor 1.3 larger than for FeMn / Ta. Similar results of the magnetoresistance have been obtained for other permalloy thicknesses \(t\) in the range between 10 and 100 Å, which we gathered in Fig. 7.9 for \(T = 10\) K and \(T = 300\) K. We like to emphasize that in all cases shown the required plateau in the magnetoresistance has been observed both at \(T = 300\) K and \(T = 10\) K, except for the NiO data point at \(t_{\text{NiO}}\) = 10 Å where the biasing is lost to some extent.
Apart from the permalloy based spin-valves we have also studied similar series of Si(100) / 35 Å Ta / 80 Å Ni$_{80}$Fe$_{20}$Co$_{18}$ / 25 Å Cu / $t_{Co$_{90}$Fe$_{10}$}$ Å Co$_{90}$Fe$_{10}$, exchange biased again by NiO or FeMn. The choice for Co-richer ferromagnetic layers, Ni$_{80}$Fe$_{20}$Co$_{18}$ and Co$_{90}$Fe$_{10}$, was inspired by the observed enhanced magnetoresistance in particular in the Co-containing systems [116–119], shown also in Fig. 7.1. The GMR-ratio for these structures, see Fig. 7.10, is however only slightly larger than the corresponding Py systems and remains more or less constant upon variation of $t_{Co$_{90}$Fe$_{10}$}$, of which the origin is not yet understood. Most probably this is related to a strong interface spin-dependence of the scattering at Co-rich interfaces [115], which shifts $t_{max}$ to smaller values, see also the calculations shown in Fig. 7.2 and 7.3. Nevertheless, the most important conclusion for these systems is, again, that systematically higher GMR-ratios are observed when NiO instead of FeMn is deposited on top of the identically grown spin-valve trilayer.

![Graph](image)

**Fig. 7.7:** Magnetoresistance relative to the resistance in parallel orientation $R_P$ at $T = 300$ K of Si(100) / 35 Å Ta / 80 Å Ni$_{80}$Fe$_{20}$ / 25 Å Cu / 40 Å Ni$_{90}$Fe$_{20}$ spin-valves, on top of which (a) 400 Å NiO, and (b) 100 Å FeMn / 35 Å Ta is grown; the arrows indicate the state of magnetization.

### 7.4 Discussion

We mentioned that our experiments were designed to facilitate a straightforward comparison between systems with insulating NiO and systems with metallic FeMn on top of a spin-valve grown under equal conditions. Keeping in mind the observed well-defined antiparallel state of the magnetic layers of the spin-valves, one is therefore tempted to directly relate the enhanced GMR-ratio in the case of NiO to the ability of the ferromagnetic/NiO interface to reflect the electron waves when they approach this potential step. However, in the comparison with the all-metal system one should not forget that the current is partially flowing through the metallic FeMn layer as well, see section 7.2, for which it is shown that the magnetoresistance data can be corrected according
Fig. 7.8: Magnetization at $T = 300$ K of Si(100) / 35 Å Ta / 80 Å Ni$_{80}$Fe$_{20}$ / 25 Å Cu / 30 Å Ni$_{80}$Fe$_{20}$ spin-valves, on top of which (a) 100 Å FeMn / 35 Å Ta and (b) 400 Å NiO is grown.
Fig. 7.9: GMR-ratio at $T = 10$ K and $T = 300$ K for the spin-valves Si(100) / 35 Å Ta / 80 Å Ni$_{80}$Fe$_{20}$ / 25 Å Cu / $t_{Ni_{80}Fe_{20}}$ Å Ni$_{80}$Fe$_{20}$ capped with FeMn (open circles) and NiO (open squares); the solid symbols represent the intrinsic GMR-ratio for the FeMn structures, after correction for the conductivity of FeMn; lines are guides to the eye.

Fig. 7.10: GMR-ratio at $T = 10$ K and $T = 300$ K for the spin-valves Si(100) / 35 Å Ta / 80 Å Ni$_{80}$Fe$_{10}$Co$_{10}$ / 25 Å Cu / $t_{Co_{90}Fe_{10}}$ Å Co$_{90}$Fe$_{10}$ capped with FeMn (open circles) and NiO (open squares); the solid symbols represent the intrinsic GMR-ratio for the FeMn structures, after correction for the conductivity of FeMn; lines are guides to the eye only.
the calculated maximum in the GMR-ratio to a lower ferromagnetic layer thickness due to the effectively enlargement of the electron trajectories by specular reflections; see e.g. Fig. 7.3. This feature is however not recovered by our data, which may again indicate that the reflectivity at NiO is far from complete.

Although we have found evidence that the NiO interface is able to enhance the GMR effect in spin-valves, we did not address the microscopic origin behind the reflecting ability of NiO. It may be very important to know how the antiferromagnetic/ferromagnetic (rough) interface and its local electronic structure may affect the scattering processes in spin-valves, and this certainly needs further (theoretical) study. Therefore, we have investigated the possibility of so-called “dead” layer formation at the NiO interface. If we plot the magnetic moment as determined from magnetization measurements in Ni$_{80}$Fe$_{20}$ / Cu / Ni$_{80}$Fe$_{20}$ as exemplified in Fig. 7.8, we observe that 8 to 10 Å of the top Py layer is not responding ferromagnetically, in both NiO and FeMn based spin-valves. This is in contrast to a CEMS study of MBE-grown Ni$_{80}$Fe$_{20}$/Fe$_{75}$Mn$_{25}$ (111) bilayers, in which no significant change in the magnetic moments of the Fe atoms near the interface was observed [133]. However, this is probably due to the differences in the preparation method. On the other hand, for the bottom Py layer we do not observe the presence of a significant dead layer at the interface between Py and Cu, which is in agreement with the investigation reported by Kools [134]. This seems to indicate that at the NiO (and also the FeMn) interface with Ni$_{80}$Fe$_{20}$ the magnetic moments are not ferromagnetically active. Apart from the relevance for exchange biasing to NiO or FeMn, the magnetic state at the interfaces may be of crucial significance for interfacial scattering processes, including the ability to reflect electron waves.

In this discussion, we should mention that the antiferromagnetic FeMn may be a source for additional scattering processes, since the electrons may penetrate the antiferromagnetic layer. Here they have the possibility to undergo spin-flip scattering, which may trouble the comparison with the NiO system. We did not take this into account in the analysis, although spin-flip scattering in principle establishes new boundary conditions for the spin-up/spin-down current densities at the pinned-layer/FeMn interface. However, as we have shown, the intrinsic conductivity of FeMn is very small and is therefore not expected to change the current polarization in the trilayer part of the spin-valve structure considerably, although we are not able to verify this further. Recently, the influence of the antiferromagnetic interface was experimentally addressed in CoO exchange biased spin-valves by Voges et al. [135]. The GMR-ratio was found to be systematically higher as compared to FeMn based spin-valves in agreement with our results for NiO. When crossing through the Néel temperature of CoO no change on the GMR-ratio due to the disappearance of antiferromagnetism was measured, apart from indirect influences caused by changes in the magnetic alignment, which clearly demonstrates that the antiferromagnetism of the interface has no considerable effect on the GMR-ratio.

Finally, we like to mention that in recent work by Egelhoff et al. [136] also evidence was found for enhanced GMR-ratios caused by specular reflectivity of electrons. In this study thin metallic Au, Ag and Cu layers were grown on top of a spin-valve, with the result that the GMR-ratio increases and the resistivity decreases, a sign of specular reflection. In contrast, the deposition of 2 monolayers of species that disorder the surface, such as Ta, Si, C, or Ni$_{80}$Fe$_{20}$ suppresses the specular scattering. Nevertheless, the interpretation of these measurements should be done with care because, intrinsically, the addition of nonmagnetic layers on top of a spin-valve results in an increase of the GMR-ratio, as has been shown in chapter 6, especially for good conducting materials, such as Au, Ag and Cu. Recently, the resistance and the magnetoresistance of
NiO / Co / Cu / Co spin-valves with a noble metal (Ag and Cu) overlayer was monitored \textit{in-situ} during deposition [137]. No evidence for a specularly reflecting surface was found in this study.

7.5 Conclusions

In conclusion, we have presented experimental evidence for the presence of specular reflectivity in metallic spin-valve structures induced by insulating NiO, inferred from the comparison with exchange biasing the same system to FeMn. This was substantiated by transport calculations using the Boltzmann equation in which reflectivity at the interfaces with an insulator has been included.
8. Tunneling magnetoresistance of sputtered FeHf(Si)O cermet films

We have studied the tunneling resistivity and magnetoresistance of reactively sputtered FeHfO and FeHfSiO thin granular films. Maximum magnetoresistance ratios at room temperature of 2.0 % and 3.2 % were observed for films with compositions Fe$_{37}$Hf$_{10}$O$_{33}$ and Fe$_{50}$Hf$_{6}$Si$_{6}$O$_{48}$, respectively. The magnetoresistance shows a decrease with temperature, which cannot be explained by spin-dependent tunneling only. We propose that spin-flip scattering in the amorphous FeHf(Si)O matrix causes this decrease as function of temperature. A two current model for the tunneling magnetoresistance, taking into account spin-flip scattering, is presented which can describe the observed temperature dependence of the magnetoresistance.

The contents of this chapter has been published in J. Appl. Phys. 84, 2749 (1998).

