Lattice-matched Magnetic Tunnel Junctions Consisting of Highly Spin-polarized Co_2FeAl Heusler Alloy Electrodes and a Spinel Barrier

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Abbreviations

AFM	atomic force microscope
AP	anti-parallel
CFA	$Co_{47.4}Fe_{24.4}Al_{28.2}$
D-ICP	direct inductively coupled plasma oxidation
DC	direct current
DOS	density of states
EDS	energy dispersive X-ray spectrometer
FFT	fast Fourier transform
FM	ferromagnet
FWHM	full width at half maximum
GMR	giant magnetoresistance
HAADF-STEM	High-resolution high-angle annular dark-field scanning transmission electron microscopy
I-ICP	indirect inductively coupled plasma oxidation
MBE	molecular beam evaporation
ML	magnetic layer
MRAM	magnetic random access memory
MTJ	magnetic tunnel junctions
NBD	nano-electron beam diffraction
NM	nonmagnetic
P	parallel
PAM	phase accumulation model
PC	personal computer
PMA	perpendicular magnetic anisotropy
RF	radio frequency
RT	room temperature
TMR	tunnel magnetoresistance
WKB	Wentzel-Kramers-Brillouin

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1 Introduction

Spintronics as we know it nowadays, is, compared to other scientific fields, a rather young research area. The term itself is a portmanteau meaning 'spin transport electronics' referring to the field of studying materials and (electronic) devices which use, besides the electronic charge, the electron spin (and its magnetic moment) to transport and store information. The beginnings reach back to the 1980's with the observation of perpendicular magnetic anisotropy (PMA) in ultrathin films by Carcia et al. [1], important for modern storage devices in which the magnetization points along the normal of the film leading to the possibility of reducing its size to create denser storage devices [2, 3]. Actual transport measurements through stacks of in-plane magnetized magnetic layers (ML) separated by a nonmagnetic conducting (NM) spacer was first demonstrated independently by Baibich et al. [4] and Binasch et al. [5]. They showed that the stack resistance changes dependent on the relative orientation of the magnetization of the two magnetic layers which can be switched by an external magnetic field with a minimum (maximum) resistance for parallel (P) [anti-parallel (AP)] magnetization orientations. Nowadays, this effect in similar structured devices (ML/NM/ML) is known as giant magnetoresistance (GMR) because of the large resistance changes even at room temperature (RT). Tunnel magnetoresistance (TMR) devices use the same effect as do GMR devices but the conducting layer is replaced by an insulating spacer. These magnetic tunnel junctions (MTJs) have already been widely studied in layered structures, i.e. by Julliere (1975) [6] and Maekawa & Gafert (1982) [7], though, receiving less attention than GMR devices. Nevertheless, inspired by the results in GMR devices research effort on MTJs also grew especially in the 90's with a breakthrough in 1995 due to the discovery of TMR higher than GMR in junctions with a ferromagnet (FM), i.e. CoFe, Fe, and an amorphous Al_2O_3 spacer layer [8, 9]. Successively, TMR in this kind of junctions increased above 70% outperforming GMR devices [10]. As common in MTJs the TMR is defined as $(R_{AP}\text{-}R_P)/R_P$, with R_{AP} (R_P) being the junction resistance in the AP (P) magnetization state. During this time, it was theoretically predicted that much higher TMR ratios can be obtained with a crystallized barrier in which a highly spin-dependent evanescent decay of specific wave-functions occurs [11]. Especially, TMR in crystallized, (100)-oriented Fe/MgO/Fe junctions was theoretically calculated to possibly reach over 1000% [12, 13] without realizing it in actual tunneling devices [14].

A breakthrough was made in 2004 by Parkin et al. with the observation of giant TMR ratio of 220% at room temperature in epitaxial, polycrystalline, sputter-deposited CoFe(100)/MgO/CoFe junctions with a low temperature spin polarization of CoFe of 85% [15]. Even higher TMR ratios in similar junctions consisting of CoFeB/MgO/CoFeB of 355% were fabricated and attributed to the flat and highly (001)-orientation of the CoFeB electrode and MgO barrier with, therefore, a smooth interface [16]. Furthermore, 410% at RT were realized in MTJs with bcc-Co(100) electrodes and an MgO barrier due to the electrode's band structure and the associated improved spin polarization compared to Fe [17]. Nevertheless, one of the highest TMR values are observed in CoFeB/MgO/CoFeB junctions with a RT TMR of over 600% by suppression of Ta diffusion in the stacks [18]. All of these junctions have features in common: (1) Usage of a highly spin-polarized FM electrode and (2) An MgO barrier. It

was early realized that these two ingredients are extremely important to achieve high TMR, with the focus on searching for highly spin-polarized electrodes. Mostly, in all high-TMR junctions MgO is used as the barrier, simply due to the lack of other materials with similar characteristics (i.e. Δ_1-symmetry filtering, easily sputter-deposited, highly oriented growth on top of FM electrodes, etc.).

In recent years, Heusler alloys have received a lot of attention from the spintronics community because they are the most promising candidates to show perfect bulk spin-polarization at RT compared to other materials, e.g. Fe_3O_4, perovskites, etc. First attempts to fabricate MTJs in the early 2000's with Heusler alloys were done with an amorphous Al_2O_3 barrier resulting in rather low TMR ratios (compared to one would expect from their theoretically high spin-polarization) at RT for junctions with, i.e. NiMnSb (9%) [19] $Co_2Cr_{0.6}Fe_{0.4}Al$ (16%) [20], Co_2MnAl (65%) [21, 22, 23], Co_2MnSi (70%) [24] (max. TMR in brackets). Problems in these junctions were the use of an amorphous barrier which does not exhibit the coherent tunneling effect and oxidation of the Heusler alloy interfaces reducing the alloy's spin-polarization. Realizing the importance of a crystalline barrier, soon after the first attempts, junctions combining high spin polarization and coherent tunneling were investigated. Giant TMR around 200% was first observed in $Co_2FeAl_{0.5}Si_{0.5}/MgO/Co_2FeAl_{0.5}Si_{0.5}$ by Tezuka et al. [25, 26]. This is a huge jump compared to junctions with Al_2O_3 barrier showing the importance of the coherent tunneling effect. With improved fabrication techniques, TMR could be increased (max. TMR in brackets): Co_2MnSi (236%) [27], Co_2FeAl (330%) [28] and $Co_2FeAl_{0.5}Si_{0.5}$ (386%) [29]. All these examples illustrate the importance of Heusler alloys in achieving giant TMR values but at the same time also reveal a downside. Although, Heusler alloys are predicted to have perfect *bulk* spin polarization, in reality those values are usually not observed, especially, in magnetic tunnel junctions in which the interface between FM electrode and NM barrier plays a crucial role. One needs to realize that the electronic structure at the interface can be greatly altered and usually differs from the bulk electronic structure. Causing effects are disordering, oxidation, etc. Therefore, developing MTJs is a delicate process which does not only require understanding of the electrode's characteristics and barrier but also its interfaces to achieve higher TMR values necessary for reducing the junction size for denser storage devices and larger signal to noise ratios.

Another approach and ongoing research is done for devices with perpendicular (to the film plain) magnetized electrodes as mentioned earlier. Although not within the scope of this thesis, it is important to know because it is closely related to in-plane magnetized MTJs and it is important for future applications. The advantage is the large PMA in these films, strong enough to withstand thermal fluctuations of magnetization at junction sizes as small as 40 nm in (001)-oriented CoFeB/MgO/CoFeB [30]. To realize PMA one has to create films that show magnetic anisotropy perpendicular to its plane. One has to consider three types of anisotropies in thin films: magneto-crystalline anisotropy, shape anisotropy and interface anisotropy. The shape anisotropy is small and usually does not play an important role. For many materials, magneto-crystalline anisotropy tends to force the magnetization in-plane and is in competition with the interface anisotropy which rotates the magnetization out-of-plane. Because the magneto-crystalline anisotropy depends on the films' volume, PMA can be achieved by drastically reducing the layer thickness. This has been realized in many thin films, i.e., Co/Pd and Co/Pt thin-film layered structures [31], ultra-thin Fe films [32, 33], CoFeB thin films [30], and Heusler alloy films (for review, see [34]) and implemented into MTJs [30, 35, 36, 37]. Here, the use of Heusler alloys is promising because of their rather high PMA, low damping constant, high Curie temperatures and

Figure 1.1: (a) Magnetic random access memory by Everspin [43] and schematic of the two states for one cell; (b) Read head [44] with schematic.

high spin-polarization. Especially, low damping constants are import for spin transfer torque (STT) devices in which, by applying a large enough current, an oscillating switching of the magnetization occurs in one layer (without the use of an external magnetic field) (for details, see [38]).
As already mentioned, the most widely used barrier material for MTJs (both in-plane and perpendicular magnetized) is MgO. The monopoly can be explained by the non-existence of other suitable barrier materials which exhibit the coherent tunneling effect (see Section 2.2 for details) and can be fabricated easily. However, MgO has some disadvantages that makes it less attractive for industrial applications, e.g. its quite large lattice mismatch with the most commonly used bcc-FM electrodes (i.e. Fe, CoFe, Heusler) which might lead to quenching of TMR for nanometer-sized MTJs, and its deliquescence reducing the MTJ endurance and hence, reducing the live time of possible devices. It is therefore necessary to discover new barrier materials with the same tunneling characteristics as MgO - that means a similar symmetry filtering effect - and incorporate them into MTJs. One possible material is spinel oxides which, although, having a special structure (see Section 2.4 for details), can be considered as having a cubic crystal structure. In 2010, MTJs with a crystalline, epitaxial $MgAl_2O_4$ barrier were reported with 120% TMR ratios at RT [39]. $MgAl_2O_4$ has the advantage of almost perfect lattice-matching with bcc-FM and non-deliquescence. Unfortunately, theoretical calculations by Miura *et al.* estimated a maximum TMR of 160% in Fe/$MgAl_2O_4$/Fe(001) junctions which is much lower than 1600% TMR as estimated for a similar stack with an MgO barrier [40]. They also calculated the band structure of the spinel to be similar to MgO. However, besides the theoretical limitation, a breakthrough was made in 2012 by Sukegawa *et al.* with giant TMR ratios over 300% in Fe/$MgAl_2O_4$/Fe(001) junctions with a cation-disordered barrier [41]. The reason for this strong improvement is the band-folding effect as explained in section 2.4. By introducing cation-disorder in the barrier, it is possible to suppress the effect resulting in higher TMR ratios. Another promising property is the wide range of RA values than can be achieved in MTJs with a post-oxidized spinel barrier without losing the high TMR by using different oxidation methods [42].

Motivation and Outlook

MTJs are widely used and can be found in many devices we use everyday. Examples for that are magnetic random access memory devices for fast and non-volatile storage of data. In these devices the high and low resistance state of an MTJ can be used to store one bit [Fig. 1.1 (a)] . Another application is the use as magnetic sensors i.e., in cars. One of the newest application is the use of MTJs in the read heads in hard disc drives in computers which sense the state of the recoding media below while rotating above it [Fig. 1.1 (b)] . All of these applications operate on the fact that the magnetization of one electrode layer can be reversed while the second electrode keeps fixed.
MTJs with a $MgAl_2O_4$ barrier facing two main problems at present which are: (1) Exploration and growth of other than already studied electrode materials (i.e. highly spin-polarized Heusler alloys) to enhance TMR seems difficult; (2) High TMR ratios are only achieved in MTJs with a *disordered* spinel barrier. Especially, latter one is a big obstacle considering the development of MTJs with other spinel oxide materials which tend to be ordered near RT and disorder at elevated temperatures [45, 46]. The enhancement of TMR is a more general problem that also concerns MTJs with an MgO barrier. Although giant TMR ratios have been achieved in CoFeB/MgO/CoFeB MTJs, they are limited to highly specialist laboratories and cannot be achieved in commercial devices. Furthermore, those reports date back to the year 2008. Since then, no improvement of TMR was reported for common bcc-FM (Fe, Co, FeCo, and CoFeB) (see Fig. 1.2). However, improving TMR ratio is needed for applications because it leads to a better separation between P and AP state which usually limits the sensing of the 0 and 1 state. Additionally, MTJ devices naturally show scattering of the R_P and R_{AP} and are sensitive to the deposition process. Sense amplifiers are required to distinguish P and AP state in nowadays MTJs with a TMR ratio of 200-300%. This means a size increase of an magnetic random access memory (MRAM) cell reducing the storage density [47]. To avoid this giant TMR values are necessary.

Figure 1.2: Development of TMR ratios with common bcc-FM (Fe, Co, CoFe, and CoFeB) with Al_2O_3 (blue diamonds) and MgO (black squares) barriers; Numbers in brackets show RT and low temperature (LT) TMR ratios respectively.

The aim of this study is the fabrication and characterization of MTJs that use a $MgAl_2O_4$ barrier with highly spin-polarized Heusler Co_2FeAl alloys. Choosing this combination, I want to achieve lattice-matched MTJs with giant TMR ratios and good bias voltage dependence. This would lead to an alternative to nowadays used MgO barriers and devices with higher storage densities for future spintronic applications.
The aim of this study is the first time fabrication and characterization of single-crystal, epitaxial MTJs using a $MgAl_2O_4$ barrier and highly spin-polarized Co_2FeAl Heusler alloys to achieve good lattice-matching at the electrode/barrier interfaces and giant TMR ratios. The dream is to exceed 1000% which thus far has not been observed in MTJs. Additionally, I expect good TMR vs. bias voltage performances of the devices which is necessary for actual applications that usually operate at non-zero bias voltages.

This thesis investigates the fabrication and characterization of MTJs that combine highly spin-polarized Heusler alloys with the $MgAl_2O_4$ spinel barrier. This work is separated into four major parts. The first section consists of the theory which is necessary to understand the results and for further discussions. First an introduction to the tunnel process between normal metals is given and connected to tunneling between magnetic metals in MTJs. Some characteristics i.e., temperature and bias voltage dependence are explained. Finally, $MgAl_2O_4$ and Heusler alloys are introduced. The experiment section contains a detailed description of the performed measurements and fabrication methods. Thereafter, in the results and discussion part, first, the results of $Co_2FeAl/MgAl_2O_4/CoFe$ MTJs followed by the section of $Co_2FeAl/MgAl_2O_4/Co_2FeAl$ MTJs. Both sections discuss temperature and bias voltage dependence, the effect of CoFe insertion at the interface and structural characterization. The final section presents the first time fabrication of MTJs with a Li-substituted $MgAl_2O_4$ barrier and Fe electrode.

2 Theory

In this section, the basic concepts of electron tunneling will be described and related to MTJs. Additionally, the characteristics of MTJs together with several models which try to explain them are presented. At the end, a theoretical background of the in this study used materials - Heusler alloys and spinel material - is given.

2.1 Physics of Tunneling

One-dimensional electron tunneling is subject to undergraduate quantum mechanics and is also the basic concept of MTJs [48]. Although, in reality, one usually deals with two-dimensional tunneling (MTJs sputtered on a substrate).
At the beginning, one starts with considering an insulator of thickness t sandwiched between two metals. A free electron with mass m and energy E is incoming at the left side of the barrier with constant height V_0, see Fig. 2.1. In good approximation, this is also the case for the conducting electrons in MTJs incoming from the electrode on the barrier. The time-independent Schrödinger equation for a particle wave is:

$$\frac{d^2}{dx^2}\psi(x) = -\frac{2m}{\hbar^2}\left[E - V_0\right]\psi(x)$$

The general solution for such a differential equation can be written as a superposition of two waves ψ_1 and ψ_2 and is $\psi = A\psi_1(x) + B\psi_2(x)$, with A and B are constants. A detailed analysis of the above equation leads to the following wave function:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

with $k = \sqrt{2m(V_0 - E)/\hbar^2}$. The constants are determined by the boundary conditions. In case of electron tunneling, the wave function will change depending on the region:

$$\begin{aligned}
\psi_1(x) &= e^{ik_1x} + re^{-ik_1x} && x \leq 0 \\
\psi_2(x) &= Ae^{ik_2x} + Be^{-ik_2x} && 0 \leq x \leq a \\
\psi_3(x) &= te^{ik_1x} && x \geq a
\end{aligned}$$

with t and r being the transmission and reflection coefficients, respectively. Both coefficients are connected by $|r|^2 = 1 - |t|^2$. A and B are coefficients that need to be determined. Using the continuity

conditions at $x = 0$ and $x = a$:

$$\psi_1(0) = \psi_2(0) \qquad \psi_2(t) = \psi_3(a)$$
$$\frac{\partial\psi_1(0)}{\partial x} = \frac{\partial\psi_2(0)}{\partial x} \qquad \frac{\partial\psi_2(a)}{\partial x} = \frac{\partial\psi_3(a)}{\partial x}.$$

Obtaining the transmission coefficient, it is possible to determine the transmission probability T:

$$T = \left|t^2\right| = \frac{1}{1 + \frac{V_0^2}{4E(V_0-E)}\sinh^2(k_2 a)} \qquad E > 0; E < V_0.$$

One can see that for $V_0 \to 0$, $T \to 1$ which reflects the case of no barrier. For low energies and wide barriers ($k_2 a >> 1$) the transmission becomes an exponential function:

$$T \propto exp\left(-2k_2 a\right) = exp\left(-2\sqrt{2m(V_0 - E)/\hbar^2} \cdot a\right). \tag{2.1}$$

The difference $V_0 - E$ is referred to as the effective barrier height Φ. In a more realistic case, the barrier height, an incoming electron sees, is different on each side of the barrier. In nature, the interfaces are never the same because of different sputtering conditions. Additionally, the potential the electrons see is not constant and varies with tunneling distance x due to an naturally imperfect barrier. Therefore, in a more general approach and under the condition of the Wentzel-Kramers-Brillouin (WKB) approximation (the potential of the barrier $V(x)$ varies slowly across the barrier), the transmission probability changes to an integral over the barrier region and is a function of $V(x)$. It can be written as:

$$T \propto exp\left(-2\int_0^a \sqrt{2m(V(x) - E)/\hbar^2}dx\right). \tag{2.2}$$

It is easily seen that for a constant barrier height, the integral is the same as for Eq. 2.1. In the case of two-dimensional tunneling the Schrödinger equation becomes more difficult to solve. In the two-dimensional case, the wave function as well as the barrier become two-dimensional functions and can be solved similarly to the one-dimensional case. In fact, if electrons reach the barrier under an

Figure 2.1: One-dimensional tunneling of an electron (displayed as a wave) from left to the right through a barrier of fixed height V_0 and width a.

off-normal angle, a non-zero parallel wave-momentum $k_{\parallel}$ needs to be taken into account. Therefore, the exponent in the equation of Eq. 2.2 gets replaced by $2m(V(x)-E)/\hbar^2+k_{\parallel}^2$. This is of importance for actual devices as it shows, that on rough electrode/barrier interfaces, at which electrons can tunnel at an angle, the tunneling probability is significantly reduced.
A tunneling current over the barrier will occur only at finite bias voltages. This current is proportional to the occupied and unoccupied density of states (DOS) at the Fermi energy of the left and right electrode, respectively. Hence, the tunneling current for small Voltages $eV << \Phi$ is:

$$I \propto N_{\mathrm{L}}(E_{\mathrm{F}})N_{\mathrm{R}}(E_{\mathrm{F}})T(\Phi,t)\int_{-\infty}^{\infty}\left(f(E-eV)-f(E)\right)dE,$$

with the DOS at the Fermi level of the left and right electrode and the transmission probability as shown in Eq. 2.1. At low enough temperatures ($eV << k_BT$), the integral is simply eV which leads to a tunnel conductance:

$$G = dI/dV \propto N_{\mathrm{L}}(E_{\mathrm{F}})N_{\mathrm{R}}(E_{\mathrm{F}})T(\Phi,t) \tag{2.3}$$

and is in this simple model dependent on the DOS of the electrodes and the tunneling probability.