8.1 Introduction

Recently there is large interest for the MagnetoResistance (MR) effect in materials which combine ferromagnetic metals and insulators. The observed MR effect in these materials is often denoted as Tunneling MagnetoResistance (TMR) or Junction MagnetoResistance (JMR) because it is ascribed to the spin-dependent tunneling of electrons between two ferromagnetic materials across an insulating barrier. This TMR effect can be found in layered structures in which a current flows from one ferromagnetic layer (e.g. Co, CoFe) across an insulating layer (often Al$_2$O$_3$) to another ferromagnetic layer in a so-called magnetic tunnel junction [5, 27]. TMR can also be observed in a different class of materials, the so-called cermet films. These are composed of metallic magnetic grains embedded in an insulating matrix, in which the probability for electrons to tunnel from one grain to another depends on the relative orientation of the magnetic moments of the grains. Several granular systems have been studied, for example CoSiO$_2$ [138], FeSiO$_2$ [139,140], CoAl$_2$O$_3$ [141–143] and FeHfO [144]. Among these materials there is particular interest in FeHfO not only for its magnetoresistance but also for its soft magnetic properties [145–147]. In this chapter we report on the observed TMR in reactive sputter deposited FeHfO and FeHfSiO thin films. We will focus on the temperature dependence of the TMR and resistivity which has not been studied in great detail so far and this yields additional insight in the mechanisms for spin-dependent conductivity. The unusual temperature dependence of the TMR of our films is in contrast with earlier studies on CoAl$_2$O$_3$ [143,148] and FeSiO$_2$ [139] and cannot be explained with spin-dependent tunneling only. We propose a model for the temperature dependence of the magnetoresistance in which we have included spin-flip scattering.
8.2 Experimental

All films were prepared by RF diode sputtering on a Perkin Elmer 2400 machine, with a base pressure better than $4 \times 10^{-7}$ Torr, at a sputter pressure of 3 - 4 mTorr from a Fe$_{85}$Hf$_{17}$ target. The composition of the films was varied by changing the partial O$_2$ pressure of the Ar/O$_2$ flow. For the sputtering of the FeHfSiO films 4 % of the target was covered with Si pellets. The films are sputtered on glass and the thickness of the FeHfO and FeHfSiO films is 2.1 and 0.7 $\mu$m, respectively. The composition of the materials was determined with Electron Probe Micro Analysis (EPMA). Resistivity and TMR measurements were done in a standard four point contact geometry with current and field in the plane of the films.

8.3 Results and discussion

Figure 8.1 shows the MR-ratio as a function of the applied field at room temperature of a Fe$_{17}$Hf$_{10}$O$_{43}$ film. The MR is measured with current either perpendicular or parallel with respect to the applied field. As can be seen, there is almost no difference between the two geometries, which shows the absence of a significant contribution of an anisotropic magnetoresistance effect. The MR curves of this film are typical for all of our FeHfO and FeHfSiO cermet materials.

![Figure 8.1: MR-ratio as a function of the applied field at room temperature for Fe$_{17}$Hf$_{10}$O$_{43}$ with current perpendicular (a) and parallel (b) with respect to the applied field. The MR-ratio is defined as $\left( \rho - \rho (\mu_0 H = 1.3 \text{ T} ) \right) / \rho (\mu_0 H = 1.3 \text{ T} ) \times 100 \%.$](image-url)
Figure 8.2 shows the Fe concentration dependence of the TMR and the resistivity at room temperature. The resistivity is extremely large and increases strongly with decreasing Fe concentration, which can be understood as follows. For a large Fe concentration a metallic conductance arises because part of the Fe grains are connected. For lower Fe content the percolation concentration will be approached [149–151] and the grains become electrically isolated by an insulating amorphous FeHf(Si)O phase resulting in tunnel-type conductivity with orders of magnitude larger resistivities as compared to metallic iron ($\rho_{Fe} \approx 10 \, \mu\Omega\cdot cm$). Note the difference in scale between the resistivity of FeHfO and the FeHfSiO films. For Fe concentrations below 45 % for FeHfO and below 40 % for FeHfSiO the layers become fully oxidized and insulating. In both cases the TMR at room temperature peaks near the percolation limit where a small barrier between the grains can be expected. The TMR for the FeHfSiO films has a maximum of about 3.2 % for the composition Fe$_{50}$Hf$_{10}$Si$_{5}$O$_{45}$. For the FeHfO films the maximum TMR of approximately 2.0 % appears at higher Fe concentration for the film with composition Fe$_{17}$Hf$_{10}$O$_{43}$.

Next we present the temperature dependence of the resistivity and the TMR-ratio of the FeHfO and FeHfSiO films. We will focus on the films around maximum TMR because they are believed...
to have an optimal grain size and separation between the grains with respect to the observation of spin-dependent tunneling. X-ray diffraction with Cu $K_\alpha$ radiation for these films, presented in Fig. 8.3, display clear Fe peaks from the grains, a large amorphous background, and a peak around 30° of which the origin is not clear, but possibly this is a combination of HfO$_2$, Fe$_2$O$_3$ and SiO$_2$ crystalline phases.

![Figure 8.3: X-ray diffraction $\theta$-2$\theta$ scan with Cu $K_\alpha$ radiation for (a) Fe$_{17}$Hf$_{10}$O$_{43}$ and (b) Fe$_{40}$Hf$_6$Si$_6$O$_{48}$. The patterns display clear Fe peaks from the grains, a large amorphous background, and a peak around 30°, which possibly results from a combination of HfO$_2$, Fe$_2$O$_3$ and SiO$_2$ crystalline phases.](image)

The temperature dependence of the resistivity of several FeHfO and FeHfSiO films, around maximum TMR, are presented in Fig. 8.4, plotted as $\log \rho$ versus $T^{-1/2}$. This proportionality should represent a thermally activated tunneling current flowing from grain to grain through an insulating matrix as calculated by Sheng et al. [149–151], viz. $\rho \propto \exp(2/\sqrt{C/k_B T})$, with activation energy $C = (2m_e \phi / \hbar^2)^{1/2} s E_c$ ($m_e$ is the electron mass, $\phi$ the effective barrier height, $s$ the separation between the grains and $E_c$ the charging energy). The solid lines are fits to our experimental data of $\rho \propto \exp(2/\sqrt{C/k_B T})$. As can be seen, the fits for FeHfSiO are rather good ($C = 2.6 \times 10^{-3}$ eV for Fe$_{40}$Hf$_6$Si$_6$O$_{48}$). On the contrary, for FeHfO there is a strong deviation between calculation and experimentally observed data ($C = 0.7 \times 10^{-3}$ eV for Fe$_{17}$Hf$_{10}$O$_{43}$). Recently [139] a similar deviation was observed for FeSiO$_2$ and this was attributed to a leak conductivity which flows through interconnected grains. As we will show later on, this seems not to be applicable to our films since a leak conductivity would lead to zero TMR at low temperature when all of the current is shunted through the interconnected grains. We also have to realize that
8.3. Results and discussion

Fig. 8.4: Temperature dependence of the resistivity, $\log \rho$ versus $T^{-1/2}$, for several (a) FeHfO and (b) FeHfSiO films with compositions around maximum TMR. The solid lines are fits to the experimental data according to $\rho \propto \exp 2\sqrt{(C/k_B T)}$, which represents a thermally activated tunneling current flowing from grain to grain through an insulating matrix.

\[ \rho \propto \exp 2\sqrt{(C/k_B T)} \]

was derived for $C > k_B T$, a condition not satisfied in our films and therefore a deviation from this proportionality may be expected at higher temperatures. The magnitude of $C$ is to a great extent determined by the average separation between the grains $s$ and the effective barrier height $\phi$. Since the values of $C$ obtained from our data are of the order of $10^{-3}$ eV, which is one to two orders smaller as compared to for example CoAl$_2$O$_3$ [141] and NiSiO$_2$ [151], this suggests that the individual grains are only poorly separated by the amorphous matrix.

In Fig. 8.5 the temperature dependence of the TMR-ratio is presented. The TMR-ratio of Fe$_{47}$Hf$_{10}$O$_{43}$ increases strongly with decreasing temperature from about 2.0 % at room temperature to about 7.0 % at 4.2 K, in contrast to the TMR-ratio of Fe$_{39}$Hf$_7$Si$_5$O$_{49}$ which increases only slightly. Inoue et al. [152] have shown that the magnetoresistance for ferromagnetic metallic clusters in an insulating matrix is equal to $P^2$ for small values of $P$, with $P = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$ the spin-polarization in the ferromagnetic material. Here, $N_\uparrow$ is the density of states at the Fermi-level with spin-up and spin-down, respectively. Within this model the magnetoresistance is independent of temperature, more or less consistent with the TMR-ratio for Fe$_{39}$Hf$_7$Si$_5$O$_{49}$, but in contrast with the data for Fe$_{47}$Hf$_{10}$O$_{43}$.

There are several possible explanations why a temperature dependent TMR may still be observed in these materials. Recently, an enhanced TMR at low temperatures also was found for CoAlO granular films [148]. The magnetoresistance shows a sharp increase to more than twice...
the value given by $P_{Co}^2$ for temperatures well below the charging energy $C/k_B (< 5 \text{ K})$, and this was explained with the successive onset of higher-order processes of spin-dependent tunneling between large granules through intervening small ones with strong Coulomb blockade. No such dramatic increase at low temperatures was observed for our FeHfSiO films, which is probably due to the fact that the charging energy is lower ($\approx 8 \text{ K for Fe}_{47}\text{Hf}_{10}\text{O}_{43}$) as compared to CoAlO cermet films ($C/k_B$ up to 110 K). The onset of these higher-order processes is therefore far below the minimum temperatures we can reach experimentally.

A second possibility is a reduction of the polarization $P$ at higher temperatures, leading to the observed decrease of the TMR. However, we expect this to be a small effect because of the high Curie-temperature of Fe. Moreover an almost temperature independent TMR was already observed for FeSiO$_2$ [139]. Furthermore, the temperature dependence of the TMR might be related to a change in magnetization behavior of the grains at low temperature. It is known that a superparamagnetic behavior of the magnetic grains in these material leads to a $1/T^2$ dependence of the TMR [152]. Therefore we have measured the field cooled and zero-field cooled magnetic moment of Fe$_{47}$Hf$_{10}$O$_{43}$ as a function of temperature as shown in Fig. 8.6. A wide peak in the zero-field cooled measurement indicates a large spread in grain sizes, with a blocking temperature between 200 and 300 K. Superparamagnetic behavior is limited to temperatures above the block-
ing temperature, which is well above the regime where the strongest temperature dependence of the TMR is observed. Moreover, Fig. 8.7 shows four magnetization loops measured at $T = 10, 75, 150$ and $300\text{ K}$ of Fe$_{17}$Hf$_{10}$O$_{43}$ with the applied field in the plane of the layers. For all temperatures the magnetization loops are similar in shape and seem to behave like a single ferromagnetic layer, with out-of-plane loops (not shown) that saturate at $H = M_s$. For the interpretation of the magnetoresistance data it is important to mention that the magnetization in-plane is well saturated at 1.3 T, the maximum field applied in the transport measurements, which ensures a good parallel alignment of the grains at all temperatures. On the other hand the remanent magnetization is close to zero, which guarantees a high degree of antiparallel alignment of the grains at zero field. It should be noted that the saturation magnetization decreases slightly with increasing temperature, which may indicate a small fraction of paramagnetic grains.

It is clear from the foregoing analysis that there is no dramatic change in magnetization behavior which can account for the large decrease of TMR at higher temperatures, and we believe another mechanism is playing a role causing the temperature dependence of the magnetoresistance. We propose that the strong decrease of TMR at higher temperatures is due to spin-flip scattering which is caused for example by magnetic impurities or iron-rich phases in the matrix. Recently, the effect of barrier impurities in ferromagnetic tunnel junctions was investigated and it was shown that these impurities can severely reduce the TMR as a result of spin-flip scattering [153]. The impact of spin-flip scattering will be analyzed here via a simple model calculation. Fert et al. [154, 155] described the temperature dependent resistance in ferromagnetic materials diluted with transition metal ions and used the resistor scheme as illustrated in Fig. 8.8 to account

![Fig. 8.6: Field cooled and zero-field cooled magnetic moment as a function of temperature of Fe$_{17}$Hf$_{10}$O$_{43}$.](image)
Fig. 8.7: Magnetization loops with the applied field in-plane at various temperatures of 
Fe$_{17}$Hf$_{10}$O$_{33}$.

for the resistivity including spin-flip scattering. The resistance of such a circuit is given by

$$\rho = \frac{\rho_+ \rho_- + \rho_{\uparrow\downarrow}(\rho_+ + \rho_-)}{\rho_+ + \rho_- + 4\rho_{\uparrow\downarrow}}, \quad (8.1)$$

where $\rho_+$ and $\rho_-$ denote the resistivities of the up and down electrons, respectively and where $\rho_{\uparrow\downarrow}$ is the spin-mixing resistivity. We apply this model directly to our granular system. The resistivities $\rho_+$ and $\rho_-$ now consist of the sum of the part of the grains with magnetization ‘up’ and magnetization ‘down’ respectively:

$$\rho_+ = \frac{N}{M} \rho_\uparrow + (1 - \frac{N}{M}) \rho_\downarrow; \quad \rho_- = \frac{N}{M} \rho_\downarrow + (1 - \frac{N}{M}) \rho_\uparrow. \quad (8.2)$$

Here, $M$ is the total number of grains and $N$ is the number of grains with magnetization ‘up’, $\rho_\uparrow$ and $\rho_\downarrow$ are the resistivities for the majority and minority spin electrons with respect to the local magnetization, respectively. The resistivity of Eq. 8.1 can now be expressed in terms of the relative magnetization $m = (2N - M)/M$, as:

$$\rho(m) = \frac{1}{4}(\rho_\uparrow + \rho_\downarrow) - \frac{1}{4} m^2 \frac{\rho_\uparrow - \rho_\downarrow}{\rho_\uparrow + \rho_\downarrow + 4\rho_{\uparrow\downarrow}}. \quad (8.3)$$

Equation 8.3 can be transformed into a similar equation for the resistivity as derived by Inoue et al. [152] with $\rho_\uparrow, \rho_\downarrow \propto \exp 2\sqrt{(C/k_B T)}$, yielding:

$$\rho(m) = \rho_0 (1 - P^2 m^2 F) \exp 2\sqrt{(C/k_B T)}, \quad (8.4)$$
with \( \rho_0 \) constant and \( F \) representing the spin-flip scattering term given by

\[
F = \frac{1}{1 + \frac{\rho_{\uparrow\downarrow}}{\rho_0} \exp 2\sqrt{C/k_B T}}.
\]  

(8.5)

and \( P \) the polarization of the ferromagnetic material (in this model given by \( (\rho_{\uparrow} - \rho_{\downarrow})/(\rho_{\uparrow} + \rho_{\downarrow}) \)).

We use Eq. 8.4 and 8.5 to describe our data of the TMR-ratio, which is defined as:

\[
\text{TMR} = \frac{\rho(m = 0) - \rho(m = 1)}{\rho(m = 1)} \cdot 100 \%
\]  

(8.6)

The spin-mixing rate at finite temperature has been modeled by Fert et al. [155], and evaluated as \( \rho_{\uparrow\downarrow} = \rho_{\uparrow\downarrow}^* \times T^n \) (\( n = 2 \) in case of electron-magnon scattering). The solid lines in Fig. 8.5 show that this model can describe the temperature dependence of the TMR-ratio very well with \( P = 0.26, \rho_{\uparrow\downarrow}^* = 138 \mu \Omega \text{cm} K^{-n} \) and \( n = 1.3 \) for FeHfO, and \( P = 0.18, \rho_{\uparrow\downarrow}^* = 38 \mu \Omega \text{cm} K^{-n} \) and \( n = 1.3 \) for FeHfSiO (\( \rho_0 \) and \( C \) are the same as for the resistivity measurements). The magnitude of \( \rho_{\uparrow\downarrow}^* \) and \( n \) are determined by the details of the spin-flip scattering mechanism, of which we at present do not know the exact origin. The spin-polarization \( P \) is for both systems lower than the polarization of iron \( P_{Fe} = 0.4 \), as reported by Meservey et al. [156], determined from Al / Al₂O₃ / Fe junctions at low temperatures. We should not be surprised by this, since our calculations are inspired by the models of Julliere [27] and Inoue et al. [152], in which the TMR is determined solely by the spin-polarization of the ferromagnetic material. However, it is theoretically argued [157] that the barrier material and the interface matching between barrier and magnetic material may determine the TMR effect as well, although no conclusive experimental data are available yet to verify this. Additionally, we have to realize that our granular films are far from an ideal system of pure Fe grains in an insulating Hf(Si)O₂ matrix and therefore negative effects on the magnitude of the polarization can be expected from for example intermixing of
Fe and Hf and oxidation of Fe. Further experimental study is necessary to determine the exact composition of the grains and the matrix and this may also reveal why spin-mixing is much more prominent in FeHfO than in FeHfSiO.

8.4 Conclusions

In summary we have measured the TMR and the resistivity of reactive sputtered FeHfO and FeHfSiO cermet films. Maximum magnetoresistance ratios at room temperature of 2.0 % and 3.2 % are observed for films with the composition Fe$_{17}$Hf$_{10}$O$_{43}$ and Fe$_{10}$Hf$_6$Si$_6$O$_{48}$, respectively. The resistivity and magnetoresistance show an unusual temperature dependence which cannot be explained by spin-dependent tunneling only. We propose that spin-flip scattering in the amorphous FeHf(Si)O matrix causes this decrease of the TMR as a function of temperature.
9. Nuclear magnetic resonance study of Co / Al + \( t_{\text{ox}} \) O\(_2\) / Ni\(_{80}\)Fe\(_{20}\) thin films

We present a NMR study of evaporated Co / Al + \( t_{\text{ox}} \) O\(_2\) / Ni\(_{80}\)Fe\(_{20}\) thin films, presently receiving much attention because of their tunneling magnetoresistive properties. It is shown that NMR is useful in determining several important fabrication parameters, such as the Co crystal structure and the optimal O\(_2\) plasma oxidation time \( t_{\text{ox}} \) of the Al spacer layer.

9.1 Introduction

As was shown in chapter 1, Tunneling MagnetoResistance (TMR) can be found in layered structures in which a current flows from one ferromagnetic electrode across an insulating barrier to another ferromagnetic electrode in a so-called tunnel junction. The first reports of a tunneling magnetoresistance effect already date from 1975 [27]. It took, however, about 20 years to develop a successful and reproducible procedure for the production of magnetic tunnel junctions, which have a high magnetoresistance [5], and are useful for applications [158]. This was probably due to the fact that the characteristics of a junction depend crucially on the properties of the magnetic layers and the insulating barrier material, which only recently are under control to an extent that reproducible tunnel junctions can be fabricated.