2.2 Magnetic Tunnel Junctions

MTJs use the tunneling principle as described above but with a difference in the electrodes. Instead of using a simple conducting electrode, (usually ferro-)magnetic conducting electrodes are used. In such devices, the spin of the electrons reaching the barrier play an important role. The spin state of the electrons is usually referred to up and down or majority and minority depending on the magnetization of the electrode. The magnetization of the electrodes can have two different states relative to each other. As seen in Fig. 2.2(a) and (b), the magnetization can be P or AP. Coming back to the tunneling probability presented in Eq. 2.1 the barrier height V_0, each tunneling electron experiences, depends on the relative orientation of the electrodes magnetization. The reason for the different tunneling probabilities can be explained by a simple two band model, called the Julière model [6]. Firstly, one considers an MTJ with the same electrodes on both sides of the barrier and electrons tunneling from left to right. In the parallel state (spin-up state in this example), most of the electrons at the Fermi energy are in the 'spin-up' state, see Fig. 2.2(a). These majority carriers can easily tunnel over the barrier into the other FM because it has a lot of empty states at E_{F}. The same happens for the minority ('spin-down') electrons but the tunneling current will be much smaller due to a lesser number of carriers at E_{F}. After switching the magnetization of the right-side electrode (Fig. 2.2(b)), the occupation the electrons changes, too. Now, the number of empty minority states at E_{F} is much larger than the number of majority states. Thus, only a few majority electrons from the left electrode can cross the barrier. Although, there are many empty minority states in the right electrode, the number of minority electrons supplied by the left electrode is still small.

2.2.1 Tunnel Magnetoresistance and the Resistance Area Product

In the P magnetization state, a larger number of electrons can tunnel as compared to the AP state. This will lead to a change in the resistance when switching the magnetization from P to an AP state,

Figure 2.2: Band model of an MTJ in parallel (a) and antiparallel (b); arrows representing electrons tunnel from left to right; arrow thickness indicates the probability for electrons to tunnel; (c) Sketch of the resistance as a function of an external magnetic field for a typical MTJ.

see Fig. 2.2(c). The relative change of the resistance (R) or conductance (G) is called the tunnel magnetoresistance (TMR) and is:

$$TMR = \frac{R_{\mathrm{AP}} - R_{\mathrm{P}}}{R_{\mathrm{P}}} = \frac{G_{\mathrm{P}} - G_{\mathrm{AP}}}{G_{\mathrm{AP}}}. \tag{2.4}$$

In general this relation is valid only for small bias voltages because only then $G = 1/R$. Of course, this gives only a quantitative number. The simple physical explanation of TMR was first described and defined by the Jullière [6] formula:

$$TMR = \frac{2P_{\mathrm{L}}P_{\mathrm{R}}}{1 - P_{\mathrm{L}}P_{\mathrm{R}}} \tag{2.5}$$

which relates the TMR to the tunneling spin-polarization $P_{\mathrm{L/R}}$ of the left and right electrode. The spin-polarization is defined as:

$$P = \frac{N_{\mathrm{maj}}(E_{\mathrm{F}}) - N_{\mathrm{min}}(E_{\mathrm{F}})}{N_{\mathrm{maj}}(E_{\mathrm{F}}) + N_{\mathrm{min}}(E_{\mathrm{F}})}, \tag{2.6}$$

the difference of majority and minority electrons at the Fermi level divided by the total number of electrons. Bear in mind that for perfectly spin-polarized electrodes ($P_{\mathrm{L/R}} = 1$) the TMR becomes infinite which can be achieved by electrode materials with a fully spin polarized band structure,

i.e. $N_{\min}(E_{\mathrm{F}}) = 0$. Note, that to obtain correct results, the spin DOS at the interface have to be considered as they are most important for the transport characteristics and can differ strongly from the bulk values. As shown later, Heusler alloys are a good example which demonstrate the difference between bulk and interface properties. Furthermore, the above shown equations only depend on the density of states but theoretical calculations show that also the properties of the barrier, i.e. barrier height, have to be taken into account [49].

The Resistance Area Product

For characterizing MTJs the resistance area is usually used and defined simply as the product of a junctions resistance in the *parallel state* R and its area A:

$$RA = R \cdot A.$$

The resistance of an MTJ is inversely proportional to its area $R \propto \frac{1}{A}$ [50, 51]. Therefore, the RA product can be regarded as an area independent resistance parameter. The resistance plays an important role in actual devices because it determines the devices resistance noise. Hence, the RA product should be as low as possible. Furthermore, the product makes it easier to compare junctions because of the microfabrication process (which varies depending on the laboratory), the junction size varies which has a large influence on the resistance according to Eq. 2.1 and 2.3. Similarly to the resistance, RA is an exponential function of the barrier thickness [52].

Electron Tunneling and the Role of the Interface

Generally, the tunneling process is determined by a few monolayers of the FM electrode. The Fermi sea in the metal is strongly shielded by the outer electrons. Therefore, electrons are only affected by the interface in close proximity to it (a few Fermi wavelengths from the interface) [53]. Several experiments have shown the crucial role of the interface by inserting layers at the interface(s) greatly affecting the transport properties [54].
Besides considering only the FM metal interface, the metal-insulator interface plays a crucial role. A good example is the exchange of Al_2O_3 with a Al_2O_3-Ta_2O_5 and $Ni_{80}Fe_{20}$ electrodes. Using the first one, a positive TMR is obtained while for the latter one a negative one is measured. The negative TMR is assumed to be due to difference between s and d dominated tunneling. It was found that the sign of the TMR depends strongly on the type of covalent bonding between the metal and insulator [55]. It shows that for Co the DOS at the Fermi level is dominated by d electrons. However, for s and p electrons the situation is reversed and the majority electrons outnumber the minority ones due to the s(p)-d hybridization. Now, considering an insulator with s-bands separated by a band gap. In case of sd hybridization at the metal-insulator interface d electrons dominate the tunneling current which leads to a negative TMR due to the negative d-electron DOS. On the other hand, if ss bonding is dominant, s bands couple with those of the insulator. Because these s states have a strongly reduced minority DOS at the Fermi level, a positive tunneling current and TMR is observed. One can alter the interface by inserting a NM dusting layer. Although, one expects TMR to be zero considering Jullières formula, experiments with Au suggesting that the spin polarization reduces rapidly with dusting layer thickness but is still considerably high [56].

Oxidation of the Barrier

The oxidation of the barrier plays a big role in optimizing MTJs with respect to TMR, RA and bias voltage dependence. Two general methods are used. (i) deposition of a metal layer (i.e. Mg) followed by a oxidation of it; (ii) sputtering from a sintered oxide target (i.e. MgO target). In order to optimize the oxidation condition, either the oxidation time is changed for a batch of samples with different barrier thicknesses or the barrier thickness is changed while keeping the same oxidation time. While the first method is rather time consuming the second method is fast using a linear shutter to create a wedge-shaped barrier. Measuring along the wedge barrier, usually one observes an over-, under- and optimal oxidized MTJ. For thick barriers, the oxidation strength is not enough leaving the barrier partially in its metallic state reducing the spin-polarization of the carriers due to inelastic tunneling processes leading to spin flips. This leads to a strongly reduced TMR. In the case of thin barriers, the oxidation is to strong leading to an oxidation of the bottom electrode directly affecting the band structure and spin-polarization at the interface. A better way to achieve more homogenous barriers is a two step process in which two barrier layers are deposited and each oxidized. This often leads to an increase of RA and a slight increase of TMR. A topic that is strongly connected to the oxidation of the barrier is the existence of pinholes (high conducting paths in the barrier between the two electrodes). Often, these are metallic due to the incomplete oxidation of the barrier or the diffusion of elements into the barrier. Pinholes drastically reduce TMR because current will run through the normal metallic contact contact instead of tunneling. Visualization of pinholes is generally difficult as there dimensions are extremely small. In general, pinholes are responsible for the break down of MTJs at rather low bias voltage compared to a pinhole-free junction. Extrinsically, the breakdown is strongly related to the quality of the deposited barrier layer. Especially if the barrier becomes really thin, pinholes may grow due to strong Joule heating. Therefore, the strong reduction of TMR and RA is associated with these growth induced pinholes. It can be partially compensated by using plasma instead of natural oxidation to reduce the number of pinholes.

Dependence on Temperature

The temperature dependence of the TMR and the underlying mechanisms are up to now still not completely understood. In general, the TMR of an MTJ decreases with increasing temperature which is of enormous importance in actual devices operating at RT. Therefore, the high TMR values observed at low temperatures, cannot be accessed in actual devices. An extreme case are Co-based Heusler alloys which have one of the strongest temperature dependencies of all electrodes. On example is a $Co_2MnSi/MgO/Co_{50}Fe_{50}$ MTJ fabricated by Tsunegi *et al.* which has a TMR of 217% at RT and 753% at 2 K [57]. An intrinsic feature of every electrode material is the thermal broadening of the Fermi states which enables electrons with higher energy to cross the barrier. Besides, three effects are believed to contribute to the temperature behavior of a junction:

(i) Reduction of spin-polarization at the interfaces because of changes of the interface magnetic moment

(ii) Defect states or impurities in the barrier leading to a hopping conductance

(iii) Electron-magnon (also spin-wave) scattering at the interface leading to inelastic tunneling effects.

The reduction of interface spin-polarization is due to thermally activated fluctuations (spin waves) of the magnetic moment with temperature. Especially, the interface magnetization is vulnerable to thermal activated switching because outer moments have a less exchange interaction and are less bound to the bulk moments. Therefore, the magnetic spin-polarization can be written as

$$P(T) = P(0)(m(T)/m(0)), \tag{2.7}$$

with $m(T)$ being the magnetic moment at temperature T and $P(0)$ and $m(0)$, the spin-polarization and magnetic moment at 0 K, respectively. When assuming spin wave excitations with increasing temperature the spontaneous magnetization can be written as:

$$m(T) = m(0)(1 - (T/T_{\mathrm{c}})^{1.5}), \tag{2.8}$$

with T_c being the temperature at which a magnetic material will become paramagnetic [58]. By combining Eq. 2.7 and 2.8 and using Jullière's formular, Shan and coworkers developed the temperature dependence of MTJs based on thermal spin wave excitation [59]. For equal interfaces (symmetric MTJ), the TMR T-dependence is:

$$TMR(T) = \frac{2P(T)^2}{1 - P(T)^2} = \frac{2P(0)^2(1 - \alpha T^{1.5})^2}{1 - P(0)^2(1 - \alpha T^{1.5})^2}. \tag{2.9}$$

Here, α is defined as a parameter that depends on the interface condition. For a symmetric junction, two free parameters ($P(0)$ and α) exist which double in the case of an asymmetric junction with different parameters. Fitting a Co_2FeAl/MgO/CoFe junction, Wang *et al.* found good agreement between experiment and theory [60]. Firstly, the spin polarization of CoFe was determined from a CoFe/MgO/CoFe junction which was assumed to be unchanged in the Co_2FeAl/MgO/CoFe MTJ. Afterward, they could extract the parameters for CFA. However, one has to be careful with choosing the right parameters because usually even symmetric barriers tend to be asymmetric in nature regarding the interfaces.

Zhang et al. [61] developed a model based on the excitation of two-dimensional magnons by tunneling electrons. This free electron model was developed for incoherent tunneling in amorphous barriers (see Sec. 2.2.2). In this model thermal smearing which should reduce the barrier height was disregarded because the effect is small compared to other extrinsic effects. However, for coherent tunneling one has to consider the opening of additional conducting channels around E_{F} with increasing temperature. This smearing effect of the bands contributes usually just a few percent to the total conductance change. But in coherent tunnel junctions (i.e. MgO), the change of conductance, especially, in the AP state with temperature is small which increases the importance of the thermal smearing of the band structure. Therefore, a thermal smearing term $G(T)/G(0) = CT/\sin(CT)$ (with $C = 1.387 \cdot 10^{-4} a/\sqrt{\Phi}$) [62] needs to be introduced in the model by Zhang *et al.* to better fit the observed behavior [63]. With this, the magnon-excitation model with thermal smearing at zero bias voltage is in first approximation:

$$R_\gamma(T,0) = R_\gamma(0,0)\frac{\sin(CT)}{CT}\left[1 + Q\beta_\gamma ln\left(\frac{k_{\mathrm{B}}T}{E_{\mathrm{C}}}\right)\right], \tag{2.10}$$

Figure 2.3: Schematic of the spin-polarized inelastic hopping transport through N localized states Z_N; γ and $\Gamma_{1,2}$ are the exchange interactions between localized states and between localized states and the electrode, respectively; Sketch after Ref. [64].

with $\gamma = (P, AP)$, $\beta_P = Sk_BT\xi/E_m$, $\beta_{AP} = Sk_BT/(\xi E_m)$ and Q describes the probability of magnons to be involved in the tunneling process. S is the spin parameter and $E_m = 3k_BT_C/(S+1)$ (T_C is the Curie temperature). $\xi = 2\rho_{maj}\rho_{min}/(\rho_{maj}^2 + \rho_{min}^2)$ is the ratio of the products of the DOS in P and AP configuration.

As mentioned above, impurities in the barrier will also effect the temperature dependence of an MTJ. Usually, R_P, R_{AP}, and TMR increase monotonically with decreasing temperature. However, impurities in the barrier can lead to an inelastic contribution that decreases with decreasing temperature. Impurity tunneling can be modeled by assuming spin-conserved hopping of electrons through N localized states Z_N in the barrier [64]. At first, it is assumed that hopping of electrons occurs through conducting chains containing N localized states, see Fig.2.3. By applying a series resistor model, the conductance through N chains can be written as a power law:

$$G_N^P \propto (k_BT)^{v_N}\left[(1+P)^{2\beta_N} + (1-P)^{2\beta_N}\right] exp\left(-\frac{2ka}{N+1}\right) \tag{2.11}$$

$$G_N^{AP} \propto (k_BT)^{v_N}\left[2\left(1-P^2\right)^{\beta_N}\right] exp\left(-\frac{2ka}{N+1}\right). \tag{2.12}$$

$v_N = N - 2/(N+1)$ and $\beta_N = 1/(N+1)$ are characteristic exponents. P is the spin polarization of *both* contacts, a the barrier thickness and k^{-1} the characteristic localization length, i.e. the distance between two localized states. The tunneling is elastic if $v_N = 0$ (for N = 0 or 1) reflecting resonant (N = 0) and direct tunneling (N = 1). The TMR can be written with this model as:

$$\mathrm{TMR(N)} = \frac{(1+P)^{2\beta_N} + (1-P)^{2\beta_N}}{2(1-P^2)^{\beta_N}} - 1. \tag{2.13}$$

Finally, one has to consider that channels contribute differently to the total TMR. This issue is attributed by a weighting factor $W = G_N^{AP}/G^{AP}$ [65]. Therefore, the total TMR is the sum over all channels: $\sum W_N(T) \cdot \mathrm{TMR(N)}$.

In general, the temperature dependence of TMR has not only one but several contribution. However, it is often possible to apply one model to fit the temperature dependence neglecting other factors.

This is possible because in i.e. optimized junctions (regarding the TMR output), the contribution of local defects in the barrier should be small. Thus, a model can be selected based on the most likely contributing factor (i.e. defects, spin-waves, etc.).

Dependence on Bias Voltage

A decrease of TMR with increasing bias voltage can be found in all MTJs. Applying bias voltage means a shift of the Fermi energies of bottom and top electrode relative to each other. For example, if E_{F} of the top electrode is lowered, electrons start to tunnel from occupied states in the bottom electrode to unoccupied states in the top electrode as displayed in Fig. 2.1. A small bias voltage is always necessary to observe a tunneling current. This is critical in devices which are biased. Hence, it is important to understand the underlying mechanism that reduce the TMR and improve the bias voltage behavior. In the simplest case of an free electron model for a symmetric and uniform MTJ using the WKB-approximation and assuming electrons tunnel elastically at small bias voltages gives (by Simmons [66]):

$$I(V) = \frac{\alpha A}{a^2}\left(\overline{\phi} - \frac{eV}{2}\right) exp\left(-\beta a\sqrt{\overline{\phi} - \frac{eV}{2}}\right) - \frac{\alpha A}{a^2}\left(\overline{\phi} + \frac{eV}{2}\right) exp\left(-\beta a\sqrt{\overline{\phi} + \frac{eV}{2}}\right). \tag{2.14}$$

$\overline{\phi}$ (A) is the average effective barrier height (area), a the barrier thickness. $\alpha = e/(2\pi h)$ and $\beta = 4\pi\sqrt{2m_{\mathrm{e}}^*}/h$ are constants with m_{e}^* being the effective electron mass in the conduction band of the barrier. One can refine this equations by taking the asymmetry of the barrier $\Delta\phi$ into account which leads to potential difference between the two interfaces. Brinkmann *et al.* modified Eq. 2.14 taking this into account. A Taylor expansion of the result gives:

$$I = R_0^{-1}\left[V - \left(\frac{\beta e t \Delta\phi}{48\overline{\phi}^{3/2}}\right)V^2 + \left(\frac{\beta^2 e^2 t^2}{96\overline{\phi}}\right)V^3\right], \tag{2.15}$$

with $R_0 = \frac{2a \cdot exp(\beta a\sqrt{\overline{\phi}})}{eA\alpha\beta\sqrt{\overline{\phi}}}$ being the low-bias resistance. If $\Delta\phi = 0$, the conductance at low bias voltages is:

$$G \equiv \frac{dI}{dV} = \frac{1}{R_0} + \left(\frac{\beta^2 e^2 t^2}{32\overline{\phi}}\right)V^2. \tag{2.16}$$

One can see that the conductance (and therefore TMR) is a cubic function of the bias voltage. Note that at higher bias voltage one has to consider the reduction of the average barrier height. Note also, that the model does not distinguish between P and AP state. Although, this model illustrates the intrinsic dependence on the applied voltage, several mechanisms are expected to contribute to the degradation of the TMR which are similar to the ones that are responsible for the temperature dependence:

(i) Defects and impurities in the barrier

(ii) flipping of spins (spin-mixing) because of electron-spin-wave scattering at the interfaces

(iii) Change of the intrinsic electronic structures of the barrier and electrodes.

Figure 2.4: Schematic of the tunneling process in an Al_2O_x (a) and MgO (b) barrier

One can see that the reduction of TMR cannot be avoided due to intrinsic factors. It can be minimized i.e. by an optimal barrier fabrication without defects. One of the most known contribution is the so called zero-bias voltage anomaly at low bias voltage $V < k_B T_C$ and is marked by dips around $V = 0$ [67]. It is attributed to the excitation of spin-waves at the electrode/barrier interface due to flipping of spins which naturally reduces the TMR.
In general, bias voltage curves are measured in the P and AP state using inelastic tunneling spectroscopy with a resolution of < 0.5 meV. Measuring at temperatures close to 0 K is preferred due to thermal contributions at higher temperatures. dI/dV and d^2I/dV^2 spectra can be obtained. The latter one can give detailed information about the electronic structure and above mentioned contributions.

2.2.2 The Coherent Tunneling Effect and Electronic Band Structure

Nowadays, two different types of tunneling are known: Incoherent and coherent tunneling. Usually, incoherent tunneling is observed in amorphous barriers (i.e. Al_2O_3) while coherent tunneling exists in crystalline barriers (i.e. MgO). In Fig. 2.4, the tunneling of electrons through an amorphous Al_2O_x (a) and crystalline and (001)-epitaxial MgO (b) barrier are displayed (after Ref. [52]). The electrode from where electrons tunnel is Fe(001). In the electrode, electrons remain in different Bloch states which have different wave function symmetries. In the case of Fe(001) different states can be found that contribute to the tunneling. The most dominant are: Δ_1, Δ_2 and Δ_5. In the case of the amorphous barrier no symmetric crystalline order is present. Therefore, Bloch states in the electrode with different symmetries can couple to the evanescent states in the barrier and tunnel through it. Hence, the term incoherent tunneling. Interestingly, Δ_1-states (spd hybridized states) have a positive spin-polarization while Δ_2-states (d states) often have a negative spin-polarization [68]. Because all states contribute to the tunneling, the overall TMR ratio reduces.
In the case of MgO, the barrier is crystalline with (001) orientation and tunneling is dominated by Δ_1- states. The highest probability of tunneling have states with a wave vector of $k_{\|}(001) = 0$ ($k_{\|}$ is the wave vector of an electron parallel to the barrier) [12, 13]. As discussed above, these electrons have different orbital symmetries. First-principle calculations revealed that in Fe Δ_1, Δ_2 and Δ_5 can tunnel in the band gap of MgO with different decay rates. The highest transmittance has the Δ_1-state followed by the Δ_5-state. The highest decay rate has the $\Delta_{2'}$-state (Note that the Δ_2-state

changes its symmetry in the barrier and decays as $\Delta_{2'}$-state because MgO grows on Fe with a 45° lattice rotation). This means for thick enough barriers that the Δ_1-states dominates in the tunneling process determining TMR. This mechanism is called the spin-filtering effect. Regarding Fe, it has a low net spin-polarization because it has several majority and minority states around E_{F}. However, the Δ_1-state is highly spin-polarized which leads to large TMR ratios [52]. The mechanism of the dominant contribution of electrons with the same symmetry is called coherent tunneling effect.
Another indication are quantum-well oscillations emphasizing the quantum mechanical origin of the tunneling effect. Due to the reflection at the metal/insulator interfaces and superposition of coherent electron waves (small phase difference), an oscillation of TMR and resistance with the change of the barrier thickness can be observed, it is known as resonant tunneling. This happens in actual MTJs in the case of close to perfect interfaces (meaning $k_{\parallel}$=0). In the case of Fe/MgO/Fe MTJs, the oscillation of the TMR can be fitted assuming the superposition of two oscillations showing the oscillation of P and AP resistance [69].
From the above explanation one can see that for giant TMR ratios two ingredients are necessary. A crystalline barrier with a spin-filtering effect and electrodes with a high spin-polarized Δ_1-band. The first effect is also theoretically predicted for other crystalline barriers, i.e. ZnSe(001) [11] and $SrTiO_3$(001) [70]. However, fabrication of high quality interfaces seems to be difficult in these materials. For the electrodes, Fe, Co and CoFe-based materials are suited because of their high spin-polarized band structure or Δ_1-band. One of the promising materials are Heusler alloys. The next section will explain Heusler alloys followed by a section introducing a barrier with similar abilities as MgO, spinel $MgAl_2O_4$.

2.3 Heusler Alloys

The first discovery of Heusler alloys was made way before the discovery of spin-dependent tunneling. In 1903, Fritz Heusler discovered the ferromagnetic alloy Cu_2MnAl which consists of elements that are not magnetic on their own [71]. In total, over 1500 different Heusler alloys are known with manifold different characteristics (i.e. shape-memory effects, superconductivity, thermoelectric, ect.). Several alloys are interesting for spintronics applications due to their magnetic and electrical properties.

2.3.1 Crystal Structure

In general, Heusler alloys have the form $X_{(2)}YZ$. Two different types of Heusler alloys exist: Full-Heusler alloys (X_2YZ) and half-Heusler alloys (XYZ). The unit cell of a full (a)- and half (b)-Heusler alloy is shown in Fig. 2.5. Heusler alloys have a face-centered (fcc) crystal structure. The unit cell consists of four interpenetrating fcc sublattices that are fully occupied in the case of full-Heusler alloys ($L2_1$ structure). In half-Heusler alloys one of the X sites is removed and only three of the fcc sublattices are occupied ($C1_{\mathrm{b}}$ structure). In full-Heusler alloys X and Y are transition metals and Z is an element of the main group. In half-Heusler alloys X and Y have a cationic and Z anionic character. Z can be a transition metal, element of the main group or a rare earth element. X and Y are main group elements from the more electronegative right side of the periodic table. In the following, I will focus on the description of full-Heusler alloys due to their importance for the use in MTJs. The space group of a full-Heusler alloy X_2YZ is the cubic space group $Fm\overline{3}m$. The most electropositive Y and Z atoms form a rock-salt type structure with an octahedral arrangement. The tetrahedral holes are filled by

Figure 2.5: Crystal structure of a $L2_1$-ordered full-Heusler alloy (a), half-Heusler alloy (b); $B2$-ordering (c) and $A2$-ordering (d) of a full-Heusler alloy due to Y-Z and Y-Z, X-Z, and X-Y disorder, respectively.

the X atoms. The crystal structure of full-Heusler alloys can be regarded as a CsCl-like structure if the Y and Z atoms are disordered. This leads to simple cubic lattice in which Y and Z occupy the center. This so called B2-type structure is shown in Fig. 2.5 (c). This is a common feature observed in half-metal Heusler systems. If additional X-Y and X-Z disorder takes place, the crystal has an $A2$-type structure, see Fig. 2.5 (d). It is of importance to note that the magnetic properties of Heusler alloys strongly depend on the ordering. Small amounts of disorder can lead to distinctive changes in their electronic structure. This is connected to changes of the magnetic and transport properties as well.

2.3.2 Magnetism and Electronic Structure

Full-Heusler alloys can show all sorts of magnetic phenomena (i.e ferro- and ferrimagnetism, half-metallic ferromagnetism). The reason is the full occupation of the X positions which enable magnetic interaction between these atoms resulting in two magnetic sublattices. What makes Heusler alloys in spintronics applications attractive is the occurrence of half-metallic ferromagnetism [72, 73]. In such a material, the DOS for majority and minority spin carriers is shifted to each other so far that for one spin direction the material is a metal and for the other spin direction it is an insulator. A schematic representation of a half-metal DOS is shown in Fig. 2.6. In the representation, the minority states are shifted downwards creating a band gap at E_F making the material insulating for minority electrons. Referring to Eq. 2.6, the absence of minority states at the Fermi energy $N_\mathrm{min}(E_\mathrm{F}) = 0$ leads to a spin polarization of $P = 1$. Theoretically, full half-metallicity can only be achieved at zero temperatures and vanishing spin-orbit interaction. Latter one is existent in many Heusler alloys containing 3d-elements (i.e. Co, Fe) which show no such interaction.

Figure 2.6: Left: Schematic spin-resolved DOS of a half-metal (dark (light) bands are occupied (unoccupied) spin states); Right: Electron band hybridization in Co_2MnSi as an example for full-Heusler alloys after Galanakis [75].

Especially, Co-based Heusler alloys Co_2YZ are interesting for MTJ applications. On one hand, they have a lattice constant similar to the most used crystalline barriers and a high Curie temperature [74]. On the other hand, they are predicted to have half-metallicity as explained above and a large magnetic moment calculated by Galanakis *et al.* [75]. They showed that the half-metallic state originates from a strong hybridization of d-states of the atoms at X sites leading to bonding and anti-bonding states, see Fig. 2.6. The highest occupied bonding state and the lowest unoccupied anti-bonding state create the observed band gap in these alloys. Further hybridization with the Y atom leads to 8 degenerated d-like orbitals (one double-degenerated and two triple-degenerated orbital). Therefore, the outmost occupied bands are as follows: one s-state and three p-states from the Z element (which are significantly lower in energy than the d-states) and 8 d-states from the hybridization. This sums up to 12 states which are occupied by one minority and majority electron, respectively, resulting in a total of 24 occupied states. Thus, one can calculate the magnetic moment M of a full-Heusler alloy by a simple Slater-Pauling rule: $M = Z - 24$ with Z being the total number of valence electrons of all the elements X, Y, and Z. The total spin moment of Heusler alloys have found to obey this rule as shown in Fig. 2.7. As shown, Co-based Heusler alloys have the highest total spin moment. Many of them are predicted to be half-metallic with Curie temperatures well above RT. A summary of several alloys is listed in Ref. [74].

Experiments on MTJs with an MgO barrier and different Heusler alloy electrodes. An overview over several MTJs is given in Fig. 2.7. The highest TMR ratios at RT are measured to be slightly over 400% which is far away from the giant TMR ratios one expects from the theoretically predicted half-metallicity. Additionally, one has to note that the MgO barriers are usually fabricated by molecular beam evaporation (MBE). This is necessary to avoid substantial defects at the interfaces due to the large lattice mismatch between Heusler alloys and MgO. Using MBE the MgO lattice stretches and is strained to match the Heusler alloy lattice increasing TMR ratios. However, using MBE is not useful and expensive when thinking about actual application and fabrication of MTJs.

The reduced TMR ratios at RT compared to what is expected from theory has also an intrinsic origin which is the reduction of the minority band gap with due to thermal activation when temperature is

increased. This can be easily seen when low temperature TMR ratios of these MTJs are measured. One example is MTJs with $L2_1$-Co_2MnSi electrodes which show a low temperature TMR ratio of 1995% (354% at RT) [76] which even exceeds the TMR of CoFeB-based MTJs with 1144% at low temperatures (604% at RT) [18]. This shows the drastically decrease of the spin-polarization of Heusler alloys with temperature due to thermal activation.

Figure 2.7: Slater-Pauling curve after Galanakis [75] (left) and history of MTJs with Heusler alloys and MgO barrier (right).

2.3.3 Co_2FeAl Full-Heusler Alloy

Among the full-Heusler alloys Co_2FeAl is an interesting material. Common to other full-Heusler alloys, it has a high Curie temperature of about 1170 K (bulk) [77] and is half-metallic in the $L2_1$-ordered state. However, the $L2_1$-ordering temperature of over 1000 K is high compared to other Heusler alloys. Nevertheless, Co_2FeAl easily crystallizes easily in the B2-structure even at RT using a common magnetron sputtering technique. As mentioned before, disorder can strongly alter the electric properties of Heusler alloys which is also the case in Co_2FeAl. In the B2-ordered state it looses its half-metallicity. However, it has been calculated that B2-Co_2FeAl still has a 100% spin-polarized Δ_1-band similar to Fe [78]. This should lead to large TMR ratios in combination with the spin-filtering effect of an MgO barrier and, indeed, over 330% (700%) at RT (10 K) was observed in Co_2FeAl/MgO/CoFe MTJs [60, 78]. The low temperature TMR ratio is still reduced as compared to other MTJs with a Heusler electrode and MgO barrier which is attributed to the use of top-CoFe and the non-half metallicity of B2-Co_2FeAl.

Besides large TMR ratios, PMA can be established at the Co_2FeAl/MgO interface. Interestingly, compared to CoFeB Co_2FeAl has a low damping constant of about 0.001 [79]. It was also demonstrated that in such MTJs the magnetization direction can be switched by current [80] making it a promising candidate as an electrode for future perpendicular magnetized MTJs.

2.4 Spinel Barrier

Humankind knows spinel materials for hundreds of years in the form of red Ruby or blue Sapphire. Around 1800 it was realized that these gemstones contain the same element $MgAl_2O_4$ with different

elemental impurities being responsible for the color. Spinel specifies the magnesium alumina $MgAl_2O_4$. However, other materials exhibit also a spinel structure AB_2O_4 with A and B being two times positive

Figure 2.8: Structure of an ordered (a) and disordered (b) $MgAl_2O_4$ spinel; Courtesy of Dr. Sukegawa.

and three times positive charged ions. It has a cubic crystal system of the space group $Fd\bar{3}m$ with a lattice constant of $a = 8.09$Å [81]. The unit cell of stoichiometric $MgAl_2O_4$ is shown in Fig. 2.8 (a). The O^{-2} ions form a cubic lattice. 1/8 of the tetrahedral empty sites are occupied by Mg^{2+}-ions (A-ion) and 1/2 of the octahedral sites are occupied by Al^{3+}-ions (B-ion). However, in real spinel materials the O^{-2} ions are displaced from there ideal positions by about 0.1 Å away from the Mg^{2+} ions expanding the tetrahedral site and reducing the octahedral site volume. In the case of an inverse spinel, 1/4 of the octahedral sites are occupied by A-ions and the B-ions occupy 1/4 of the octahedral and 1/8 of the tetrahedral sites. The disorder of the cation sub-lattice is usually measured by an inversion parameter i which varies from 0 (fully ordered spinel with all Mg^{2+} ions on the tetrahedral sites) to 1 (perfect inverse spinel with all tetrahedral sites are occupied by Al^{3+}).
The remaining interstices in the tetrahedral and octahedral sites of the normal spinel can be occupied by other divalent and trivalent cation species. The atomic radii these atoms can have, are 0.044-0.100 nm changing the lattice constant from 0.80 to 0.84 nm in the case of $MgAl_2O_4$ [82]. A phase diagram is shown in Fig 2.10 taken from Ref. [83]. The left and right side of the phase diagram below 2000°C indicate two phases, namely MgO-$MgAl_2O_4$ and $MgAl_2O_4$-Al_2O_3. The dashed curve is a metastable state. The stoichiometric spinel contains 71.8% Al_2O_3 and 28.2% MgO with a melting point of about 2100°C. The band structure is similar to the one of MgO as calculated by Miura *et al.* [40]. The calculated band gap is about 5.84 [84] (5.5 [12]) eV for $MgAl_2O_4$ (MgO) between O2p states and Mg3s+Al3p (Mg3s) states. However, an evanescent state with Δ_1 symmetry in the energy gap exists which explains the observed high TMR ratios in MTJs with a spinel barrier. $MgAl_2O_4$ spinel has a relatively high density and hardness of 8 and therefore is harder than many other materials, i.e. MgO (6-6.5).
Firstly, spinel-like barriers were first fabricated by postoxidation of an Mg/Al double layer [85, 59]. In 2010, $MgAl_2O_4$ were incorporated as a barrier in an Fe/$MgAl_2O_4$/Fe MTJ by Sukegawa *et al.* [39, 86]. The barrier was fabricated by sputtering of a Mg and Al layer followed by a postoxidation process. The MTJs reached TMR ratios of 117% at RT (165% at 15 K). From High-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images the formation of an ordered spinel barrier which is indicated by {022} reflection peaks in the Nano-beam diffraction (NBD) was found. Compared to a Fe/MgO/Fe barrier (TMR > 180%), the TMR is significantly lower [14]. Using first-principles calculation, Miura *et al.* [40] found a significant reduction of TMR

Figure 2.9: Lattice constant of Mg-Al-O alloys dependent on the total Mg composition

in Fe/$MgAl_2O_4$/Fe MTJs due to the large difference in in-plane unit cell size of Fe and $MgAl_2O_4$ ($2a_{\mathrm{Fe}} = a_{\mathrm{CFA}}$). This so called band-folding effect causes the electronic bands at the edge of the Brioullin zone in Fe to be folded back to center leading to the appearance of minority-spin states that can couple to the Δ_1 evanescent state of $MgAl_2O_4$ (see Fig. 2.13 for a schematic explanation). Therefore, these states can contribute to the tunneling current reducing the resistance in the anti-parallel state. After realizing the problem, Sukegawa *et al.* could overcome it by fabrication of a cation-disordered $MgAl_2O_4$ barrier [41] achieving a TMR ratio 188% at RT (308% at 15 K) which is of the order of the TMR in an MTJ with an MgO barrier. The barrier was fabricated by post-oxidation of a Mg/MgAl layer. The MgAl was sputtered from an Al-rich target. To crystallize the barrier, the Mg-underlayer is needed which leads to a stoichiometry close to spinel after annealing. In the case of a MgAl target with higher Mg content, the Mg underlayer can be omitted or its thickness can be reduced. In a cation-disorderd spinel, the Mg and Al are intermixed together with vacancies reducing its unit cell size to one half of the unit cell of an ordered spinel as shown in Fig. 2.8 (b). The cation-disorder barrier avoids the band-folding effect in Fe keeping the spin filtering effect of the $MgAl_2O_4$ barrier. For further explanation of the effect, see below.
The spinel barrier has some advantages over an MgO barrier. They are:

- Good lattice matching with Fe- and Co-based (i.e. CoFe(B), Heusler alloys) FM which is necessary for the future miniaturization of MTJs. It improves the TMR and reliability of devices (higher breakdown voltages).