The insulating barrier material now commonly used is Al\(_2\)O\(_3\), which is usually fabricated by in-situ glow-discharge oxidation of a metallic Al layer. In order to observe a high TMR it is important that this layer is thin (of the order of 10 Å). Electrodes and barrier layers must be extremely flat to avoid any direct contacts (pinholes) between bottom and top electrodes. Another important fabrication parameter is the optimal oxidation time (\( t_{\text{ox}} \)) of the Al barrier layer. When the Al is not oxidized long enough, there will be Al left, which has a negative effect on the TMR. On the other hand, when the Al layer is oxidized too long, oxidation of the bottom electrode could occur. In general, there is no unique optimal oxidation time. The optimum conditions vary from system to system and should be optimized for each specific configuration.

In a recent study by van de Veerendonk et al. [159], for example, there were indications that, for 80 Å Co + 12 Å Al + \( t_{\text{ox}} \) O\(_2\) + 80 Å Ni\(_{80}\)Fe\(_{20}\) tunnel junctions, oxidation of the bottom Co electrode starts at about 150 s. This is demonstrated in Fig. 9.1, taken from Ref. [159]. At 300 K the resistance \( R_{\text{p}} \) of the tunnel junctions increases exponentially with the oxidation time, until saturation is reached at about 150 s. Upon a decrease of the temperature from 300 to 10 K, the resistance increase is about 15 - 20 % for the short oxidation times (< 150 s). For the longer oxidation times (> 150 s), however, the tunneling seems to be thermally activated, and the resistance increase upon decreasing temperature is much higher. On the other hand, the magnetoresistance as
function of the oxidation time, shown in Fig. 9.1.b, shows an overall decrease with increasing oxidation time, which is more progressive at 300 K (The apparent maximum in the magnetoresistance at $t_{\text{ox}} = 150$ s and $T = 300$ K is due to a noncomplete antiparallel alignment of the magnetic layers for lower oxidation times). Both the resistance and magnetoresistance behavior can be understood by CoO formation for oxidation times longer than 150 s. The observed thermally activated conductivity is in agreement with semiconducting/insulating properties of CoO. Furthermore, CoO is paramagnetic at room temperature and its uncoupled spins act as an efficient spin-mixer, which lowers the magnetoresistance dramatically. At lower temperatures an antiferromagnetic ordering takes place, which fixes the magnetic moments and reduces spin-mixing.

Fig. 9.1: (a) Resistance for parallel alignment of the Co and Ni$_{80}$Fe$_{20}$ layers ($R_P$) and (b) tunneling magnetoresistance for 10 Å Si + 80 Å Co + 12 Å Al + $t_{\text{ox}}$ O$_2$ + 80 Å Ni$_{80}$Fe$_{20}$ + 20 Å Al tunnel junctions as function of the oxidation time $t_{\text{ox}}$ at 10 and 300 K. For the open squares no full antiparallel alignment of the magnetic layers was reached. The lines are guides to the eye only. The data are taken from Ref. [159].

In this chapter a NMR study is presented of Co / Al + $t_{\text{ox}}$ O$_2$ / Ni$_{80}$Fe$_{20}$ magnetic tunnel junction layers. It is shown that NMR is useful in determining several important fabrication parameters, such as the Co crystal structure and the optimal O$_2$ plasma oxidation time of the Al spacer layer. NMR can be used complementary to other techniques, such as Rutherford Backscattering Spectrometry (RBS), Auger Electron Spectroscopy (AES), or X-ray Photoemission Spectroscopy (XPS). The main advantage of NMR, however, is that it is one of the few techniques capable of
analyzing an oxidized Al layer embedded between Co and Ni$_{80}$Fe$_{20}$ layers.

The organization of this chapter is as follows. After a brief experimental introduction, the structure of the Co layers is determined from $^{59}$Co NMR spectra. Next the optimal oxidation time is determined from $^{59}$Co spin-spin relaxation time measurements. Finally, a first $^{27}$Al NMR spectrum is presented, showing two distinct lines for Al and AlO$_x$.

9.2 Experimental

The layers used for this study have been produced at the Francis Bitter Magnet Laboratory (Massachusetts Institute of Technology) by evaporation in the same deposition facility as used in Ref. [159]. Because of sensitivity reasons it is impossible to measure only one junction produced by shadow mask evaporation (typical junction areas are of the order of $100 \times 100 \mu m^2$). Consequently, we have grown large areas ($4 \times 12$ mm$^2$) without the shadow mask to obtain an acceptable signal to noise ratio in the NMR measurements. The layers have the following composition: $80 \text{ Å Co} + d_\text{Al} \text{ Å Al} + t_\text{ox} \text{ Å O}_2 + 100 \text{ Å Ni}_{80}\text{Fe}_{20}$, with $d_\text{Al} = 12, 14, \text{ or } 16$ Å and oxidation time $t_\text{ox}$ ranging from 30 to 360 s. The layers were grown on $4 \times 12$ mm$^2$ SiO$_x$ substrates with a 10 Å Si seed layer and covered with Al or Ag. The Si adhesion layer, the Co bottom layer, and the Al layer have been grown at cryogenic temperatures to reduce surface roughness. The oxidation of the Al spacer layer took place at room temperature using a DC glow-discharge in an O$_2$ pressure of about $1 \times 10^{-1}$ bar.

9.3 Results and discussion

9.3.1 Co NMR

In Fig. 9.2 the $^{59}$Co NMR spectrum of $10 \text{ Å Si} + 80 \text{ Å Co} + 14 \text{ Å Al} + 150 \text{ s O}_2 + 100 \text{ Å Ni}_{80}\text{Fe}_{20} + 10 \text{ Å Al}$ at $T = 1.5$ K is presented. The spectrum can be divided into two parts: a bulk peak around 218 MHz and an interface part for frequencies lower than about 200 MHz. The intensity of the bulk peak arises from Co atoms with only Co nearest neighbors, whereas the interface signal arises from Co atoms at the bottom and top interfaces with, respectively, Si and Al (and possibly Al$_2$O$_3$) nearest neighbors. The bulk peak consists of a mixture of fcc, hcp$\parallel$ (magnetization parallel to the c-axis), hcp$\perp$ (magnetization perpendicular to the c-axis), and stacking faults (distributed between fcc and hcp), indicating a polycrystalline nature of the Co.

A rough estimation of the interface roughness can be given by evaluating the relative contributions in the interface and bulk spectral range of the spectrum. This is done in Fig. 9.2 by fitting the main peak with a Gaussian distributed line, resulting in 84 % Co (67 Å) with Co neighbors only and 16 % Co (13 Å) with nearest neighbors of a different kind (Si and Al). Unfortunately, no clear satellite resonance peaks in the interface region of the spectrum are visible, which would have allowed for an analysis of the interface region in terms of different nearest neighbor atoms and configurations. However, it is known that when Co is deposited on Si, several cobalt-silicides can be formed, similar to Fe on Si (see chapter 3). Therefore, in our opinion most of the intensity in the interface region of the spectrum is due to cobalt-silicide formation at the bottom interface.

Figure 9.3 shows the NMR spectra of $10 \text{ Å Si} + 80 \text{ Å Co} + 12 \text{ Å Al} + t_\text{ox} \text{ Å O}_2 + 100 \text{ Å Ni}_{80}\text{Fe}_{20} + 30 \text{ Å Ag}$ for $t_\text{ox} = 30, 90, 150$ and 280 s. The spectra are normalized to a total Co thickness
of 80 Å. In general, all the spectra are similar in shape and no systematic changes are observed as a function of the oxidation time, although there are some minor differences in the specific intensity distributions of the bulk peak. Whereas the spectrum for 30 s oxidation time seems to favor slightly more fcc stacking, the spectrum for 280 s oxidation time is more hcp like. These differences, however, seem not systematic and therefore we can only speculate about their origin.

It is obvious that no systematic changes are observed in the spin-echo NMR spectra as function of the oxidation time. However, as was shown in Fig. 9.1, for tunnel junctions grown under equal conditions in the same deposition facility, oxidation of the bottom Co layer seems to start at about 150 s for a 12 Å Al spacer layer. Therefore we expect that antiferromagnetic CoO is also present in our sample for oxidation times longer than about 150 s, although we have seen no changes in the NMR spectra indicating its presence. Possibly, a few monolayers of CoO are not enough to show up in our NMR spectra, but, more likely, the resonance frequency of CoO is not within the range of 150 - 240 MHz. Unfortunately, the resonance frequency of antiferromagnetic CoO is not known. To our knowledge there has been only one NMR study of antiferromagnetic CoO, showing a broad satellite line at about 250 MHz [160]. However, these results have never been reproduced and no resonance signals were observed in our samples at 250 MHz.

Nevertheless, there is an indirect way to establish the presence of CoO via the spin-spin relaxation time of the adjacent Co atoms. In general, the hyperfine field at the nucleus site can be separated in a thermal average, responsible for the resonance frequency shifts, and a fluctuating part which induces random rotations or spin-flips of the nuclear moments, responsible for the relaxation phenomena. Fluctuations are also induced via the thermal motion of the electronic mo-
9.3. Results and discussion

Fig. 9.3: $^{59}$Co NMR spectra of 10 Å Si + 80 Å Co + 12 Å Al + $t_{\text{ox}}$ O$_2$ + 100 Å Ni$_{80}$Fe$_{20}$ + 30 Å Ag at $T = 1.5$ K for various oxidation times $t_{\text{ox}}$ as indicated in the figure.