- Non-deliquescence (chemical stability) of the material as opposite to MgO.

- The lattice constant of the spinel barrier can be tuned based on the Mg-content in the sample, see Fig. 2.9.

- A wide range of different spinel are available for possibly barriers, i.e. $LiAl_5O_8$; doping of the barriers is also possible. With this, the properties of the barrier. i.e. barrier height can be tuned for different applications.

Figure 2.10: Phase diagram of the magnesium aluminate $MgAl_2O_4$ from Ref. [42].

Especially, the defect free interface due to the lattice matching is important. The lattice matching of $MgAl_2O_4$ and MgO with different FM materials is shown in Table 2.1. The lattice-matching is expected to increase the V_{half} (bias voltage at which TMR drops to 50%) above 1 V in Fe/$MgAl_2O_4$/Fe MTJs which is larger than in MTJs with an MgO barrier [39].

Usually, the $MgAl_2O_4$ barrier is fabricated by post-oxidation. One can vary the oxidation strength by changing the oxidation procedure. Three different oxidation methods are known: natural oxidation (Nat), indirect inductively coupled plasma oxidation (I-ICP), and direct inductively coupled plasma oxidation (D-DCP). The oxidation conditions are schematically shown in Fig. 2.11. Natural oxidation means the oxidation with pure O_2-gas. For the plasma oxidation, the an Ar-O_2 gas mixture is used. In the indirect plasma oxidation process a shutter is placed between the plasma and the sample. The direct is similar to the indirect plasma oxidation but without a shutter in between. Therefore, the strength of the oxidation can be adjusted by the method used. The weakest method is the natural oxidation followed by indirect plasma oxidation. The direct plasma oxidation provides the strongest type. A detailed description of the oxidation process is given in Sec. 3.1. In MTJs with $MgAl_2O_4$ barriers, RA can be tuned with the different oxidation conditions while keeping a large TMR ratio, see Fig. 2.12 from Ref. [42]. This shows that the barrier properties can be tuned to match the needs of applications of high-performance MTJs.

Table 2.1: Lattice mismatch of $MgAl_2O_4$ and MgO with various FM materials

Ferromagnet	a (nm)	Mismatch vs MgO	Mismatch vs $MgAl_2O_4$
bcc-Fe	0.2866	-3.8%	-0.3%
bcc-CoFe	0.2851	-4.3%	0.3%
$L2_1$-Co_2FeAl	0.5730	-3.8%	-0.3%

Figure 2.11: Oxidation methods for a $MgAl_2O_4$ barrier.

2.4.1 The Band-folding Effect in $MgAl_2O_4$ Barriers

The band-folding effect occurs always when one assumes a double-sized unit cell. This happens on the interface between two films (film A and B) having a large difference in unit cell size, i.e. $a_A = 2a_B$. In reciprocal space the situation is reversed, $2\pi/a_A > 2\pi/a_B$. At the interface both Brioullin zones have to match leading to a shrinking of the film A Brioullin zone. This results in a folding of the bands at the edge of the Brioullin zone into its center. For the $Fe/MgAl_2O_4$ case and a two-dimensional zone the band-folding of the Δ_1-bands is shown in Fig. 2.13 after Miura *et al.* [40]. In this case, electrons tunnel in k_z-direction and the folding of a band from the outside of the zone in k_y-direction is sketched. It should be noted that tunneling is usually assumed for electrons with $k_{x,y}$=(0,0). Therefore, here electrons with k_y=0 will tunnel. Without the band-folding effect (Fig. 2.13(a)) the Δ_1-states are fully spin-polarized around E_F at k_y=0. With the band-folding effect (Fig. 2.13(b)) the bands from k_y=2π/a are folded into the center k_y=0 resulting in the appearance of the band around E_F for the minority states. This leads to a reduced spin-polarization and subsequently the reduction of TMR ratio.
Now, Heusler alloys are theoretical half-metals which means a band gap for all symmetries and k-directions. The question is what happens in the case of combining Heusler alloys with a $MgAl_2O_4$ barrier. One can think of two scenarios:

1. The Heusler alloy is $L2_1$-ordered having a unit cell size (two times the one of Fe) similar to the one of $MgAl_2O_4$. In this case the band-folding effect does not occur.

2. The Heusler alloy is B2-ordered having a unit cell size similar to the one of Fe. In this case the band-folding effect does occur because no foldable bands exist around E_F due to the half-metallicity in all k-directions and the spin-polarization remains.

Figure 2.12: TMR vs. RA for a Fe/$MgAl_2O_4$/Fe MTJ with a wedge-shaped barrier oxidized under different conditions (see text); Taken from Ref. [].

Figure 2.13: Schematic illustration of the band-folding effect in a two dimensional unit cell of Fe in the vicinity of a disordered (a) and ordered (b) $MgAl_2O_4$ barrier.

Therefore, by using Heusler alloys in combination with the $MgAl_2O_4$ barrier, large TMR ratios can be expected that exceed the up to now observed ratios.

3 Experiment

3.1 Device Fabrication

Sputtering

All multilayers were fabricated with an ULVAC magnetron sputter which is operated and controlled by a PC. The sputter itself consists of three - load-lock, transfer, and main - chambers (see Fig. 3.1),

Figure 3.1: Illustration of the used sputter; Orange circles mark the target positions. The robot arm can extend to reach into the Load-Lock- and Main-chamber; The gray circle represents the disk with two holes for the sample holder.

each evacuated by a rotary and turbo pump and separated by valves with interlocks. Samples are set in the load-lock chamber and automatically transferred from there. The transfer chamber has three targets (S1 to S3) and is used for post-oxidation of the barrier. The oxide nozzle is around the S2 target position. S3 is equipped with an electron beam evaporator for the deposition of MgO. This chamber has a robot arm with a fork at the end which can extend and rotate 275°. The arm is used to transfer the sample holder from the load lock to the main chamber and to the target positions in the transfer chamber. During deposition in the transfer chamber the sample holder rests at the end of the arm. The main chamber contains 10 different targets, labeled A1 to A10. From positions A2 to A7 heating lamps are installed. Positions A9 and A10 are used as cooling stages. The pumps, cathodes, and heating lamps are water-cooled by a Neslab ThermoFlex3500 (Thermo Scientific) chiller. Targets at positions S1 to S3 are sputtered using a RF voltage and at positions A1 to A10 DC voltage is used. The base pressures are $<1\times10^{-5}$ Pa and about 4×10^{-7} Pa for the transfer and main chamber, respectively. The deposition of films is controlled by a PC that uses a user-defined sputter program. A program consists of different steps which like building blocks can be individually arranged. Each step consists of different, so called, pages in which the target position, sputter time, temperature,

Figure 3.2: MTJ stacks fabricated in this thesis and presented in Sec. 4.1 (a), 4.2 (b), and 4.3 (c); Numbers in brackets are layer thicknesses; Annealing temperatures are written outside of brackets.

Ar-pressure, etc. can be defined and controlled. After loading the sample in the load-lock chamber and connecting the PC to the sputter, the whole sample fabrication is controlled by the program. The only exception is the deposition of a non-uniform wedge-shaped film (at position S1 & S3) which is done manually because the respective linear shutters are not connected to the PC.

Information of Sputtered Layers

Multilayers are sputtered on a MgO(001) single crystal. The substrates are cleaned in an ultrasonic bath with Isopropanol and distilled water. In the sputter, before the layers are sputtered, the MgO is degassed and cleaned at 800°C for one hour. Three different types of MTJs are fabricated: CFA/$MgAl_2O_4$/CoFe, CFA/$MgAl_2O_4$/CFA, Fe/Li-$MgAl_2O_4$/Fe. Here CoFe means $Co_{50}Fe_{50}$ and Li-$MgAl_2O_4$ is a Li-substitute $MgAl_2O_4$ barrier. The structures are displayed in Fig. 3.2. The number in brackets indicate the layer thickness in nm and the respective annealing temperatures are written thereafter. The nominal compositions are $Mg_{16.5}Al_{83.5}$ (MgAl), $Li_{10}Al_{90}$ (MgAl) $Co_{47.4}Fe_{24.4}Al_{28.2}$. The thin film compositions were determined through inductive coupled plasma analysis to be $Mg_{19}Al_{81}$, $Li_{11}Al_{89}$, and $Co_{49}Fe_{26}Al_{25}$.

Barrier Oxidation

The barrier was formed by post-oxidation after deposition of the MgAl or LiAl layer. The barrier was formed by D-ICP (CFA/$MgAl_2O_4$/CFA) or I-ICP (CFA/$MgAl_2O_4$/CoFe and Fe/Li-$MgAl_2O_4$/Fe) (see 2.11). The plasma was formed near a one-turn coil and a sputtering cathode (diameter: 50.8 mm). Introducing an O_2 + 20% Ar mixture gas and applying power, the gas mixture pressure was kept at 5 Pa while a power of 5 W (50 W) for the cathode (coil). The total barrier thickness is $d_{\mathrm{Mg}} + d_{\mathrm{MgAl}} + d_{\mathrm{Oxide}}$ due to the oxidation of the metallic layers. In case of a wedge-shaped barrier, d_{MgAl} linearly increases (see Fig. 3.3). The wedge-shape is determined by the shutter speed and the deposition rate/time. Note that the actual barrier thickness will be even larger due to the post-oxidation process. To improve the interface quality, insertion of CoFe with different thicknesses d_{CoFe} was used. The layer thicknesses and annealing temperatures can be found in the respective sections.

Figure 3.3: Sketch of the wedge-shape barrier sputter process.

Microfabrication

Junctions were microfabricated in a class-1000 (ISO 6) clean room and patterned into 50 to 288 m^2 scale junctions using photolithography and Ar^+-ion etching. The number of junctions in a row on a substrate is 22 or 46 for substrates with a width of 1 cm or 2 cm, respectively. Films with a wedge-shaped barrier were prepared on a 2×1 cm substrate. Films with a fixed thickness were prepared on a 1×1 cm substrate. The detailed microfabrication procedure is described in Appendix A.

Magnetic Annealing

The magnetic annealer is shown in Fig. 3.4. The magnet is water cooled and can be ramped up to 10 kOe. The vacuum is generated by a rotary and turbo pump. The pressure is below 10^{-4} Pa. The sample stage can be rotated 360° for different annealing directions. The temperature curve can be programmed. The different characteristics for the fabricated stacks are shown below. Stacks were annealed at 200°C or 300°C for a CoFe or CFA top electrode, respectively, under a magnetic field of 5 kOe applied parallel to MgO[100]‖Heusler[110] direction (no rotation of the sample stage). The annealing program was as follows for a maximum temperature of 200°C (300°C) for Fe and CFA (CoFe) top-electrode:

Figure 3.4: Magnetic annealer to establish exchange bias.

1. RT → 190°C(290°C) in (30 min) for 40 min
2. 190°C (290°C) → 200°C (300°C) for 20 min
3. 200°C (300°C) for 30 min
4. cool-down

3.2 Electron Transport Measurements

In-plane 4-probe measurements at Room Temperature

All transport measurements are done with an in-plane magnetic field. The in-plane prober in Fig. 3.5 (a) has a 360° rotatable magnet and sample stage. The magnet can reach fields up to 3 kOe. The two probe electrodes have 2-channels each with a distance of 200 μm to allow a four point measurement as in Fig. 3.5 (b). One electrode of each probe is connected to a current source and the other one is connected to a voltage source by two coaxial cables. Between the sources and the probe electrodes a band-pass filter is inserted to reduce noise. The current for a TMR measurement flows from the bottom electrode to the top electrode. For positive bias voltage this current flow is the same. For negative bias voltages the electrons flow from the top to the bottom. The measurements are PC-controlled. TMR and bias voltage loops are loaded from a text-file in which the measurement intervals, steps, and time (for each point) can be defined. Conductance spectra ($dI/dV = G$) are obtained by numerical differentiation of the measured I-V curves.

Figure 3.5: (a) In-plane proper for RT measurements; (b) Top-view of a microfabricated MTJ with electrodes

In-plane 4-probe measurements at Low Temperatures

Low temperature measurements are done in a self-build machine. It consists of a vacuum chamber in which a chip carrier can be placed in the chip holder on a copper sample stage. The stage is decoupled from the chamber walls and can be heated. The sample stage is cooled with a Helium cryostat down to 5 K. For the measurement, the microfabricated device is glued to the chip carrier with a resin adhesive. Wires are contacted from the, to be measured, devices to the contacts of the chip carrier with a wire-bonder. The measurement is PC-controlled. The measurement is done for P and AP state separately. Firstly, the sample is brought in the P or AP state by tuning the external magnetic field. Thereafter, the system is cooled down to about 5 K. This field cooling preserves the AP magnetization state down to low temperatures. For heat-up, the sample stage will be heated while the cryostat is

still working. This allows for a better temperature control. During heat-up, the AP or P resistance state will be measured in a point-by-point manner. Conductance spectra are measured at both low RT and 5 K with the same procedure as for the resistance measurement. First, the sample is cooled down in P or AP state. After that, the respective I-V curves are measured.

3.3 Structural Characterization

Atomic Force Microscope

Surface morphologies of the bottom electrodes are obtained with a SPA400 atomic force microscope (AFM) using a SPI 3800N probe station. The surfaces are measured in dynamic force mode. Areas of 1 μm^2 were used to determine the roughness of the layers (using the arithmetic roughness R_a). Images were processed with the included Hitachi software and with the open source software Gwyddion. [87]

X-Ray Diffraction

X-ray diffraction (XRD) patterns are measured with a four-axis Rigaku diffractometer at RT using a Cu Kα-radiation ($\lambda = 0.154059$ nm), a current of 200 mA and a voltage of 45 kV. The diffractometer has the option of a 0D- and 2D-detector. The latter one allows fast 2θ and ω measurements simultaneously with a reduced resolution compared to the 0D-detector which has a longer count time but better resolution. The proper horizontal alignment of the sample surface was done using the MgO(002) substrate peak.

TEM & EDS

High-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), nano-electron beam diffraction (NBD), and energy dispersive X-ray spectrometer (EDS) were carried out using a Titan G2 80-200 TEM to investigate the microstructure of the MTJs.

4 Results and Discussion

In this chapter the results of $Co_2FeAl/MgAl_2O_x/CoFe$ and $Co_2FeAl/MgAl_2O_x/Co_2FeAl$ MTJs are presented in different sections. Due to the difficulty of separating the discussion from the results both are presented at the same time. If information from other chapters are necessary they will be referred to in the text. First the transport measurements are discussed followed by a detailed analysis of the MTJ crystal structure by TEM.

4.1 $Co_2FeAl/MgAl_2O_4/CoFe$ MTJs

In order to obtain high TMR ratios, the bottom layers are of great importance and should be of high quality. Therefore, firstly, the bottom layers were optimized with respect to the smoothness as obtained from AFM measurements and its rocking curve obtained from XRD measurements. The stacking structure of the bottom layers are as follows: MgO(001) substrate// Cr (40)/ CoFe(5)/ CFA (5)/ Ru (2) (number in brackets in nm). The Cr-buffer was post-annealed at 800°C, the CoFe-buffer was not annealed. The smoothest surface was found for a CFA post-annealing temperature of 250°. In Fig. 4.1 the out-of-plane XRD scan and the rocking curve are shown together with an AFM-scan. One can see that the bottom layers grow epitaxial on the MgO substrate in (001) direction. The full width at half maximum (FWHM) of the rocking curve was found to be 1.2°. The R_a height was measured to be 0.11 nm.

4.1.1 MTJ with a wedge-shaped barrier

After confirming a smooth bottom electrode, an MTJ stack with a wedge-shaped barrier was fabricated. The stacking structure was already shown in Fig. 3.2. The top CoFe electrode was post-annealed at 250°C. Relating to previous publications on $MgAl_2O_4$ barriers, the post-annealing temperature was set to 250°C [41, 42]. To achieve a sufficient AP state, IrMn was used to create an exchange bias between it and the CoFe electrode (pinned layer). The whole stack was *ex-situ* annealed at 300°C parallel to the MgO[001] direction to establish the exchange bias. In Fig. 3.2, an insertion layer of CoFe can be seen between CFA and the barrier. Refer to the CoFe insertion part below for further information.

In Fig. 4.2 (a), the TMR (left axis, red) and RA (right axis, black) values as function of the nominal MgAl thickness d_{MgAl} (representative for the total barrier thickness) of the MTJ with the wedge-shaped barrier are presented. Note that the RA axis is logarithmic. The highest TMR ratios (∼235%) are reached at barrier thicknesses of 0.6-0.8 nm. The TMR decreases slowly with decreasing barrier thicknesses below 0.6 nm. The thickness dependence of the RA is found to be an exponential function of thickness for 0.8 nm $< d_{\mathrm{MgAl}} <$ 1.6 nm. Above 1.6 nm, tunneling breaks down due to strong underoxidation [42]. Below 0.8 nm, the junctions get overoxidized which might lead to an oxidized bottom interface. Interestingly, in the overoxidized region the TMR decreases linearly but slowly with

Figure 4.1: (a) Out-of-plane XRD measurement of the bottom electrode (see text); (b) Rocking curve of the corresponding CFA(002) peak from (a); red line is the fit to obtain FWHM.

decreasing barrier thickness. This is not observed in wedge-shaped $Fe/MgAl_2O_4/Fe$ junctions [42] in which the TMR drops when RA reduces. Additionally, TMR vs RA ratio is plotted in Fig. 4.2 (b). Note that the RA axis is logarithmic. One can see that TMR increases slightly with decreasing RA values which is usually not observed in such junctions. Thus, it might be possible to reduce the barrier further and obtain rather high TMR ratios at low barrier thicknesses with low RA values. This is interesting for applications as the thermal noise ($\sqrt{RT}$) in devices reduces with the resistance [88].
In the next step the normalized bias voltage dependence was measured at different barrier thicknesses. A positive bias voltage is related to electrons tunneling from bottom to top and for negative bias voltages vice verca. It gives information about the electronic structure. The spectra were measured

Figure 4.2: (a) TMR (left axis, red) and RA (right axis, black) vs d_{MgAl} at RT; (b) TMR vs RA from (a).

at RT and contain thermal noise. This however does not change the following discussion much because the curve measured at RT and LT are quite similar. In Fig. 4.3, the at $V = 0$ V normalized conductance curves in the P (a) and AP (b) state at RT are displayed for several barrier thicknesses. In the P state, the conductance varies strongly with the barrier thickness. At negative bias voltages, conductance shifts upwards with increasing thicknesses as indicated by an arrow. At positive bias

Figure 4.3: Normalized conductance spectra at $V = 0$ V for several barrier thicknesses of for P (a) and AP (b) state at several barrier thicknesses d_{MgAl}; (c) TMR (left axis, red) and RA (right axis, black) vs d_{MgAl} at RT; (d) deepness of the minima (left axis, black circles) and its position (right axis, blue squares) in (a) as a function of the barrier thickness.

voltages, the minimum shifts monotonically to higher voltages with increased barrier thickness. The deepest minimum is observed between 0.7-0.9 nm barrier thicknesses which corresponds to the barrier thickness that shows the highest TMR. The dip is less pronounced for thinner and thicker barriers. In Fig. 4.3 (d), the deepness of the minimum (left axis, black circles) and its position (right axis, blue squares) are displayed as a function of the barrier thickness. Here, I plot again the TMR and RA ratios as a function of d_{MgAl} in Fig. 4.3 (c) to emphasize the relation between the two graphs. Interestingly, the position of the minimum shifts linearly to lower bias voltages and shows a break point around $d_{MgAl} = 0.8$ nm which corresponds to a MTJ with one of the largest TMR. In the AP state, the conductance curve at negative bias voltages shifts to higher conductance when the barrier is increased up to 0.9 nm. The conductance remains almost unchanged beyond this thickness. Note that the observed changes coincide with changes in TMR and RA as marked by the dashed lines.
It has been shown by Miura *et al.* [40] that the spinel barrier has a similar electronic structure as MgO and the coherent tunneling effect is present in $MgAl_2O_4$ barriers. The high TMR values observed in Fig. 4.2 is another prove that coherent tunneling occurs in the here fabricated junctions. Consequently, the anomalies observed in barriers with coherent tunneling can be related to the band structure of the bottom and top interface $Fe/MgAl_2O_4/Fe$ junctions [89]. This should be also the case in the spinel-based MTJs. The shoulder at about -400 mV in Fig. 4.3 (a) is fading out with increased barrier thickness hinting to a participating band that decays rather fast in the barrier. The dip at positive bias voltages lies between 280-360 mV depending on the barrier thickness. It is difficult to assign a specific electron band to this dip because the top interface changes depending on the barrier thickness and, hence, the oxidation. Naturally, this holds also for the shoulder at neg. bias voltages. However,

in this case the shoulder does not shift its bias voltage position which means that the responsible band

Figure 4.4: Temperature dependence of (a) TMR and normalized R_P (b) and R_{AP} (c) for two junction thicknesses; the black curve corresponds to a junction with the highest TMR.

Figure 4.5: Fit (red line) of the TMR temperature dependence for three samples with different barrier thicknesses according to Eq. 2.9.

does not shift in energy. It only is less transmitted when the barrier thickness is increased. The possible band will be discussed further below in Sec. 4.1.2

Lastly, the temperature dependence of the TMR was measured down to 5 K for three junctions with an overoxidized barrier (d_{MgAl}=0.38 nm), an optimized barrier (the highest TMR, d_{MgAl}=0.87 nm) and with an underoxidized barrier (d_{MgAl}=1.58 nm). The TMR curve as a function of temperature T for the different barrier thicknesses are shown in Fig. 4.4 (a). The junctions are chosen from an overoxidized, well oxidized and underoxidized region of the wedge-shape sample in Fig. 4.2. $R_P(T)$ and $R_{AP}(T)$ are normalized to $R_P(5\,K)$ and $R_{AP}(5\,K)$ and shown in Figs. 4.4 (b) and (c), respectively. As commonly observed, TMR and R_{AP} increase with reducing the temperature for both junctions. Interestingly, $R_P(T)$ of the two junctions differ greatly compared to $R_{AP}(T)$. That is, for the larger TMR junction $R_P(T)$ reduces monotonically with temperature. On the other hand, $R_P(T)$ of the thin barrier junction increases down to 150 K from where it decreases again. As introduced in Sec. 2.2.1,

the temperature dependence has different origins. As mentioned, a positive contribution is in theory only observed if a non-tunneling current flows through the barrier due to, i.e. defects or pinholes in

Figure 4.6: (a) Fit (red line) of the TMR temperature dependence for three junctions with d_{MgAl} = 0.38 nm (blue), 0.87 nm (black), and 1.58 nm (yellow) using the spin-wave excitation model according to Eq. 4.1; (b)-(d) Fit (red lines) of the normalized parallel and antiparallel resistance curves of the same junction and with the same model.

the barrier. This seems reasonable in the case of thinner barriers in which pinholes play a bigger role than in thicker junctions. In the optimized MTJ case, such a defect mediated tunneling process is not observed. Although, a contribution of defects to the tunneling current cannot be excluded in this junction the contribution is negligible small, so that no change in the monotonically decrease of $R_P(T)$ can be observed. Therefore, fitting the temperature dependence of the three MTJs is tried by using different models as introduced in Sec. 2.2.1.

TMR Temperature Dependence

At first, the temperature dependent Bloch wall model was used to fit the temperature dependence. Note, that it should be difficult to use this model for the thin barrier MTJ due to the non-monotonically decrease of $R_P(T)$. With Eq. 2.9, the TMR can be fitted. However, in this junctions the electrodes are not the same, hence, different interfaces exist as observed in the conductance spectra in Fig. 4.3

(a) which leads to four free parameters $P_1(0)$, $P_2(0)$, α_1 and α_2 (1, 2 refer to the two interfaces). It is not possible to explicitly determine the four parameters. One rather ends up with a range of possible fitting parameters. Therefore, I assume a symmetric junction which reduces the number of parameters to two: $P(0)$ and α but also leads to a loss of information. With this, a distinction of both interfaces is not possible. One rather ends up with average values. The fitting result is shown in Fig.4.5. The fits are similar with similar fitting parameters. However, the parameters cannot be used to draw conclusions from the actual spin polarizations. It is obvious that the fit is better for the MTJs with a thicker barrier but also deviates significantly from the curve at low temperatures $T < 25\,\mathrm{K}$. This means that another contribution (besides the natural decrease of the spin-polarization) has to be taken into account for the thinner barrier MTJ.

In the next step, curves are fitted with the spin-wave excitation model extended with thermal smearing as described in Eq. 2.10. To fit the curves, several parameters are necessary which are summarized in Tab. 4.1 together with the from the fit obtained values. The fits are shown in Fig. 4.6. The inset show the fit of the to 5 K normalized resistance in parallel (R_P) and antiparallel (R_AP) state. It is obvious that similar to the previous fit, the thicker barriers is better fitted by the spin-wave excitation model than the thinner barrier. Especially, at higher temperatures the fit deviates significantly from the measured curve for the thinnest barrier MTJ. The reason is R_P which cannot be fitted by this model. The from the fit extracted values are similar to Ref. [63] for the optimized barrier MTJ. The value C can be converted to the amount of thermal smearing in the MTJ using: $\alpha = 1-\sin(C\cdot 300\mathrm{K})/(C\cdot 300\mathrm{K})$. C should depend only on the barrier and not the used electrodes. For the same barrier, one expects similar C values. However, due to the different oxidation condition and thickness, the properties of it changes. The thermal smearing for the thin barrier junction is below 1%, for the optimized one it is 3.8% and the thickest barrier 12.1%. It increases with increasing barrier thickness or with the reduction of oxygen in the barrier. The parameter Q which gives the probability that a magnon gets excited during the tunneling process. It is 4% larger for the thicker barrier compared to the one with optimized thickness. Interestingly, the probability drops for the thickest barrier to 13.6%. Taking all of these into account, it is obvious that the thicker barrier junction can be fitted quite well with this model while for the thinnest, overoxidized barrier, especially, the positive slope of R_P below 150 K is the problem and cannot be covered by this model.

It is known that a positive slope in the temperature dependence of R_P and/or R_AP can be related to the existence of metallic impurities or defects in the barrier [90, 64]. The impurities can be either magnetic or non-magnetic. In the case of magnetic impurities, the Kondo effect might be observed which leads to a strong degradation of TMR at low temperatures [91, 92]. This is clearly not observed in the here fabricated and shown junctions. Thus, the contribution of non-magnetic impurities or defects seems to be likely. A model for this process dealing with spin-polarized inelastic tunneling via hopping conductance through localized states in the barrier was proposed by Lu *et al.* [64] (see Sec. 2.2.1). According to their work, if a hopping contribution is present and dominant, it can be observed by plotting the conductivity difference ΔG which is free of spin-independent contributions. In the case excited magnons contribute mainly to the temperature dependence of the conductance, $\frac{\mathrm{d}(\Delta G)}{\mathrm{d}T} < 0$. In the case of a *strong* hopping mediated temperature dependence, $\frac{\mathrm{d}(\Delta G)}{\mathrm{d}T} > 0$ because the hopping follows a power law $G_\mathrm{hop} \propto T^N$ (N is the number of hopping channels through the barrier) which contributes to the temperature dependence of ΔG. This means, for a large enough amount of hopping channels, the temperature dependence gets dominated by the hopping at higher temperatures.

The dependence of the conductance is shown in Fig. 4.7. For both the thinner and thicker junction, $\frac{\mathrm{d}(\Delta G)}{\mathrm{d}T} < 0$ which hints to a non-dominant contribution of localized states to the tunneling process. However, a contribution of theses states cannot be ruled out. Firstly, the number of localized channels N net to be known in order to fit the TMR ratio according to Eq. 2.11. In the case of hopping transport, the conductance in the AP state follows a power law:

$$G_{\mathrm{AP}}(0,T) = G_0 + \sum_{N\geq 2}^{N_{\max}} G_{\mathrm{N}} T^{N-2/(N+1)}.$$

The fit is shown in Fig. 4.7 (top). For all thicknesses, up to $N = 3$ localized channels are assumed to be present in the barrier. Therefore, the fit is $G_{\mathrm{AP}}(0,T) = G_0 + G_2 T^{1.33} + G_3 T^{2.5}$. Note, that G_0 has to be considered as an average value for $(G_0 + G_1)/2$ which cannot be distinguished because both are temperature independent in this model. The obtained coefficients are shown in Table 4.2. Note that for the thicker barrier, the contribution of all values G_0, G_2, and G_3 are significantly reduced compared to the thinner barrier. The contribution of each channel to the tunneling can be calculated according to $W(\mathrm{N,T}) = G_{\mathrm{AP}}(N,T)/G_{\mathrm{AP}}(T) \times 100$ and is shown in Fig. 4.7 (2nd from top). $G_{\mathrm{AP}}(N,T)$ are taken from the fit of G_{AP}. In general, the resonance and direct tunneling contributions reduce due to thermal smearing and activation of magnons. The contribution of the hopping conductance however, increases with increasing temperature. In the case of the thinner barrier, the contribution of 2-localized states are larger at RT than for the thicker barrier. On the other hand, 3-localized states are negligible for the thinner barrier while the thicker barriers shows contributions of this channel of ∼12% (0.87 nm) and ∼7% (1.58 nm) at RT. Higher order localized states contributions are more likely for thicker barriers due to the large distance between the electrodes favoring transport through longer chains of localized states. Therefore, direct and resonant tunneling at RT are reduced for thicker barriers and the tunneling is more promoted by hopping through localized states. In the next step, the conductance difference $\Delta G = G_{\mathrm{P}} - G_{\mathrm{AP}}$ is fitted using:

$$\Delta G(0,T) = G_0 \frac{CT}{\sin(CT)} \mathrm{TMR}(0,T) + \sum_{N\geq 1}^{N_{\max}} G_N \mathrm{TMR}(N,T) T^{N-2/(N+1)} \tag{4.1}$$

Here, the model assumes a thermal smearing $\frac{CT}{\sin(CT)}$ of the resonant tunneling contribution, equal to the one in the magnon fitting. $\mathrm{TMR}(0,T) = 2P^2/(1-P^2)$ is the standard ratio as obtained from the Jullière model. $\mathrm{TMR}(N,T)$ are defined as in Eq. 2.13. The temperature dependence of the TMR ratio originates from the spin polarization temperature dependence and is assumed to follow Bloch's law: $P = P_0(1 - \alpha T^{1.5})$, P_0 and α being the spin polarization at $T = 0$ and an interface parameter, respectively. Note, that $P = \sqrt{P_1 P_2}$ is the averaged spin polarization of both electrodes. The fitted curves are shown in Fig. 4.7 (3rd from top) and the obtained values are summarized in Table 4.3.

Table 4.1: Parameters used to fit the temperature dependence (S, E_{m} and ξ) of two MTJs according to Eq. 2.10 and obtained values (Q, E_{C}, C) from the fit.

Junction (d_{MgAl})	S	E_{m} (meV)	ξ	Q	E_{C} (meV)	C (K^{-1})
0.38 nm	1	161	0.201	0.202	0.06	0.000024
0.87 nm	1	161	0.201	0.247	1.90	0.001600
1.58 nm	1	161	0.201	0.136	0.90	0.002899

Figure 4.7: Fitting using the hopping model for three different thicknesses: 0.38 nm (a), 0.87 nm (b), and 1.58 nm (c); red curves are fits to the respective curves; Top graph is the conductance G_{AP} in the AP state from which the number of localized channels was extracted; their weighted contribution W to G_{AP} are shown second from top; third row is the fit of $\Delta G = G_P - G_{AP}$ with Eq. 4.1; bottom graphs show the fit of TMR with the hopping model.

Table 4.2: Parameters obtained from the temperature fit of G_{AP} assuming three localized states $N = 3$.

Junction (d_{MgAl})	G_0 ($1/\Omega$)	G_2 ($10^{-6}/(\Omega K^{1.33})$)	G_3 ($10^{-10}/(\Omega K^{2.5})$)
0.38 nm	0.017	4.570	6.030
0.87 nm	0.004	0.835	5.060
1.58 nm	0.002	0.541	1.963

One can see, that the model cannot fit the maximum at low temperatures in ΔG and therefore was excluded from the fit. C is a measure for the amount of thermal smearing. The amount at RT is given by 1-sin$(C \cdot 300\text{K})/(C \cdot 300\text{K})$ and is shown in the table in brackets following the C values. The thermal smearing in the case of the thin barrier is much larger than for the thicker one. Interestingly, the fit of the barrier with $d_{\text{MgAl}} = 1.58$ nm shows no thermal smearing with this model. α is two times larger for the thicker barrier. It strongly depends on the interface condition [59, 64]. Hence, the different interface parameters reflect a change in the interfaces due to a change in the oxidation (which originates from the different barrier thicknesses). Interestingly, the obtained spin polarization are similar for $d_{\text{MgAl}} = 0.38$ and 0.87 nm. The lowest value is found in the case of the thickest barrier, reflecting the lower TMR ratios. In the case coherent tunneling would be assumed in this model, i.e. by assuming different decay rates depending on the symmetry on the electrons, the spin polarization would reduce [64]. Therefore, the spin polarization is not effected by an overoxidation of the barrier but strongly by underoxidation. Finally, the obtained values are used to model the temperature dependence of TMR according to TMR $= \sum \text{W}_\text{N} \cdot \text{TMR(N,T)}$. The achieved dependencies together with the measured curves for the TMR ratios are displayed in Fig. 4.7 (bottom). One can see that the curves can be well fitted with the model. Especially in the case of the optimized barrier (d_{MgAl} = 0.87 nm), around RT the model fits the measured values much better than the magnon model or Bloch wall model. This might hint to the existence of localized states even in the optimized barrier.