The spin-spin relaxation time was measured with the CPMG sequence, as explained in chapter 2. As an example, the behavior of $T_2$ as a function of the frequency for 10 Å Si + 80 Å Co + 14 Å Al + 150 s O$_2$ + 100 Å Ni$_{80}$Fe$_{20}$ + 10 Å Al at $T = 1.5$ K is shown in Fig. 9.4. The spin-spin relaxation time is lower for the bulk resonance frequencies than for the interface parts, probably because there are less Co atoms at the interfaces and hence less relaxation possibilities than for the bulk. However, this has not been systematically studied and verified.

Figure 9.5 shows the spin-spin relaxation time at 220 MHz of 10 Å Si + 80 Å Co + 12 Å Al + $t_{\text{ox}}$ O$_2$ + 100 Å Ni$_{80}$Fe$_{20}$ + 30 Å Ag at $T = 1.5$ K as function of Al oxidation time $t_{\text{ox}}$. The relaxation time is constant up to about 150 s and increases strongly for longer oxidation times, showing that beyond 150 s antiferromagnetic CoO adjacent to the Co layer acts as a pinning force. The optimal oxidation time of 150 s, inferred from these results, is in perfect agreement with the resistivity measurements of Fig. 9.1. Finally, it should be mentioned that the ferromagnetic enhancement factor decreases dramatically for larger oxidation times, indicating the formation of CoO as well, as was shown also recently by de Gronckel et al. [161].
9. Nuclear magnetic resonance study of Co/Al + $t_{ox}$ O$_2$ / Ni$_{80}$Fe$_{20}$ thin films

Fig. 9.4: $^{59}$Co spin-spin relaxation time $T_2$ versus frequency of 10 Å Si + 80 Å Co + 14 Å Al + 150 s O$_2$ + 100 Å Ni$_{80}$Fe$_{20}$ + 10 Å Al at $T = 1.5$ K. The resonance frequencies of fcc and hcp Co are indicated by dashed lines.

Fig. 9.5: $^{59}$Co spin-spin relaxation time $T_2$ at 220 MHz of 10 Å Si + 80 Å Co + 12 Å Al + $t_{ox}$ O$_2$ + 100 Å Ni$_{80}$Fe$_{20}$ + 30 Å Ag at $T = 1.5$ K as function of Al oxidation time $t_{ox}$. The solid lines are guides to the eye only.
9.3.2 Al NMR

The progressive oxidation of the Al spacer layer with oxidation time can, in principle, also be monitored by NMR. Metallic Al is paramagnetic and can therefore be distinguished by its Knight shift of 0.162 % [46] from diamagnetic AlO\textsubscript{x} with zero Knight shift. However, because Al is not ferromagnetic, no enhancement of the resonance signals, like for Co, occurs. This causes serious sensitivity problems, because a few monolayers of Al (1 monolayer \( \approx 1 \times 10^{15} \) atoms) is certainly at the lower sensitivity limit of our NMR equipment.

As a first test, we have measured 16 Å Al oxidized for 60 s, confined within 200 Å Co and 60 Å Ni\textsubscript{80}Fe\textsubscript{20} [162]. The results are shown in Fig. 9.6. Clearly, two distinct lines are observed, corresponding to Al and AlO\textsubscript{x}. The Al Knight shift of 0.18 % compares well to previous studies [46]. However, the signal to noise ratio is extremely poor (about 4 for the Al peak) and does not allow for a quantitative interpretation of the data. Nevertheless, some qualitative information can be obtained from this spectrum. It seems that the Al layer oxidizes to AlO\textsubscript{x} layer by layer,

![Fig. 9.6: \textsuperscript{27}Al NMR spectrum of 10 Å Si + 200 Å Co + 14 Å Al + 60 s O\textsubscript{2} + 60 Å Ni\textsubscript{80}Fe\textsubscript{20} + 30 Å Ag at 4.2 K, showing two distinct lines for Al and AlO\textsubscript{x}. The line is a guide to the eye only.

because two separate peaks are observed for Al and AlO\textsubscript{x}, rather than one broad distribution. The Al and AlO\textsubscript{x} lines are dipole broadened by stray fields emerging from the Co and Ni\textsubscript{80}Fe\textsubscript{20} layers. It is known that these dipole fields cause a ferromagnetic magnetostatic (orange peel) coupling between the Co and Ni\textsubscript{80}Fe\textsubscript{20} layers, as was observed recently [163]. The observed linewidth of about 0.004 T is in agreement with the magnitude of the coupling fields deduced in Ref. [163] from magnetization measurements.
Although some qualitative conclusions could be drawn from these experiments, it is obvious that a more systematic study, for example as a function of the oxidation time or the Al spacer layer thickness, is necessary to obtain more quantitative information.

9.4 Conclusions

To summarize, first results were presented of a structural NMR study of evaporated Co / Al + $t_{ox}$ O$_2$ / Ni$_{80}$Fe$_{20}$ thin films. $^{59}$Co NMR shows that the Co layers are not single crystalline, but consist of a mixture of fcc and hcp Co. The spin-spin relaxation time shows that Co is oxidized, when the Al spacer layer is exposed to oxygen longer than 150 s. $^{27}$Al NMR shows two distinct lines of Al and AlO$_x$, dipole broadened by stray fields emerging from the Co and Ni$_{80}$Fe$_{20}$ layers, which might be related to the magnetostatic coupling between the two ferromagnetic layers.
10. Magnetization of Fe₃O₄ / MgO multilayers studied with Mössbauer spectroscopy

The magnetic behavior and structure of Fe₃O₄ / MgO multilayers has been investigated with Mössbauer spectroscopy in field, magnetization measurements and scanning tunneling microscopy. It is shown that detailed structural knowledge of the size of the structural domains and the width of the antiphase boundaries are indispensable in understanding the magnetization behavior of the films and the contradictory results reported in literature.

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10.1 Introduction

In view of possible technological importance of half-metallic Fe₃O₄ (magnetite) in for example all-oxide tunnel junctions, there have been an increasing number of studies addressing the magnetization behavior of thin films of Fe₃O₄ / MgO. However, not all of these studies are in agreement with each other and some contradictory observations are reported.

In a recent study extremely high saturation fields, up to 70 kOe, were observed in 500 - 10 000 Å thick sputtered Fe₃O₄ films [164]. It was suggested that this was related to the presence of AntiPhase Boundaries (APBs) which are formed as a consequence of the nucleation of Fe₃O₄ on MgO [165–167], as illustrated schematically in Fig. 10.1. Because the Fe₃O₄ unit cell \((a_0 = 8.3967 \text{ Å})\) is nearly twice the size of the MgO unit cell \((a_0 = 4.213 \text{ Å})\), Fe₃O₄ can nucleate at different positions on the MgO. Where two domains meet, the oxygen lattice is continued but the cation lattice is rearranged. This has significant influence on cation-anion-cation superexchange interactions between A (Fe³⁺) and B (Fe².₅⁺) sublattice Fe atoms (A-O-A, B-O-B and A-O-B). In contrast to the bulk [165] (1) the number of A-O-A interactions is increased by a factor of 2 and the angle A-O-A is increased towards 180°; (2) a number of B-O-B with an angle of 180° is created; and (3) the number of A-O-B interactions is reduced by a factor of 2. As a consequence, the antiferromagnetic interaction between A sublattice Fe is greatly enhanced and a strong antiferromagnetic interaction between B sublattice Fe atoms is created, while the normal A-O-B interactions is strongly reduced. This favors an antiparallel alignment of the net moment of adjacent structural domains, which explains the observed high saturation fields. Although this can be considered an intrinsic effect of the growth of Fe₃O₄ on MgO, it was observed that in contrast to sputtered layers, 10 - 500 Å thick films produced by means of Molecular Beam Epitaxy (MBE) display much lower saturation fields [168].

A second issue in this field is the question whether or not a magnetically inactive or “dead” interface layer of the order of 10 Å is present in these layers. From neutron reflectometry [169],
10. Magnetization of Fe\textsubscript{3}O\textsubscript{4} / MgO multilayers studied with Mössbauer spectroscopy

![Fig. 10.1: Schematic illustration of the growth of Fe\textsubscript{3}O\textsubscript{4} on MgO. Because the Fe\textsubscript{3}O\textsubscript{4} unit cell is nearly twice the size of the MgO unit cell, Fe\textsubscript{3}O\textsubscript{4} can nucleate at different positions on the MgO. Where two domains meet a so-called AntiPhase Boundary (APB) is formed.](image)

the thickness dependence of the magnetic moment [168], Mössbauer spectrometry [170] and also from the resistivity [171] and the magnetocrystalline anisotropy [172], such a “dead” layer was reported. Nevertheless, in another study [167] Fe\textsubscript{3}O\textsubscript{4} / MgO multilayers with an Fe\textsubscript{3}O\textsubscript{4} layer thickness below 53 Å were characterized by Mössbauer spectroscopy and magnetization measurements, showing no surface effects. In these thin films the presence of APBs is believed to result in a frustration of the superexchange interactions between the domains, permitting the magnetic moments of the domains to fluctuate more or less freely in a superparamagnetic manner.

In this chapter a study is presented of a set of MBE grown Fe\textsubscript{3}O\textsubscript{4} / MgO layers for which magnetic and structural properties from magnetization, Mössbauer and Scanning Tunneling Microscopy (STM) measurements, are combined. It will be shown that, when detailed knowledge of the size of the structural domains and the width of the APBs is available, the magnetization behavior can be fully understood. This suggests that contradictions reported in literature are due to differences in the size of the domains and differences in the width and microstructure of the APBs caused by different preparation conditions.

10.2 Experimental

The films were prepared on MgO(100) single crystalline substrates using the MBE system at Philips Research Laboratories, described in section 2.1.2. The system is equipped with electron-gun evaporators for the deposition of Fe and Ni and with Knudsen cells for $^{57}$Fe and Mg. Oxidation of the layers is achieved by supplying oxygen through a ring-shaped doser located close to the substrate. Fe enriched with 95 $^{57}$Fe is used for the $^{57}$Fe\textsubscript{3}O\textsubscript{4} probe layers. Atomic fluxes are controlled by a cross-beam quadrupole mass-spectrometer system. Prior to deposition the substrates
are annealed for 20 minutes at 550°C in an oxygen atmosphere. Deposition rates are 0.16 Å/s for Fe₃O₄, 0.03 Å/s for ^{57}\text{Fe}_3\text{O}_4, 0.15 Å/s for MgO and 0.15 Å/s for NiO. In-situ Reflection High Energy Electron Diffraction (RHEED) indicated epitaxial growth of MgO and both ^{57}\text{Fe}_3\text{O}_4 and natural iron Fe₃O₄ layers.

A set of 4 multilayers with the following composition was grown: MgO(100) + 4 × (300 Å Fe₃O₄ + 30 Å MgO) + 30 Å NiO, in which each Fe₃O₄ layer was enriched with 2 parts of ^{57}\text{Fe}_3\text{O}_4, positioned symmetrically at 0, 25, 75 and 125 Å distance from the MgO interfaces; see the illustration in Fig. 10.2. The total enriched thickness is 50 Å per Fe₃O₄ layer, which ensures that the observed Mössbauer signal arises mainly from the enriched parts of the multilayer.¹

10.3 Results and discussion

Figure 10.3 shows the Conversion Electron Mössbauer Spectroscopy (CEMS) spectra at room temperature of the multilayers as a function of the position of the enriched ^{57}\text{Fe}_3\text{O}_4 part relative to the MgO interface. The spectra consist of two Zeeman splitted sextets which partly overlap at positive velocities corresponding to Fe^{3+} (A-sites) and Fe^{2.5+} (B-sites). The hyperfine fields for A- and B-sites are 48.6 T and 45.7 T and the isomer shifts are 0.25 mm/s and 0.64 mm/s, respectively, which is in agreement with literature. The relative intensities of A-site and B-site spectrum is 36 % : 64 %, which corresponds to almost perfectly stoichometric Fe₃O₄ [173]. Hyperfine fields,

¹ At the time of these experiments we did not have the disposal of a second Knudsen cell for the deposition of ^{56}\text{Fe}, which would have removed the background signal from the natural iron in the CEMS measurements and would have enabled us to use thinner ^{57}\text{Fe}_3\text{O}_4 layers.
Fig. 10.3: Mössbauer spectra with no external applied field as a function of the position of the enriched part of the Fe$_3$O$_4$ layers. In the top spectrum the fitted two sub-spectra are shown which correspond to Fe at tetrahedral sites (dotted line) and octahedral sites (dashed line). The crystallographic positions of Fe$^{3+}$ and Fe$^{2+}$ are illustrated at the right-hand side in the figure.
isomer shifts and intensity ratios are independent of the enriched layer position, which means that within experimental accuracy there is no indication for a magnetically different layer near the interfaces with MgO. In a way this is surprising since one expects that the magnetic symmetry break at the interfaces disturbs the delicate balance of the ferrimagnetic ordering. Apparently, if such an effect is present, the current 25 Å probe layer is too thick to sense the resulting changes. Alternatively, the concept of a “dead” layer of constant thickness on top of a perfectly aligned ferrimagnetic array might be too simple and the interface effect may propagate through the whole layer. In that case the interface effect results in a homogeneous magnetization which gradually decreases when the thickness is reduced to only a few elementary Fe$_3$O$_4$ cells. Nevertheless, one also has to realize that the observation time period of the CEMS measurements of about 10$^{-8}$ s is short compared to the DC magnetization measurement time ($\approx$ 1 s) allowing the possibility that slow fluctuations of the magnetic spins at the interface are of influence on the measured saturation magnetic moment. Additional experiments are needed to confirm this. In the remainder of this chapter we will focus on the field dependence of the magnetization as observed in the magnetization and CEMS measurements and its relation to the structural domains and the APBs.

The relative intensities for the individual lines in one sextet is $3 : x : 1 : 1 : x : 3$. For all the zero-field spectra $x$ is approximately 2, which means that the magnetic moments either make an angle of 54.7° with respect to the film normal (along [111] direction) or that they are randomly out-of-plane
distributed. In Fig. 10.4 the magnetization hysteresis loop, measured with a Superconducting Quantum Interference Device (SQUID), with the field along the [100] direction is shown of the multilayer with the enriched part in the middle of the Fe$_3$O$_4$. For all the samples the magnetization curves are identical. The magnetization is not saturated up to fields of at least 1.5 T, which is too high to explain in terms of a competition between the different anisotropy contributions, as already was pointed out by Margulies et al. [164] for sputtered Fe$_3$O$_4$ layers. At a field of 0.5 T and 0.8 T, 92 % and 95 % of the saturation moment is reached (relative to the saturation moment for fields higher than 3 T). The inset of Fig. 10.4 is a magnification of the magnetization loop at low fields which shows a remanence of 58 %. This perfectly corresponds to the magnetic moments not randomly distributed but pointing in the easy [111] directions since its projection along [100] yields a remanence of 57.7 %.

![Mössbauer spectra in an external field of 0, 0.5 and 0.8 T in the plane of the layers for the enriched part at the interface and in the middle of the Fe$_3$O$_4$ layers.](image)

Figure 10.5 shows the CEMS spectra of the multilayers with the enriched part at 0 and 125 Å from the MgO interfaces for applied fields of 0, 0.5 and 0.8 T in-plane along the [100] direction. The signal to noise ratio for the spectra in field is somewhat less than without field due to the disturbing influence of the field on the conversion electron paths. Nevertheless, it is again evident that no significant difference can be observed between the spectra for the enriched layer at the interfaces and in the middle, which also holds for the spectra with the probe layer at 25 and 75 Å from the MgO interfaces (not shown). The relative intensities of the lines in both sextets $3:x:3$ increases from $x = 2.0$ without applied field to $x = 3.0$ in an applied field of 0.5 T and up to $x = 3.3$ in an applied field of 0.8 T. From these relative line intensities the
angle $\theta$ between the incoming $\gamma$-rays and the magnetization direction can be calculated, yielding $\theta = 54.7^\circ$, $\theta = 67.8^\circ$ and $\theta = 72.0^\circ$ for 0, 0.5 and 0.8 T, corresponding to a relative in-plane magnetization component of 58, 93 and 95 %, respectively, in almost perfect agreement with the magnetization loop of Fig. 10.4.

From the foregoing CEMS and magnetization measurements we can conclude that the magnetization points along the $[111]$ directions in zero field and cannot be saturated in fields up to at least 0.8 T. As was shown recently [165] this can be explained by the presence of structural domains separated by APBs. The moments of two adjacent domains are antiferromagnetically coupled which leads to frustration when for example three domains meet.

![Image](image_url)

Fig. 10.6: (a) STM image of a $1200 \times 1200$ Å$^2$ region of MgO(100) + 400 Å Fe$_3$O$_4$. Large terraces with steps of 2 Å high can be seen, which is also illustrated in the line profile. APBs are visible on the terraces which is in some cases extend over steps and form large structural domains. (b) Magnification of an APB, which shows that the APBs are broad disordered regions.

Experimental evidence for the existence of APBs in our films we have obtained from STM. In Fig. 10.6.a we present a $1200 \times 1200$ Å$^2$ STM image of MgO(100) + 400 Å Fe$_3$O$_4$, grown under exactly the same conditions as the multilayers. Broad plateaus (different gray shades) of several hundreds of Ångströms wide are visible, separated by monoatomic steps of 2 Å high, corresponding to the distance between two adjacent planes of oxygen or equivalent iron atoms.
On these terraces broad lines are observed which are the APBs separating two regions of the same height rotated over 90°, as shown in Fig. 10.6.b (see also Gaines et al. [166]). The fact that the APBs extend in some cases across steps indicates that the APBs are not induced by the steps but are an intrinsic feature related to the nucleation of \( \text{Fe}_3\text{O}_4 \) on MgO. The large structural domain in the middle of the figure has a width of 550 Å and a length of 1100 Å, which is comparable to the size of the domains observed by Margulies et al. [165]. From STM it is difficult to obtain an average grain size, but recent TEM pictures [174] of a 2000 Å thick MBE grown layer show that the average domain size is of the order of 3000 Å, which is an order of magnitude larger than the domains observed by Margulies et al. We do not know, however, whether the average domain size in this 2000 Å thick film is the same as in our 300 and 400 Å thick films.