4.1.2 CoFe Insertion at the Bottom Interface

In 2009, Tsunegi *et al.* inserted an ultrathin CoFeB insertion layer at the bottom interface of a $Co_2MnSi/MgO/Co_2MnSi$ MTJ to enhance the TMR ratio [93]. It was attributed to the stabilization of the Co_2MnSi interface magnetic moments. Similarly, I used a thin CoFe insertion layer at the bottom interface to increase the TMR ratio. Here, CoFe instead CoFeB was used because it has a crystalline cubic structure when sputtered. Contrarily, CoFeB is amorphous after sputtering making it difficult to grow an epitaxial barrier on top [94]. For this experiment the MgAl thickness was fixed to $d_{\text{MgAl}} = 0.9$ nm and insertion of CoFe with a thickness of $d_{\text{CoFe}} = 0 - 1.5$ nm was used. The TMR and RA ratios as a function of d_{CoFe} are displayed in Fig. 4.8 (a). For comparison, an MTJ with a CoFe-bottom electrode with the following stack was fabricated: MgO(001) substrate//Cr (40)/CoFe (10)/Mg (0.45)/MgAl (0.9)/CoFe (5)/ IrMn (12)/ Ru (12) (thickness in nm). The same annealing conditions as for the MTJ with a CFA electrode were used, see Sec. 4.1.1. The inset shows the TMR curves of two junctions with $d_{\text{CoFe}} = 0$ and 1 nm. The TMR (RA) increases (reduces) when CoFe is inserted. The largest (lowest) TMR (RA) of 280% at RT (453% at 5 K) is observed for junctions with $d_{\text{CoFe}} = 1$ nm. Compared to the MTJ with a CoFe bottom electrode the TMR (RA) ratio is larger (lower). Note that the TMR ratio is lower than the one in $CoFe/MgAl_2O_4/CoFe$ junctions (308%) in Ref. [41] which is due to the different annealing conditions and buffer layers used.

Table 4.3: Parameters obtained from the temperature fit of ΔG using the values for G_N obtained from the previous fit.

Junction (d_{MgAl})	C (K^{-1}) (smearing)	α ($\text{K}^{-1.5}$)	P
0.38 nm	$(3.21 \pm 0.01) \times 10^{-3}$ (14.6%)	$(4.08 \pm 0.08) \times 10^{-6}$	0.87
0.87 nm	$(1.68 \pm 0.09) \times 10^{-3}$ (4.2%)	$(9.04 \pm 0.07) \times 10^{-6}$	0.88
1.58 nm	$(6.84 \pm 43) \times 10^{-10}$ (0.0%)	$(6.04 \pm 0.01) \times 10^{-6}$	0.79

Figure 4.8: (a) TMR (top) and RA (bottom) ratios vs d_{CoFe} measured at RT for $d_{MgAl} = 0.9$ nm; "CoFe" denotes a $CoFe/MgAl_2O_x/CoFe$ MTJ for comparison; inset shows the TMR curves for two MTJs with $d_{CoFe} = 0$ and 1 nm; (b) TMR temperature dependence of MTJs with $d_{CoFe} = 0$ (red) and 1 nm (black); inset: R_P and R_{AP} normalized to the resistance at $T = 5$ K.

For further discussion the temperature dependence of two MTJs with $d_{CoFe} = 0$ and 1 nm are shown in Fig. 4.8 (b). One can see that the slope for both MTJs is almost the same. Interestingly, R_P for the MTJ with $d_{CoFe} = 1$ nm shows a similar positive slope as the junction with a thin barrier, see Fig. 4.4 (b). Similarly, one can conclude for this junction that defects or impurities in the barrier are present which leads to this unique behavior. This fact is further supported by the EDS profile as discussed in Sec. 4.1.3 which shows a segregation of Mg in the barrier at the bottom interface. Therefore, incomplete mixing of Al and Mg can lead to defects in the barrier resulting in the here observed TMR temperature dependence.

The lower TMR of MTJs with CoFe electrode compared to one with CoFe insertion is evidence for a strong contribution of CFA, especially, to the TMR ratio. On the other hand, the RA monotonically reduces with d_{CoFe}. The RA for $d_{CoFe} = 0$ nm was 2.5 kΩμm^2, which was 10 times higher than that for $d_{CoFe} = 1.5$ nm. This behavior suggests that the interface between the CFA and $MgAl_2O_4$ barrier for $d_{CoFe} = 0$ nm can be partly degraded (i.e., monolayer oxidation of CFA, intermixing, etc.) due to the damage in the oxidation process, even if the dislocation-free interface is maintained. Such imperfections may reduce the coherency of electron transport and cause an undesirable increase in the effective barrier thickness. Here, a higher RA for the CoFe-MTJ than the MTJs with $d_{CoFe} > 1$ nm means the difference in electronic structure between the $CoFe/MgAl_2O_4$ and the CFA/ultrathin $CoFe/MgAl_2O_4$ interface as discussed later. Consequently, we can conclude that the CoFe insertion up to $d_{CoFe} \approx 1$ nm on the CFA reduces the oxidation damage and intermixing, and a further increase of d_{CoFe} reduces the bulk contribution from the highly spin-polarized CFA layer. Note that the degradation of the $CFA/MgAl_2O_4$ interface cannot be detected in an STEM image as will be shown below. This also suggests that the spin-dependent transport is very sensitive to only slight differences in the chemical and electronic states.

In Fig. 4.9 the conductance spectra of the junctions shown in Fig. 4.8 (a) are displayed. Additionally, for comparison the spectra of a CFA/MgO/CoFe(001) junction are shown. The curves are normalized to $V = 0$ V. the strong asymmetry in the conductance spectra was already observed in the

Figure 4.9: Conductance spectra of MTJs with $d_{CoFe} = 0$, 0.5 and 1 nm for P (top) and AP (bottom) states; Spectra of a CFA/MgO/CoFe MTJ and a $CoFe/MgAl_2O_4/CoFe$ MTJ are also shown for comparison.

wedge-shaped sample in Fig. 4.3 for P (top) and AP (bottom) state. When inserting CoFe at the bottom interface ($d_{MgAl} = 0.5$ and 1 nm) the spectra becomes symmetric. The CFA/MgO/CoFe and $CoFe/MgAl_2O_4/CoFe$ MTJs have also a symmetric spectra. This hints to a symmetric electronic interface structure for these MTJs. Obviously, the CFA-barrier interface structure differs significantly from the CoFe-barrier interface structure. Junctions with symmetric spectra show two minimum in the P state. The minimum at negative bias voltages are below 0.5 V and for positive bias voltages 0.3∼0.5 V. These minimum were observed in previous publications with CFA/MgO/$Co_{75}Fe_{25}$ MTJ [60] and CoFe(B)/MgO/CoFe(B) MTJs [95, 96, 97]. This behavior in the MgO barrier MTJ suggests that a high quality and well-defined CFA/MgO interface was achieved. For the $MgAl_2O_4$ barrier MTJ with $d_{CoFe} = 0$ nm, we clearly observed an asymmetric feature in both the P and AP state. Especially, a significant increase of G for $V < 0$ may suggest a degradation of the CFA/$MgAl_2O_4$ interface since the spectra in $V < 0$ mainly reflect the electronic structure of the bottom $MgAl_2O_4$ interface. A more detailed analysis of the electronic structure at the interface will be given below.

The normalized TMR vs bias voltage for junctions with $d_{CoFe} = 0$, 0.5 and 1 nm and a CFA/MgO/CoFe junction are shown in Fig. 4.10 (a). The curve for $d_{CoFe} = 0$ nm is asymmetric due to the asymmetry observed in the conductance spectra. V_{half} [$=(V_{half+} - V_{half-})/2$] for this MTJ (0.47 V) is also smaller than that for the MgO barrier MTJ (0.52 V); V_{half+} (V_{half-}) is the bias voltage at which TMR is 50% of the zero bias voltage value. The V_{half} values here are much smaller compared to $Fe/MgAl_2O_4/Fe$ junctions [39, 42] due to different electronic structures of Fe and CFA. By inserting the CoFe layer, nearly symmetric curves are obtained due to a shift of the positive voltage branch of the TMR and V_{half} approach the value for the MgO barrier MTJ (0.53 V for $d_{CoFe} = 0.5$ nm and 0.50 V for $d_{CoFe} = 1$ nm).

Figure 4.10: Bias voltage dependence of the normalized TMR ratio (a) and the output voltage V_{out} (b) at RT for MTJs with $d_{CoFe} = 0$, 0.5 and 1 nm, Values correspond to the maximum V_{out}; dependence of a CFA/MgO/CoFe junction is also shown.

Interestingly, I observe improved TMR ratios in high-V regions ($|V| > 0.5$ V) for the MTJs with the CoFe insertion compared with the MgO barrier MTJ. The improved TMR ratio in the high-V regions substantially enhances the output voltages ($V_{out} = |V|\,(R_{AP} - R_P)/R_{AP}$) as shown in Fig. 4.10 (b). The maximum V_{out} for the $MgAl_2O_4$ MTJ with $d_{CoFe} = 1$ nm reaches 0.448 V, which is higher than that for the MgO barrier MTJ (0.396 V) and that for the reported one in the CFA/MgO/$Co_{75}Fe_{25}$ MTJ (0.425 V) [28]. By reducing the in-plane lattice mismatch which will be shown in Sec. 4.1.3, TMR ratios in high-V regions are improved since TMR reduction due to the inelastic tunneling at the dislocations becomes negligible. Therefore, the enhancement of the TMR ratios in high-V regions and V_{out} in the CFA-MTJs with the $MgAl_2O_4$ barrier may be attributed to the reduction of the lattice mismatch between barrier and electrode.

4.1.3 TEM and EDS Characterization

To obtain information of the barrier and the element distribution, TEM and EDS measurements were done for different samples and related to the transport characteristics of the respective junctions. For this one three different junctions were used. The characteristics of all three junctions are shown in Table 4.4. Here, RA_P (RA_{AP}) corresponds to the resistance are in the P (AP) state. One can see that MTJ-2 and MTJ-3 are the same as MTJs with $d_{CoFe} = 0$ and 1 nm in the previous section. For further understanding of the interface electronic structure later a third sample MTJ-1 is given. For this sample the CFA layer was not annealed and no CoFe insertion was used. Firstly, low magnification

Table 4.4: Characteristics of three different samples for TEM analysis.

Sample	d_{CoFe}	T_{CFA}	d_{MgAl}	TMR	RA_P	RA_{AP}
MTJ-1	0 nm	none	0.55 nm	120%	1500 $\Omega\mu m^2$	3500 $\Omega\mu m^2$
MTJ-2	0 nm	250°	0.70 nm	228%	1800 $\Omega\mu m^2$	5750 $\Omega\mu m^2$
MTJ-3	1 nm	250°	0.90 nm	280%	270 $\Omega\mu m^2$	880 $\Omega\mu m^2$

Figure 4.11: Low-magnification HAADF-TEM images of MTJ-1, MTJ-2, and MTJ-3; Respective layers are shown on the right with thickness in caption.

cross-sectional HAADF-TEM images of MTJ-1, MTJ-2, MTJ-3 are shown in Fig. 4.11 (a)-(c), respectively. Here, a brighter contrast means a larger average atomic number (Z). The respective stacks are shown next to the TEM images with the respective thicknesses in brackets behind. Each layer can be well distinguished from its contrast. This means low intermixing between the layers and a high quality of the MTJ stack. The different top electrodes of MTJ-1 (white stripe in the bottom electrode corresponds to Ru (0.8 nm) spacer layer) and MTJ-2 and MTJ-3 are clearly visible. They are used to ensure a sufficient exchange bias. The barriers of all three junctions are well defined with smooth bottom interfaces. The top interfaces appear to be rougher than the bottom ones which might be related to the formation mechanism of an $MgAl_2O_4$ barrier using the post-oxidation process [41]. A clear contrast between CoFe and CFA in the bottom electrode of MTJ-1 can be seen. It fades out in MTJ-2 and MTJ-3 when the CFA layer is annealed which hints to diffusion of elements (i.e. Al).
For a better verification of the barrier area, high resolution images were taken around the barrier in Fig. 4.12 (a)-(c). The barrier thicknesses are larger than the designed one ($d_{Mg} + d_{MgAl}$) due to the incorporation of oxygen during the postoxdiation process. Next to the TEM images fast Fourier transform (FFT) filtered with respect to the $MgAl_2O_4$(200) atomic planes (Fig. 4.12 (d)-(f)) and with

respect to the $MgAl_2O_4(002)$ atomic planes (Fig. 4.12 (g)-(i)) are shown. Around the barrier of MTJ-1

Figure 4.12: High resolution HAADF-STEM image of MTJ-1 (a), MTJ-2 (b), and MTJ-3 (c) around the barrier; FFT filtered image with respect to $MgAl_2O_4(200)$ ((d)-(f)) and $MgAl_2O_4(002)$ ((g)-(i)) planes; Markers show dislocations.

several defects can be observed, especially, for the $MgAl_2O_4(200)$ filtered image. From the density of the defects at the interface a lattice mismatch of ∼1.7% (number of defects/number of lines) at the top spinel/CoFe interface was calculated. For the $MgAl_2O_4(004)$ filtered images up to two defects are found. This can be attributed to the missing annealing temperature of CFA which leads to a modified growth and a somewhat strained crystal structure of the layers grown on CFA. Already slight changes in the CFA layer can lead to significant changes of the crystal structure of the layers grown on top of CFA. For MTJ-2 and MTJ-3 no defects are observed which is attributed to a perfect lattice-matching between CFA and the $MgAl_2O_4$ spinel barrier. This is also expected theoretically.

In Fig. 4.13, the NBD patterns of the bottom-CoFe buffer, B2-CFA bottom electrode and top-CoFe top electrode close to the interface, and the $MgAl_2O_4$ barrier for all three samples are shown. The planes responsible the respective reflection spots are labeled in the images. The corresponding reflection indices are labeled in the images. A cation-discorded spinel barrier without any superlattice reflections from {220} planes is observed. The patterns do not differ much because the barriers are annealed at the same temperature. The top-CoFe has a bcc structure. The CFA electrodes have a B2-ordered

Figure 4.13: NBD pattern of MTJ-1, MTJ-2, and MTJ-3 of bottom-CoFe, B2-CFA electrode, $MgAl_2O_4$ barrier, and top-CoFe electrode; Respective reflection spots are labeled.

structure because of the absence of {111} reflection spots. No difference in the ordering of CFA in MTJ-1 and MTJ-2 and MTJ-2 cannot be found. However, one expects a better ordering of CFA in MTJ-2 and MTJ-3 due to the low temperature annealing at 250°C which should effect the ordering but is too small to be observed in the NBD pattern. Changes at the CFA interface cannot be excluded either because they also cannot be detected. However, the tunneling transport properties are sensitive to slight changes at the barrier/electrode interfaces.

In Fig. 4.14, the EDS element distribution profiles are shown with each layer and element labeled. The element ratios are in units of atomic percent. Note that a background of 10-15 at.% of Oxygen can be observed which is an artifact of the measurement. The element distribution of Co and Fe at the bottom interface shows a longer tail into the barrier for MTJ-1 compared to MTJ-2 and MTJ-3. Because the element profiles are taken over a long lateral distance, the broad tail reflects the rougher bottom interface of MTJ-1. In the same junction, the stoichiometry of the CFA electrode is similar to the nominal composition. The stoichiometry of the CFA electrode in MTJ-2 displays a small reduction of Al from the CFA layer. A small Co-peak and a minimum in the Al distribution in CFA close to the barrier interface are observed. This can be attributed to diffusion of elements when the layer is annealed. In MTJ-3, the insertion of CoFe at the bottom interface is clearly reflected in the element distribution. Inserting CoFe reduces the amount of Al at the bottom interface greatly. This is also reflected in the stoichiometry of CFA which improves (increase of Al content) compared to MTJ-2. Therefore, CoFe acts as a diffusion barrier for light elements (i.e. Al). Segregation of Mg at the bottom interface is also observed in MTJ-3 which is caused by the change in the underlying structure. The CoFe insertion might block the supply of Al from the CFA layer which may be necessary to form

a uniform barrier together with the Mg at the bottom. The top interface and electrode are similar for all junctions showing stoichiometric CoFe.

In Fig. 4.15, the HAADF image together with the corresponding element maps of Co, Fe, O, Al, and Mg of the same junction are displayed. The element distributions are well confined within their respective layers. The CoFe, CFA and barrier layers can be distinguished from the Al and Fe map. As already observed in Fig. 4.14, the rough top interface is reflected in the element distribution. The Al shows slight diffusion out of the barrier into the top-CoFe electrode and out of CFA into the bottom-CoFe layer.

Figure 4.14: EDS element profiles for MTJ-1 (a), MTJ-2 (b), and MTJ-3 (c) for all elements; Corresponding layers are shown in the top of the graphs; 10-15 at.% of Oxygen in the metallic layers is an artifact.

Figure 4.15: EDS elemental maps for the elements and HAADF-STEM image of barrier and electrodes for MTJ-1, MTJ-2, and MTJ-3.

4.1.4 Discussion on the Electronic Interface Structure

In the previous section the crystal structures of three MTJs were investigated. The crystal structures were found to be similar. A difference could be only observed in the element distribution for the bottom electrode and interface. In this part, I want to discuss the electronic interface structure and relate it to the transport properties of the three samples and the structural observations. In Fig. 4.16, the TMR, and RA products in the parallel (RA_{P}) and antiparallel (RA_{AP}) are shown. Note that the RA axis is logarithmic. The values can also be found in Table 4.4. For comparison, the values of the CoFe introduced in Sec. 4.1.2 are shown. The lowest TMR is observed in MTJ-1 without any bottom CFA annealing and CoFe insertion. Annealing CFA at 250°C increases the TMR while (RA_{P}) remains constant (MTJ-2). The lowest (highest) RA_{P} (TMR) is observed when keeping the CFA post-annealing temperature and inserting 1 nm of CoFe at the bottom interface between CFA and the spinel barrier. The $CoFe/MgAl_2O_4/CoFe$ junction has a higher (lower) RA_{P} (TMR) ratio than MTJ-3 but lower R_{AP} compared to MTJ-1 and MTJ-2. In Fig. 4.17, the bias voltage dependence of the conductance normalized at $V = 0$ V of all MTJs in the P (a) and AP (b) magnetization states at RT are shown. Although, low temperature measurements are preferable due to the minimization of thermal contributions to the conductance curves, it does not change the discussion in the following. At positive bias voltages electrons tunnel from CFA to CoFe and for negative bias voltages vice versa. MTJ-1 and MTJ-2 show a strong asymmetry in both states. In the P configuration, both junctions

have a

Figure 4.16: TMR (a), RA_{P} (shaded) and RA_{AP} (unshaded) (b) values for the junctions MTJ-1, MTJ-2 and MTJ-3 are shown. 'CoFe' indicates the values for the $CoFe/MgAl_2O_4/CoFe$ junction.

minimum at positive bias voltage and a small shoulder at negative bias voltage. They coincide with shoulders in the AP state at the respective bias voltages indicated by dashed lines. After annealing CFA, the minimum is more pronounced and shifts to higher bias voltages. The shoulders in the P and AP state curve remain almost unchanged after the post-annealing.