Most striking in our films is the width of the APBs which is of the order of 10 to 100 Å, because in the models of Margulies et al. [165] and Voogt et al. [167] it was assumed that the oxygen lattice is continued at an APB, which is clearly not the case. Since the APBs are strongly disordered regions with numerous stacking faults, the magnetic state of this region is not clear [166], which means that the antiferromagnetic superexchange interaction across the APBs is probably strongly suppressed or even absent. It is even not unlikely that also magnetostatic interactions between domains contribute to the frustration of the magnetization [175]. This also explains why different saturation fields are observed in different studies, because the specific preparation conditions may very well determine the width of these APBs and therefore the strength of the antiferromagnetic interactions.
coupling across the boundaries. Detailed knowledge of the size of the domains and the width of the APBs via STM is therefore essential. To quantify the impact of APBs on the magnetization behavior further, we have described the approach to saturation of our layers according to

\[ M \propto 1 - b/H^n, \]  

(10.1)

describing a macroscopic antiferromagnetic chain [165]. Figure 10.7 shows the magnetization curve of Fig. 10.4 for positive fields and the fit according to Eq. 10.1 (The actual fit shown in Fig. 10.7 is \( M \propto 1 - b/(H + c)^n \) which takes into account a small field shift as a consequence of hysteresis). We obtain \( n = 0.5 \), as expected for a competition between Zeeman and exchange energies and \( b = 8.8 \) Oe\(^{1/2}\). Saturation is reached faster than for the films of Margulies et al. [165], which is in agreement with the broad APBs observed in our films as compared to the films of Margulies et al.

### 10.4 Conclusions

In conclusion, CEMS measurements of Fe\(_3\)O\(_4\)/MgO do not show a significant difference between bulk layers and interface layers. The magnetic moments point along the [111] directions in zero field according to CEMS and gradually align along the field consistent with the experimentally observed magnetization, which can be understood by frustration of the moments due to the presence of structural domains in the Fe\(_3\)O\(_4\).
References


[41] W. Kuhn, Phil. Mag. 8, 625 (1929).


[91] The anodic alumina filters were obtained from Whatman International Ltd., Maidstone England.


[162] This spectrum was measured at the Forschungszentrum Jülich, Germany, in cooperation with dr. H.J.M. de Gronckel.


Summary

Magnetic Nanostructures
an experimental study of structural, magnetic and transport properties

In the last decade the research in solid state magnetism is shifting from bulk materials towards smaller structures. Not only fabrication techniques have improved, to an extent that it has become possible to make flat magnetic layers of only a few atomic layers thick, but also nanostructures with even smaller dimensions, such as wires and dots, are attracting more and more attention.

The research of these magnetic nanostructures is driven by exciting physical phenomena occurring in these systems with reduced dimensions, such as interlayer exchange coupling, Giant MagnetoResistance (GMR) and Tunneling MagnetoResistance (TMR). When two magnetic layers are separated by a nonmagnetic spacer (for example Co / Cu / Co), spontaneous antiparallel alignment of the moment directions of the two magnetic layers can be observed, so-called interlayer exchange coupling. It turned out that on application of a magnetic field, which aligns the two moments parallel, a reduction of the resistance can be observed, the giant magnetoresistance effect. This reduction in resistance also occurs for magnetic layers separated by an insulating spacer, which is only in the order of 1 - 2 nm thick so that electrons can tunnel through; so-called tunneling magnetoresistance. The above physical properties can be applied in, for example, magnetic read and write heads, magnetic discs, and Magnetic Random Access Memories (MRAM).

This thesis describes the research of these physical properties in a number of magnetic nanostructures. Much attention is paid to a thorough structural characterization of the materials, because this is essential in understanding the exchange coupling and magnetoresistance effects. A number of experimental techniques were used, such as Nuclear Magnetic Resonance (NMR), Conversion Electron Mössbauer Spectroscopy (CEMS), magnetization measurements (SQUID, MOKE), resistivity measurements, X-ray diffraction (XRD), Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), Scanning Tunneling Microscopy (STM), and Scanning Electron Microscopy (SEM).

The most important results are listed below:

- Chapter 3 deals with the interlayer exchange coupling in Fe / Si / Fe trilayers. With CEMS, AES and LEED it is proven that an Fe$_{1-x}$Si interlayer with CsCl structure is formed, corroborating recent explanations for the interlayer coupling. In chapter 4 it is shown that 90 degree coupling in Fe / Si / Fe is due to so-called “loose spins” in the interlayer.

- In chapter 5 the magnetization behavior of arrays of Co nanowires, grown by electrodeposition in the pores of anodic alumina, is discussed. These wires have a diameter of 20 and 100 nm and vary in length between 0.5 and 40 \( \mu \)m. It is shown that the wires are mag-
netically coupled via direct magnetostatic dipole-dipole interactions. The magnetization direction is determined by a competition of demagnetizing fields and dipole-dipole fields and can be tuned parallel or perpendicular to the wires by changing the length of the wires.

- The GMR effect in Co / Cu / Co layers with very thin Co was studied in chapter 6. In a detailed experimental analysis, substantiated by theoretical arguments, it is shown that spin-dependent scattering at the Co / Cu interfaces is the primary source of the GMR in Co / Cu. Nuclear magnetic resonance measurements show that, for a Co layer thickness of 5 Å the layers are broken up into clusters, which explains the observed reduction of the GMR effect for these thin layers.

- In chapter 7, it is proven, by a direct comparison between FeMn and NiO exchange biased spin-valves, that partial specular reflection of electrons at the NiO interface leads to an increase of the GMR effect. This is substantiated with model calculations, which show the impact of specular reflectivity on the magnitude of the GMR.

- In chapter 8 TMR properties are studied of reactive sputtered FeHfO and FeHfSiO thin granular films, which are composed of Fe clusters surrounded by an insulating FeHf(Si)O matrix. The magnetoresistance shows a decrease with temperature, which cannot be explained by spin-dependent tunneling only. It is proposed that spin-flip scattering in the amorphous FeHf(Si)O matrix causes this decrease as function of temperature.

- In chapter 9 a structural study is presented of Co / oxidized-Al / NiFe thin films, presently under much attention for their tunneling magnetoresistive properties. $^{59}\text{Co}$ nuclear magnetic resonance shows that the Co layers are not single crystalline but consist of a mixture of fcc and hcp Co. The oxidation of Al is the most crucial step in the fabrication of these layers, and our measurements of the spin-spin relaxation time show that Co becomes oxidized when the Al spacer layer is exposed to oxygen too long. This formation of CoO leads to a decrease of the tunneling magnetoresistance.

- In chapter 10 we have investigated the magnetic behavior and structure of Fe$_3$O$_4$ / MgO multilayers with Mössbauer spectroscopy, magnetization measurements and scanning tunneling microscopy. Magnetite (Fe$_3$O$_4$) is a half-metallic ferromagnet and therefore of technological importance for all-oxide tunnel junctions with possibly an infinite tunneling magnetoresistance. A detailed analysis of the direction of the magnetization as function of an externally applied magnetic field showed that these films have a high saturation field because of so-called structural domains in the magnetite.
Samenvatting

Magnetische Nanostructuren
een experimentele studie naar structurele, magnetische en transport eigenschappen

In het laatste decennium heeft het onderzoek naar magnetische materialen zich meer en meer toegelegd op steeds kleinere structuren. Niet alleen zijn de fabricagetechnieken zo sterk verbeterd dat het mogelijk is geworden om vlakke dunne magnetische lagen te maken die maar enkele atoomlagen dik zijn, maar ook gaat men zich meer en meer toeleggen op het onderzoek naar magnetische nanostructuren met nog kleinere afmetingen zoals draadjes, kubussen en bolletjes.

Enkele van de interessante fysische verschijnselen die zich in deze nanostructuren voordoen zijn onder andere de interlayer exchange coupling, het giant magnetoresistance effect (GMR) en daarvan afgeleid het tunneling magnetoresistance effect (TMR). Interlayer exchange coupling is het verschijnsel dat in twee magnetische lagen gescheiden door een niet magnetische tussenlaag (bijvoorbeeld Co / Cu / Co) de magnetische momenten spontaan een antiparallelle oriëntatie kunnen aannemen. Het blijkt dat als deze momenten door een uitwendig magneetveld parallel worden gericht, dit leidt tot een verlaging van de elektrische weerstand, het zogenaamde GMR effect. Deze weerstandsverandering treedt ook op wanneer de magnetische lagen worden gescheiden door een dunne isolator waar de elektronen doorheen kunnen tunnelen. In dit geval noemt men de weerstandsverandering TMR. Deze verschijnselen kunnen worden toegespast in magnetische lees- en schrijfkoppen, informatiedragers en magnetic random access memory (MRAM).

In dit proefschrift wordt het onderzoek beschreven naar deze fysische verschijnselen in een aantal magnetische nanostructuren. Hierbij is er veel aandacht besteed aan de structurele karakterisatie van de materialen, omdat deze essentieel is bij de interpretatie van verschijnselen zoals interlayer exchange coupling en magnetoweerstand. Er is gebruik gemaakt van een aantal experimentele technieken, waaronder kernspinresonantie, Mössbauer spectroscoïpie, diverse technieken voor het meten van magnetisatiecurves, weerstands metingen en diverse structurele analyse technieken waaronder Röntgen diffractie (XRD), Auger elektronen spectroscoïpie (AES), lage energie elektronen diffractie (LEED), raster tunnel microscopie (STM) en elektronen microscopie (SEM).

Hier volgen de belangrijkste resultaten:

- In hoofdstuk 3 is het onderzoek beschreven van de interlayer exchange coupling in Fe / Si / Fe lagen. Met behulp van Mössbauer spectroscopy en LEED is aangetoond dat er in de tussenlaag Fe$_{1-x}$Si in de CsCl structuur wordt gevormd, hetgeen van groot belang is voor het begrijpen van de grootte en dikteafhankelijkheid van deze koppeling. In hoofdstuk 4 is aangetoond dat de 90 graden koppeling in Fe / Si / Fe lagen wordt veroorzaakt door zogenaamde loose spins in de tussenlaag.
Hoofdstuk 5 beschrijft het onderzoek naar Co draadjes die gemaakt zijn met behulp van elektrodepositie in de poriën van aluminiumoxide filters. Deze draadjes hebben een diameter van 20 en 100 nm en variëren in lengte tussen de 0.5 en 40 μm. Het is aangetoond dat magnetostatische interacties tussen de individuele draadjes zorgt voor een voorkeursrichting van magnetisatie loodrecht op de draadassen. Deze voorkeursrichting kan veranderd worden door de lengte van de draadjes aan te passen.