Comparing MTJ-1 and MTJ-2, the increase in TMR after post-annealing origins from an increase in the RA_{AP} product. The crystal structures shown above deviate only slightly from each other, although, one expects an increased B2-ordering after annealing CFA at 250°C. A change in the ordering can affect the electronic structure of Heusler alloys at the interface [98, 99]. Therefore, the increase of RA_{AP} is a result of an improved electronic interface structure due to a sharper interface as observed in the element distribution in Fig. 4.14 and the absence of top interface defects. This might lead to an opening of the minority band gap reducing the probability of minority tunneling electrons increasing the resistance. This will be further discussed below. MTJ-3 with 1 nm of CoFe inserted at the bottom interface shows the lowest (highest) RA_{P} (TMR). Interestingly, also RA_{AP} decreases greatly after the insertion. The EDS maps and NBD patterns of sample MTJ-2 and MTJ-3 are similar without strong deviations from each other. The largest changes are observed at the bottom interface. As seen in the elemental graphs, a small segregation of Mg at the bottom interface of $MgAl_2O_4$ can be found. However, it cannot be responsible for the strong change of RA_{P} and, especially, RA_{AP}. When

Figure 4.17: Normalized conductance vs. bias voltage of parallel (a) and anti-parallel (b) state at RT for MTJ-1, MTJ-2, MTJ-3 and the $CoFe/MgAl_2O_4/CoFe$ junction; Electrons tunnel from bottom to top for positive bias voltages.

comparing MTJ-2 with the $CoFe/MgAl_2O_4/CoFe$ junction, one can see that the MTJ with a Heusler electrode shows a higher RA ratio than the one with a CoFe electrode. Interestingly, this also holds for CoFe(B) and Heusler electrodes with a MgO barrier. In Table 4.5, the RA_P ratios of MTJs presented in this and several other works are compared using CoFe(B) or Heusler alloys as a bottom electrode. MTJs with a similar barrier thickness are chosen. Junctions with a CoFe(B) electrode show a lower RA ratio than junctions that have at least one Heusler electrode. This holds for MgO and $MgAl_2O_4$

Table 4.5: Comparison of the RA_P ratios between CoFe(B) and Heusler alloy electrodes for epitaxial MTJs at RT; $Co_{50}Fe_{50}$ electrodes are denoted CoFe.

Junction	$d_{Barrier}$ (nm)	TMR (%)	RA_P ($\Omega\mu m^2$)	Reference
$Co_{70}Fe_{30}/MgO/(Co_{70}Fe_{30})_{80}B_{20}$	2.0	220	10^4	[15]
CoFeB/MgO/CoFeB	2.0	~140	2×10^3	[100]
$Co_2FeAl_{0.5}Si_{0.5}/MgO/Co_{75}Fe_{25}$	2.0	130	10^6	[100]
$Co_2FeAl/MgO/Co_{75}Fe_{25}$	1.8	328	10^4	[60]
$Co_2MnSi/MgO/Co_2MnSi$	2.4	330	$\sim3\times10^5$	[76]
$CoFe/MgAl_2O_4/CoFe$	~1.9	200	8×10^2	this work
$Co_2FeAl/MgAl_2O_4/CoFe$	~1.7	235	1.7×10^3	this work

barriers. The different RA seem to be an intrinsic feature of CoFe(B) and is most likely related to a larger number of electronic states around the Fermi energy in these materials enhancing the number of tunneling electrons. In our junctions, this holds for both majority as well as minority states because RA_{P} and RA_{AP} drop as well.

The increased TMR in MTJ-3 is related to an improved interface structure [101]. By inserting CoFe, CFA is protected from oxidation. The second reason might be disordering of the CFA interface itself. Although, B2-crystallized CFA is theoretically expected to have a spin polarized Δ_1-state, the ordering of the CFA interface is unknown but most likely varies from the bulk one. Despite, observation of oxidation or diffusion at the interface with TEM is almost impossible, the latter one is supported by the element maps which show slight diffusion of Al out of CFA changing its stoichiometry in the case of MTJ-2. It is known that disorder in Heusler alloys introduces additional states at the Fermi level and destroys their half-metallicity [60, 102, 103]. Therefore, the spin polarization of CFA in our samples is likely to be far away from the theoretically expected value. By inserting CoFe, Al diffusion to the interface can be reduced.

Considering the conductance spectra in Fig. 4.17, a similar asymmetry in the P state can be found in $Co_2MnSi/MgO/CoFe$ MTJs [57]. Similar to our junctions, they show a deeper minimum after annealing the MTJ stack. The dip structure is attributed to the coherent tunneling effect which is present in the crystalline MgO barrier. This is clearly the same case in our junctions and should be associated with the underlying band structures of the electrodes as observed in Fe/MgO/Fe MTJs [89]. The shift of the minimum to higher voltages with increasing CFA annealing temperature should correspond to a shift of the responsible band(s) at the CFA interface to higher energies. The shoulder at negative bias voltage should also be a fingerprint of another electron band. The conductance curves of MTJ-3 and the $CoFe/MgAl_2O_4/CoFe$ MTJ are symmetric showing two minimum in the P state at positive and negative bias voltages representing similar electronic structures at both interfaces. In the AP state anomalies appear at positive and negative bias voltages, indicated by the dashed lines in Fig. 4.17. Again, the features in the conductance curves should reflect the underlying electronic structure and relate to closing or opening of bands at the respective energies. The same features are observed in CoFe(B)/MgO/CoFe(B) junctions [95, 97, 96]. Because these features in P and AP state occur at the same bias voltages, a contribution of minority bands seems likely.

The shoulder in the P state in Fig. 4.17 at negative bias voltages fades out with increasing barrier thickness (see Fig. 4.3 (a)) which hints to an electronic state that decays rather fast in the barrier. The conductance curves show that the coherent tunneling effect is present in our junctions. Therefore, the symmetric filtering effect as observed in MgO based MTJs is also present in the spinel barrier [41]. Assuming a similar decay behavior of the electronic states as in MgO [12] and referring to other works on CoFe(B)/MgO/CoFe(B) MTJs ([104] and references therein), the observed shoulder at negative bias voltages when electrons tunnel from CoFe into CFA can either be a Δ_2- or Δ_5-symmetry state. A recent work by Ringer *et al.* investigating the anomalies in CoFeB/MgO/CoFeB in detail, points to a Δ_2-symmetry state [104]. The absence of a strong minimum in our sample might be due to the absence of a Δ_2-symmetry state in CFA around the Fermi energy as calculated by Wang *et al.* for B2-ordered bulk [78].

At this point, the minimum in the P state conductance curve cannot be assigned clearly to a specific electronic band. It should be a mixing of the band gap structure in CFA and the closing or opening of specific bands in CoFe which can be seen due to the symmetric filtering effect of the spinel barrier.

The influence of the CFA band structure on the minimum can be seen in Fig. 4.17. When CFA is annealed, a shift of the minimum occurs. This effect is also observed in $Co_2MnSi/MgO/CoFe$ MTJs [57]. Therefore, the minimum is not closely related to the barrier material. The shift of the minimum (Fig. 4.3 (d)) should be related to a shift of the underlying bands to higher energies. Note, that the observed break point at the optimal barrier thickness (∼0.8 nm) coincides with the change of the exponential slope of RA. The behavior seems to be related to the oxidation of the barrier [101]. However, further studies are necessary in order to clarify the origin of the minimum.

4.1.5 Summary

Fabrication of MTJs with a CFA bottom electrode and spinel $MgAl_2O_4$ barrier are possible and large TMR up to 230% can be achieved. Insertion of CoFe at the CFA/barrier interface increased the TMR and reduced RA drastically. This is attributed to the change in the electronic interface structure and avoiding the oxidation of the CFA interface because no clear changes in the MTJ crystal structure was found. The temperature dependence was investigated using three different models. Interestingly, positive resistance slopes in R_P could be best fitted with an electron hopping model. The MTJs proved to be lattice-matched with only slight diffusion of elements. NBD proved the existence of B2-CFA and a cation-disordered barrier. Furthermore, the interface electronic interface structure based on differential conductance curves was discussed.

4.2 $Co_2FeAl/MgAl_2O_4/Co_2FeAl$ MTJs

From the last chapter it got clear that high TMR ratios can be achieved when using a CFA Heusler alloy as a bottom electrode and this TMR can be further increased by inserting CoFe at the interface. However, it clearly shows that the CFA/barrier interface is not optimal and the spin polarization should be significantly lower than what it is expected from theory. In order to improve the TMR ratio further, half-metallic Heusler electrodes for both the top- and bottom-$MgAl_2O_4$ sides seems promising. However, the growth of high quality metallic films directly on oxide materials is often challenging due to difference in their surface energies between metals and oxides [105]. Therefore, the interaction of the surfaces is less for the growth of an FM layer on a barrier, and thus a three-dimensional growth is often energetically favorable resulting in a non-uniform coverage of the oxide surface for ultra-thin films and a rough interface [106]. Therefore, controlling the interfacial state at the barrier/top ferromagnetic electrode is the important factor toward a high performance MTJ stack. In addition, to obtain a high TMR ratio in $MgAl_2O_4$-based MTJs using typical 3d-transition FM materials (Fe or CoFe) or B2-ordered alloys, the $MgAl_2O_4$ barrier generally is needed to have a cation-disordered spinel structure having a half size lattice of an ordered spinel structure; that is, the band-folding effect in the FM electrodes must be suppressed by controlling the $MgAl_2O_4$ structure when non-half-metallic electrodes are used (see Sec. 2.4).

4.2.1 Top-Co_2FeAl Electrode Annealing

As mentioned, it is difficult to grow metallic thin films on oxides. Therefore, at first the grow condition of CFA on the $MgAl_2O_4$ barrier was investigated. For this, stacks with the following structure were prepared: MgO(001) substrate//Cr (40)/CoFe (10)/Mg (0.45)/MgAl (0.75)/oxidation/CFA (10)/Ru(2) (thickness in nm). The Cr buffer, bottom-CoFe electrode and spinel barrier were annealed at 500°C, 300°C, and 250°C, respectively. The barrier was oxidized using the direct plasma method (see Sec. 2.4) and the Ru-cap protects the CFA film from oxidation. The stack with the respective layer annealing temperatures is shown in Fig. 4.18 (a). In the bottom electrode, CFA was replaced by CoFe to observe the XRD-peaks of the B2 superlattice peak (002) of the CFA layer. Fig. 4.18 (c) and (d) show the XRD out-of-plane and in-plane profiles for different CFA annealing temperatures T_{CFA}, respectively. The in-plane profiles are normalized to the peak at $2\theta \approx 65°$ which contains the overlapped peaks of B2-CFA(400), CoFe(200) and Cr(200) peak. The XRD profiles indicate that the 10 nm thick CFA layers grow as continuous and epitaxial films in a (001)-orientation on the $MgAl_2O_4$ barrier independent of the CFA. The FWHM values of the rocking curves for the B2-CFA(001) peaks (out-of-plane) were 2.18° (T_{CFA} = 250°C), 1.43° (T_{CFA} = 450°C) and 1.22° (T_{CFA} = 600°C), indicating that the annealing at a higher T_{CFA} improves the (001) orientation. The out-of-plane patterns show a shift of the CoFe(004) peak to lower angles and a drop of the Cr peak intensity at T_{CFA} = 600°C. It coincides with a ∼0.003 nm increase of the out-of-plane lattice parameter $a^{\mathrm{out}}_{\mathrm{CoFe}}$ = 0.286 nm (a_{bulk} = 0.285 nm) at T_{CFA} = 600°C and is attributed to a relaxation of the CoFe lattice. Note that a shift of the in-plane CoFe peak cannot be observed due to the overlap with Cr(200) and CFA(400) peaks ($a^{\mathrm{in}}_{\mathrm{Cr}} = a^{\mathrm{in}}_{(\mathrm{CFA}(B2))} \sim 0.287$ nm). The drop of the Cr peak intensity is speculated to originate from diffusion of Cr into other layers. The measured out-of-plane lattice parameter for the CFA is $a^{\mathrm{out}}_{(\mathrm{CFA}(B2))} \sim 0.286$ nm for all temperatures, similar to the theoretical bulk value ($a_{\mathrm{bulk}}(L2_1)/2$ = 0.2865 nm [107]). In the in-plane scan the intensity of the CFA(200) with respect to the CFA(400) peak (including the

Figure 4.18: (b) Out-of-plane XRD scan normalized to the substrate MgO(002) peak; (c) In-plane scan normalized to the overlapped CFA(400) peak.

Cr(200) and CoFe(200) intensities) increases with T_{CFA}, indicating that the B2-order of the CFA layer improves with T_{CFA} by assuming no change in the overlapped Cr(200) and CoFe(200) peak intensities. Therefore, if the interdiffusion between each layer can be neglected, a highly (001)-oriented and highly B2-ordered CFA film grows directly on an $MgAl_2O_4$ barrier by sputtering in combination with a post-annealing process at a high temperature; this is clearly different from the case of the direct sputter deposition of CFA on the MgO barrier [60].

Multilayers were deposited on an MgO(001) single crystal substrate with the following stacking structure, see Fig. 3.2: substrate//Cr buffer (40)/$Co_{50}Fe_{50}$ (hereafter CoFe) buffer (5)/bottom-CFA (5)/CoFe ($d_{\text{b-CoFe}}$ = 0-1 nm)/Mg (0.45)/Mg-Al (0.75)/oxidation/CoFe ($d_{\text{t-CoFe}}$ = 0-0.5 nm)/top-CFA (5)/CoFe (0.5)/IrMn (12)/Ru (12) (in nanometer). The post-annealing temperatures are shown in the stacking structure. The ultrathin CoFe insertion between the bottom-CFA and Mg is to control the bottom-CFA/$MgAl_2O_4$ interface for high TMR ratio. The CoFe inserted between the top-CFA and IrMn is to increase the exchange bias field by the IrMn layer. The same was tried by inserting CoFe at the top interface. The whole stack was ex-situ annealed at 300°C under a magnetic field of 5 kOe applied parallel to the CFA magnetic easy axis (MgO substrate [100] ∥ CFA [110]) direction.

Fig. 4.19 (a) displays the TMR ratio (top) and RA (bottom) of MTJs with a CFA/$MgAl_2O_4$/CFA structure with $d_{\text{t-CoFe}} = d_{\text{b-CoFe}} = 0$ nm (no insertion) as a function of the post-annealing temperature for the top-CFA (= T_{CFA}), measured at RT. The post-annealing temperature of 300°C was used for the bottom-CFA layer, which was optimized before, see Sec 4.1. The lines in Fig. 4.19 (a) show the maximum TMR values of the above reported CFA/$MgAl_2O_4$/CoFe (red, dashed) and CFA/CoFe (1 nm)/$MgAl_2O_4$/CoFe (blue, dash-dotted) MTJs. With increasing T_{CFA}, the TMR ratio increases. The TMR ratio at T_{CFA} = 400°C (450°C) is comparable to the values obtained in a CFA/MgO/CoFe MTJ (CFA/$MgAl_2O_4$/CoFe MTJ). Importantly, at T_{CFA} = 500°C, the TMR ratio of the CFA/$MgAl_2O_4$/CFA MTJ exceeds the values in the CFA/$MgAl_2O_4$/CoFe MTJ. Therefore, the high spin polarization owing to the high B2 order of the top-CFA layer is responsible for the enhanced TMR ratio. Interestingly, the RA also increases with T_{CFA}, suggesting the significant change of the interfacial electronic states with the post-annealing.

In the next step, the bias voltage dependence of the conductance at RT of a sample with T_{CFA} = 300°C, 400°C and 500°C were measured. One expects more symmetric curves in both P and AP state compared to CFA/$MgAl_2O_4$/CoFe MTJs because of a similar electronic interface structure at bottom and top. The normalized at $V = 0$ V conductance vs bias voltage is displayed in Fig. 4.19 (c) and (d).

Figure 4.19: (a) TMR (top) and RA (bottom) vs. top-CFA annealing temperature T_{CFA}; red, dashed (blue, dash-dotted) line indicate the maximum TMR for $CFA/MgAl_2O_4/CoFe$ (CFA/CoFe (1nm)/$MgAl_2O_4$/CoFe) junctions; (b) TMR curves at RT for different T_{CFA}; (c) and (d) normalized conductance at $V = 0$ V vs. bias voltage at RT in parallel and antiparallel state.

The dotted curve represents a $CFA/MgAl_2O_4/CoFe$ junction with the same barrier thickness (d_{MgAl} = 0.75 nm). A positive bias voltage means electrons tunnel from bottom to top. As expected, the junctions with a top-CFA electrode are more symmetric than $CFA/MgAl_2O_4/CoFe$ MTJs. Minima at positive and negative bias voltages in the P state can be observed. by replacing CoFe with CFA at the top the shoulder at negative bias voltages becomes a minimum which is due to the change in the top electronic interface structure. Interestingly, the minimum at positive bias voltages becomes shallow leading to higher conductivity. This can be associated with the increase of the amount of carriers that can tunnel through the barrier. The possible electronic structure at the interface will be discussed further below. Annealing top-CFA leads to a upward shift of the conductance curves. The effect is larger for the positive bias voltage branch which hints to major change at the top interface. At low negative (positive) bias voltages ($|V| \leq 0.2$ V), a minimum (maximum) appears. The origin is still unclear. It might be related to diffusion processes at high temperatures. The conductance in the AP increases with increasing T_{CFA}. The curves are symmetric. Especially, the positive branch moves upwards when exchanging CoFe with CFA as a top electrode.