Het GMR effect in Co / Cu / Co lagen met zeer dunne Co lagen werd bestudeerd in hoofdstuk 6. In een uitgebreide analyse onderbouwd met theoretische argumenten is met behulp van deze structuur onomstotelijk aangetoond dat spin afhankelijke verstrooiing aan de Co / Cu grenslagen de belangrijkste bijdrage levert voor het GMR effect in Co / Cu. Met behulp van kernspinresonantie is aangetoond dat afwijkingen voor zeer dunne laagdiktes (< 5 Å) veroorzaakt worden door het opbreken van de continue Co laag in clusters.

In een rechtstreeks vergelijking tussen FeMn en NiO exchange biased spin-valves is aangetoond in hoofdstuk 7 dat gedeeltelijke spiegelende reflectie van elektronen aan het isolerende NiO zorgt voor een verhoging van het GMR effect. Dit is uitgebreid onderbouwd met modelberekeningen van de invloed van spiegelende reflecties aan de verschillende grenslagen op het GMR effect.

In hoofdstuk 8 is het TMR effect in granulaire FeHf(Si)O materialen onderzocht. Deze materialen bestaan uit Fe clusters omgeven door een FeHf(Si)O isolerende matrix. De temperatuursafhankelijkheid van het TMR effect kan begrepen worden als wordt aangenomen dat er in de matrix verstrooiingsprocessen optreden die de spin van het elektron niet behouden, zogenaamde spin-flip verstrooiing.

Hoofdstuk 9 beschrijft het onderzoek naar Co / geoxideerd-Al / Ni$_{80}$Fe$_{20}$. Deze structuren staan de laatste tijd onder grote belangstelling omdat ze een groot TMR effect vertonen. Met behulp van kernspinresonantie is aangetoond dat de Co laag bestaat uit een mengsel van fcc en hcp kristallieten. De geoxideerde-Al laag wordt gemaakt door eerst een Al laag te deponeren die daarna met een zuurstof plasma geoxideerd wordt. Er is aangetoond dat CoO wordt gevormd als de Al laag te lang aan zuurstof wordt blootgesteld. Dit is van belang omdat dit CoO een negatieve invloed heeft op het TMR effect.

Met behulp van Mössbauer spectroscopie zijn magnetiet/magnesiumoxide multilagen bestudeerd, zoals beschreven in hoofdstuk 10. Deze lagen zijn belangrijk voor de ontwikkeling van structuren met een oneindig hoge tunnel magnetoweerstand. Hierbij werd een nauwkeurige analyse gedaan van de richting van de magnetisatie als functie van een uitwendig aangelegd magneetveld waarbij eenduidig is aangetoond dat de magnetisatie moeilijk te verzadigen is tengevolge van zogenaamde structurele domeinen in het magnetiet.
List of publications

- **Loose spins in Co / Cu(100),**
  J.J. de Vries, G.J. Strijkers, M.T. Johnson, A. Reinders, and W.J.M. de Jonge,

- **Analysis of scattering lengths in Co / Cu / Co and Co / Cu / Co / Cu spin valves using a Ru barrier,**
  G.J. Strijkers, M.M.H. Willekens, H.J.M. Swagten, and W.J.M. de Jonge,

- **Analysis of scattering lengths in Co / Cu spin-valves using a Ru barrier,**
  H.J.M. Swagten, G.J. Strijkers, M.M.H. Willekens, and W.J.M. de Jonge,

- **Enhanced giant magnetoresistance in spin-valves sandwiched between insulating NiO,**
  H.J.M. Swagten, G.J. Strijkers, P.J.H. Bloemen, M.M.H. Willekens, and W.J.M. de Jonge,

- **Giant magnetoresistance induced by ultrathin magnetic layers,**
  G.J. Strijkers, H.J.M. Swagten, A.H.M. Mettler, M.M.H. Willekens, and W.J.M. de Jonge,

- **Interface selective determination of spin-dependent scattering,**
  H.J.M. Swagten, G.J. Strijkers, G.L.J. Verschueren, M.M.H. Willekens, and W.J.M. de Jonge,

- **Observation of an exponential FeSi spacer thickness dependence of the antiferromagnetic exchange coupling in Fe / Si-based multilayers,**
  J.T. Kohlhepp, J.J. de Vries, F.J.A. den Broeder, R. Coehoorn, R.M. Jungblut, A. Reinders,
  G.J. Strijkers, A.A. Smits, and W.J.M de Jonge,

- **Temperature dependence of the resistivity and tunneling magnetoresistance of sputtered FeHf(Si)O cermet films,**
  and K.M. Schep,
• Specular reflection in spin-valves bounded by NiO layers,
  H.J.M. Swagten, G.J. Strijkers, R.H.J.N. Bitter, and W.J.M. de Jonge,

• Strong anti-ferromagnetic coupling in \( \tau \)-MnAl/Co perpendicular magnetic superlattices on GaAs,
  C. Bruynseraede, G. Lauhoff, J.A.C. Bland, G. Strijkers, J. De Boeck, and G. Borghs,

• Compositional dependence of the giant magnetoresistance in Fe\(_{x}\)Rh\(_{1-x}\) thin films,
  J. van Driel, R. Coehoorn, G.J. Strijkers, E. Brück, and F.R. de Boer,

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  H. Nishihara, K. Sato, N. Suzuki, T. Kanomata, G.J. Strijkers, W.J.M. de Jonge, F. Wagatsuma, and T. Shinohara,

• Magnetization of Fe\(_x\)O\(_y\) / MgO multilayers studied with Mössbauer spectroscopy,
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• Structure and magnetization of arrays of electrodeposited Co wires in anodic alumina,
  G.J. Strijkers, J.H.J. Dalderop, M.A.A. Broeksteeg, H.J.M. Swagten, and W.J.M. de Jonge,

• Direct observation of the formation of nonmagnetic c-Fe\(_{1-x}\)Si in antiferromagnetically coupled epitaxial Fe / Si / Fe,
  G.J. Strijkers, J.T. Kohlhepp, H.J.M. Swagten, and W.J.M. de Jonge,

• Nuclear magnetic resonance study of thin Co layers on single crystal substrates,
  G.J. Strijkers, J.T. Kohlhepp, H.J.M. Swagten, and W.J.M. de Jonge,

• Origin of biquadratic exchange in Fe / Si / Fe,
  G.J. Strijkers, J.T. Kohlhepp, H.J.M. Swagten, and W.J.M. de Jonge,
  to be submitted for publication (1999).
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Curriculum vitae

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Magnetic Nanostructures, an experimental study of structural, magnetic and transport properties
STELLINGEN

behorende bij het proefschrift

Magnetic Nanostructures

an experimental study of structural, magnetic and transport properties

door

Gustav Jacob Strijkers

Eindhoven, 30 september 1999
1. De identificatie van hcp en fcc satellietlijnen in het NMR spectrum van een dunne Co laag gegroeid op een Cu(111) één-kristal kan niet worden gedaan op grond van een vergelijking van bulk en satelliet intensiteiten.

2. Biquadratische koppeling in Fe / FeSi / Fe is geen intrinsiek hogere orde term van de bilineaire koppeling maar wordt veroorzaakt door zogenaamde “loose spins” in de FeSi laag.
   - Dit proefschrift, hoofdstuk 4.

3. In de experimenten gedaan door Bailey e.a., die het doel hadden spiegelende reflecties van elektronen in NiO / Co / Cu / Co met een Ag of Cu afdeklaag aan te tonen, is de bovenste Co laag te dik. Om spiegelende reflecties eenduidig aan te kunnen tonen, moet deze Co laag dunner zijn dan die dikte waarbij een maximum in het reuzenmagnetoweerstandseffect optreedt.

4. Bij de interpretatie van de afname van het tunnelmagnetoweerstandseffect in magnetische tunneljuncties met een extra metalische laag op of onder de Al₂O₃ tunnelbarrière, dient terdege rekening gehouden te worden met de structuur en de magnetische eigenschappen van deze extra laag.

5. De geïnduceerde Kerr rotatie en ellipticiteit, zoals gemeten in ultrasnelle spindynamica experimenten aan ferromagnetische materialen, is niet direct gerelateerd aan een verandering van de “magnetisatie”.
6. De rol van de raster tunnel microscoop bij de karakterisatie van steeds kleinere nanostructuren kan in de toekomst worden overgenomen door de magnetische resonantie kracht microscoop, omdat deze de mogelijkheid gaat bieden driedimensionale afbeeldingen op atomaire schaal te maken.


7. De elektrische doorslag in magnetische tunneljuncties kan op een microscopische schaal zichtbaar worden gemaakt met behulp van de raster tunnel microscoop.

W. Oepts e.a., Appl. Phys. Lett. 73, 2363 (1998).

8. De verklaring van het magnetoweerstandseffect, waargenomen bij twee op elkaar gedrukte nikkel draden, in termen van spin-afhankelijke geleiding is niet in overeenstemming met het feit dat eenzelfde effect ook wordt waargenomen als de draden worden bedekt met een relatief dikke laag koper.