To get a rough image of the barrier properties, the conductance curves in the AP state were fitted with the Brinkmann model (see Sec. 2.2.1). Because for bottom and top electrodes CFA was used the AP state is symmetric and parabolic. Due to this fact, $\Delta\Phi$ is assumed to be zero. Again, it should be

Figure 4.20: (a) Polynomial fit used for the Brinkmann model in the case of $T_{CFA} = 500°C$; the fit was always carried out between ±0.4 V; (b) obtained values for the barrier height and thickness using Eq. 2.16 of the Brinkmann model; Errors bars are obtained from the fitting according to (a).

emphasized that this model is based on free electrons with parabolic energy dispersions and does not include any interface properties (i.e. DOS) and doesn't distinguish between P and AP state. Because the model is only valid at low bias voltages, the fit was done between $|V| \leq 0.4$ V using a parabolic fit. The fit is shown in Fig. 4.20 (a) for the sample with $T_{CFA} = 500°C$. For the fit, the effective electron mass m_e^* in the barrier is necessary but is unknown. From literature the value for bulk $MgAl_2O_4$ was used: $m_e^* \approx 0.36 m_e$ [108]. Note, that for a thin film this value can differ. The extracted barrier height Φ and thickness t are plotted in Fig. 4.20 (b) as a function of T_{CFA}. The extracted effective barrier height (thickness) are too large (small) when compared to MgO or TEM images of the barrier (see Sec. 4.1.3). The barrier height seems to be almost constant between 7.9 and 8.5 Å within the error while the effective barrier height reduces with T_{CFA}. The constant barrier thickness hints to hot spot (i.e defects, vacancies) free tunneling. If electrons tunnel through hot spots usually a decrease of Φ and t is observed. Therefore, the decrease of the effective barrier height might be due to an improved band matching of the bottom and top interface which leads to a reduced barrier height allowing more electrons to tunnel. This can be seen in Fig. 4.19 (c) in which the conductance curves become more symmetric at higher T_{CFA}.

4.2.2 CoFe Insertion

In $CFA/MgAl_2O_4/CoFe$ junctions an improvement of the bottom interface and an increase (reduction) of TMR (RA) with CoFe insertion. To check if the top interface is degraded and improvement is possible, the CoFe insertion method was probed at both top and bottom interface with different CoFe insertion thicknesses $d_{\text{t-CoFe}}$ and $d_{\text{b-CoFe}}$, respectively.

Top-CoFe Insertion

First, the insertion at the top interface was probed. The used insertion thickness is $d_{\text{t-CoFe}} = 0\text{-}0.5$ nm. TMR and RA vs. insertion thickness is shown in Fig. 4.21. $d_{\text{b-CoFe}} = 0$ here. With inserting CoFe TMR and RA decreases. The decrease of RA is less than in $CFA/CoGe/MgAl_2O_4/CoFe$ MTJs but follows the same trend. This is attributed to the modified interface electronic structure after insertion. The less reduction of RA is attributed to a higher quality top interface which cannot be improved by

Figure 4.21: (a) TMR (top) and RA (bottom) vs. $d_{\text{t-CoFe}}$; (b) and (c) conductance vs. bias voltage for thicknesses shown in (a) in P and AP state, respectively.

the CoFe insertion. The decrease of TMR supports this. It means that the $MgAl_2O_4$/CFA interface has a higher spin polarization than the $MgAl_2O_4$/CoFe/CFA interface. It is the result of the high annealing temperature of the top CFA leading to a better B2-ordering which should improve the spin polarization bringing the electronic structure close to the theoretical structure of B2-CFA as calculated by Wang *et al.* [60].

In Fig. 4.21 (b) and (c) the conductance vs. bias voltage curves at P and AP state, respectively, are shown for the different $d_{\text{t-CoFe}}$ shown in (a). The changes of the conductance spectra are small when CoFe is inserted. Interestingly, in the P state the negative branch is effected by the insertion.

In the AP state positive branch is slightly effected. Furthermore, the respective conductance branches increase (decrease) in P (AP) state. In the P state the curves become more asymmetric with increasing $d_{\text{t-CoFe}}$. The observed minimum fades out and becomes a shoulder similar to the CFA/$MgAl_2O_4$/CoFe MTJ. It seems that after insertion the top interface becomes more 'CoFe like' which means a worse matching of the bottom and top interface electronic structures. Electrons have less empty states to tunnel into and/or less electrons are available for tunneling. Therefore, the top interface cannot be improved by inserting CoFe.

Bottom-CoFe Insertion

In the CFA/$MgAl_2O_4$/CoFe MTJs, ultra-thin CoFe insertion at the bottom $MgAl_2O_4$ interface was substantially effective to improve the TMR ratio and to obtain a clean interface structure. Therefore, the effect of the insertion for the CFA/$MgAl_2O_4$/CFA structure is also investigated. In Fig. 4.22 (a), the $d_{\text{b-CoFe}}$ dependencies of the TMR ratio (top) and RA (bottom) are plotted for the CFA/CoFe ($d_{\text{b-CoFe}}$ = 0)/$MgAl_2O_4$/CFA MTJs with T_{CFA} = 500°C (black squares) and 550°C (blue circles), respectively. For T_{CFA} = 500°C, the TMR ratio increases slightly by inserting CoFe with a maximum at $d_{\text{b-CoFe}}$ = 0.5 nm. In the case of T_{CFA} = 550°C, the peak of the TMR ratio is also found at $d_{\text{b-CoFe}}$ = 0.5 nm, where the TMR ratio of 341% was observed (see the corresponding TMR-magnetic field curves in Fig. 4.22 (b)). The observed TMR ratio is higher than the value in the CoFe/$MgAl_2O_4$/CoFe MTJ (308% at RT) [41] indicating the effectiveness of the use of the highly spin-polarized Heusler layers for both the electrodes. The RA in the bottom of Fig. 4.22 (a) decreases with increasing $d_{\text{b-CoFe}}$ similar to the CFA/CoFe/$MgAl_2O_4$/CoFe MTJs.

To clarify the influence of the CoFe insertion at the high T_{CFA} = 500-550°C, the conductance curves of three different MTJs are plotted in Fig. 4.23. At T_{CFA} = 500°C, the insertion of $d_{\text{b-CoFe}}$ = 0.5 nm leads to a downward shift of the curve near the local minimum of the negative bias (see the

Figure 4.22: (a) TMR ratio (top) and RA (bottom) as a function of CoFe insertion thickness $d_{\text{b-CoFe}}$ for $T_{\text{CFA}} = 500°\text{C}$ (blue) and 550°C (black); (b) TMR curve for the MTJ with the highest TMR ($T_{\text{CFA}} = 550°\text{C}$ and $d_{\text{b-CoFe}} = 0.5$ nm).

red arrow) while the positive branch remains almost unchanged. A similar behavior was previously observed in the CFA/CoFe insertion/$MgAl_2O_4$/CoFe MTJs; this means that the bottom $MgAl_2O_4$ interface state was tuned by the ultra-thin CoFe insertion. Another reason might be interdiffusion of Al into the inserted CoFe due to the high T_{CFA} as observed in the EDS plot shown later. At $T_{\text{CFA}} = 550°\text{C}$, the whole conductance curve shifts upwards as indicated by the dark arrows and a plateau-like feature appears at negative bias voltages. In the AP state the negative branch moves downwards with CoFe insertion while at $T_{\text{CFA}} = 550°$ and $d_{\text{b-CoFe}} = 0.5$ nm the positive branch moves upwards. CoFe insertion is affecting mainly the negative branch which resembles electrons tunneling from top to bottom resembling the bottom interface. Therefore, the insertion affects only the bottom electronics structure. On the other hand, increasing the annealing temperature leads to a complete shift of the conductance curve in the P state. Remembering the conductance curve in P state without CoFe insertion at different annealing

Figure 4.23: Conductance vs. bias voltage at RT in P (a) and AP (b) state; The temperature in the graph is T_{CFA} and the thickness is $d_{\text{b-CoFe}}$; arrows in the P state curve mark the shift of the respective curve.

Figure 4.24: TMR temperature dependence of four junctions; red line presents a fit with the Bloch model according to Eq. 2.9.

temperatures in Fig. 4.19 (c), one can see that with CoFe insertion both interfaces are affected by the annealing temperature. Inserting of CoFe makes the bottom interface sensitive to temperature changes which is not the case without CoFe insertion. Together with the observed changes in P state conductance curve this hints to diffusion of Al at the bottom interface. By changing T_{CFA} and $d_{b\text{-}CoFe}$, the amount of Al (which is easy to diffuse [109]) can be tuned which leads to a change in the conductance curves. Although it is difficult to fully explain the observed changes in the curve at present, the optimum conditions for the CoFe insertion and T_{CFA} may lead to a high quality interface structure and thus the highly spin-polarized states at the interface through increase in the amount of Al at the bottom $MgAl_2O_4$ interface. The decrease in the RA with $d_{b\text{-}CoFe}$ could also be attributed to a change in the interfacial electronic states (i.e. DOS) caused by the bottom interface modification.

4.2.3 Low Temperature Measurements

Similar to $CFA/MgAl_2O_4/CoFe$ junctions shown above, the TMR temperature dependence is evaluated with the three models introduced in Sec. 2.2.1. The temperature dependence is plotted in Fig. 4.24 for four different junctions with different T_{CFA} = 400°C-550°C and bottom CoFe insertion $d_{b\text{-}CoFe}$ = 0-0.5 nm. The red line is a fit using the Bloch model according to Eq. 2.9. The extracted spin polarizations $P(0)$ and interface parameter a are shown in Table 4.6. The best fit is obtained for the sample with T_{CFA} = 550°C and $d_{b\text{-}CoFe}$ = 0.5 nm while the MTJ with T_{CFA} = 500°C and $d_{b\text{-}CoFe}$ = 0.0 nm cannot be fitted well due to the strong curvature of the curve. Additionally, the model has

problems with fitting the TMR at low temperatures. The zero temperature TMR is overestimated in all cases which means that the corresponding spin polarizations at zero temperature is slightly overestimated too. The spin polarization increases with increasing T_{CFA} as expected and a is similar for all junctions. Due to the used fitting method, the contribution of the top and bottom interface and electrode in $P(0)$ and a cannot be distinguished. As has been observed from the bias voltage dependence in the previous section, the bottom interface electronic structure without CoFe insertion seems to be almost unaffected by the high annealing temperature. However, when CoFe is inserted at the interface, the top CFA annealing temperature greatly affects the bottom interface electronic structure. Therefore, for the MTJs without CoFe insertion the increased spin polarization is linked to the improved top interface. After CoFe insertion $P(0)$ increases stronger which might be related to an improved top and bottom interface as observed in the bias voltage spectra.

Because the extracted information from the above model is quite sparse, the temperature dependencies are fitted with the more extensive Magnon model (see Sec. 2.10). The normalized resistance curves (black) with the respective fits (red) are shown in Fig. 4.25. The input (used) values and the extracted parameters are shown in each plot. The best fit is obtained for the MTJs with CoFe insertion. Without CoFe insertion, the fit of the AP resistance deviates strongly from the measured curve. The magnon cut-off energy E_{C} is around 3 meV and the thermal smearing constant C ranges between 0.0018-0.0025 which corresponds to 5%-10% of thermal smearing at RT. These values are larger compared to the $CFA/MgAl_2O_4/CoFe$ MTJ with a similar barrier thickness ($d_{\mathrm{MgAl}} = 0.87$ nm) due to the different barrier oxidation conditions used. Interestingly, the CFA annealing temperature does not affect C as strongly as a different oxidation of the barrier does.

The largest contribution of magnons to the tunneling process as calculated from Q is 12.4% which is found for the highest TMR MTJ. For the other junctions, the contribution reaches from 6.6% to 9.5%. Compared to the $CFA/MgAl_2O_4/CoFe$ junction, the contribution of magnons is significantly smaller which might be due to a better top interface as seen in the TEM images shown in next section which suppresses the creation of magnons.

Finally, the spin-dependent hopping model was used, similar to the case of $CFA/MgAl_2O_4/CoFe$ MTJs. Before, the fit is done, a plot of the conductance difference $\Delta G = G_{\mathrm{P}} - G_{\mathrm{AP}}$ normalized to the value at 5 K is shown in Fig. 4.26. For the junctions with $T_{\mathrm{CFA}} = 500°\mathrm{C}$, $d_{\text{b-CoFe}} = 0$ nm and $T_{\mathrm{CFA}} = 550°\mathrm{C}$, $d_{\text{b-CoFe}} = 0.5$ nm a positive slope is shown which was not observed in $CFA/MgAl_2O_4/CoFe$ MTJs. Although, the hopping model is expected to fit such a temperature dependence, it was found, that the model greatly underestimates the TMR. This comes from the model itself which assumes such a conductance temperature dependence for thick barriers $d_{\mathrm{Barrier}} \geq 3$ nm. For such a thickness hopping transport is expected. Due to the large distance between the electrodes, electrons start to tunnel through pinholes. In the following, the hopping model was used to fit three of the temperature

Table 4.6: Extracted spin polarization and interface parameter from the Bloch model used on the MTJs shown in Fig. 4.24.

T_{CFA}	$d_{\text{b-CoFe}}$	$P(0)$	a
400°	0.0 nm	0.80	1.71×10^{-5}
500°	0.0 nm	0.81	1.13×10^{-5}
500°	0.5 nm	0.84	1.52×10^{-5}
550°	0.5 nm	0.87	1.74×10^{-5}

Figure 4.25: Magnon fits (red) of the temperature dependence of the resistance (black) for four different MTJs with different T_{CFA} and $d_{b\text{-}CoFe}$; the curves with the largest negative slopes are R_{AP}.

Figure 4.26: ΔG temperature dependence of four different CFA/CoFe($d_{b\text{-}CoFe}$)/$MgAl_2O_4$/CFA(T_{CFA}) MTJs.

Figure 4.27: Fitting using the hopping model for three different MTJs: $T_{CFA} = 450°C$ & $d_{b\text{-}CoFe} = 0$ nm (a), $T_{CFA} = 500°C$ & $d_{b\text{-}CoFe} = 0$ nm (b) and $T_{CFA} = 500°C$ & $d_{b\text{-}CoFe} = 0.5$ nm (c); red curves are fits to the respective curves; Top graph is the conductance G_{AP} in the AP state from which the number of localized channels was extracted; their weighted contribution W to G_{AP} are shown second from top; third row is the fit of $\Delta G = G_P - G_{AP}$ with Eq. 4.1; bottom graphs show the fit of TMR with the hopping model.

dependencies. It will be shown that the TMR of MTJs with positive ΔG-slope cannot be fitted with the hopping model on the example of the MTJ with $T_{CFA} = 500°C$, $d_{b\text{-}CoFe} = 0$ nm. In Fig. 4.27, the used curves necessary for the TMR fitting are displayed. The fits are done for three MTJs: $T_{CFA} = 450°C$ & $d_{b\text{-}CoFe} = 0$ nm (a), $T_{CFA} = 500°C$ & $d_{b\text{-}CoFe} = 0$ nm (b) and $T_{CFA} = 500°C$ & $d_{b\text{-}CoFe} = 0.5$ nm (c). The top curves show the fit of G_{AP} with the assumption of three different hopping channels in the barrier. For all junctions this assumption seems to be the best as it is the minimum number of channels that can fit the measured curves well. The plots in the second row show the weighted contribution of each channel in percent to the total conductance. Obviously, the direct and indirect channel have the largest contribution even at RT. However, for the MTJ in (a) and (c) the second order contribution is larger compared to the third order contribution. For the MTJ in (b) this is reversed and the third order contribution gets larger above 150 K than the second order contribution which might be the reason for the positive observed slope in the ΔG temperature dependence.
With the calculated contributions, ΔG was fitted using Eq. 4.1. The fitting of ΔG is shown in the third graph from the top. The bottom graph shows the fitted TMR with the values extracted from

the ΔG fit. The obtained fitted values are listed in Table 4.7. Obviously, ΔG of the first two MTJs cannot be fitted well with the hopping model. This results in significant underestimation of the TMR for theses two cases. The strongest underestimation is found for the MTJ with a positive ΔG slope. At low temperatures, the fitted curve underestimates the actual value by 50% of the measured TMR. The reason is the low spin polarization value for the second junction. Interestingly, ΔG and TMR of the MTJ with the highest TMR can be fitted reasonably well with the hopping model, although, the fit deviates quite strongly from the measured one at low temperatures. Additionally, the interface parameter α is one order of magnitude lower compared to the ones obtained from the Bloch model fit. For comparison, the parameters of the CFA/$MgAl_2O_4$/CoFe MTJs from the Bloch and hopping model resulted in similar results.
It is easily seen that the hopping model cannot be used for the CFA/$MgAl_2O_4$/CFA junctions. The reason lies most likely in the assumption of the model which predicts hopping for thick barriers much thicker than the ones used here. However, the temperature dependencies of CFA/$MgAl_2O_4$/CoFe could be fitted even when a thin barrier is used. It might be argued that the spinel barrier in the CFA/$MgAl_2O_4$/CFA MTJs is of better quality, i.e. stoichiometry, due to the high annealing temperatures or the use of CFA as a top electrode which reduces the amount of Al that can diffuse out of the barrier. It will be shown in the next section that the EDS map verifies the good stoichiometry of the barrier.

4.2.4 Discussion on the positive Resistance and ΔG Slope

In Fig. 4.28, the resistance and ΔG temperature curves for three different MTJs which were shown previously are plotted. The first MTJ (Fig. 4.28a and b) represents the normally observed resistance and ΔG curves with a negative slope. In Fig. 4.28c and d, the curves of an MTJ with $\mathrm{d}R_\mathrm{P}/\mathrm{d}T > 0$ and $\mathrm{d}(\Delta G)/\mathrm{d}T < 0$ is shown. Finally, in Fig. 4.28e and f, an MTJ with $\mathrm{d}R_\mathrm{P}/\mathrm{d}T < 0$ and $\mathrm{d}(\Delta G)/\mathrm{d}T > 0$ is shown which is the opposite of the second MTJ. A junction with $\mathrm{d}R_\mathrm{P}/\mathrm{d}T > 0$ and $\mathrm{d}(\Delta G)/\mathrm{d}T > 0$ was not found. In the following, the parallel resistance is discussed.
In general doing resistance measurements vs. temperature, a negative slope $\mathrm{d}R_\mathrm{P}/\mathrm{d}T$ is found. The same is observed for $\Delta G = G_\mathrm{P} - G_\mathrm{AP}$ temperature curves. That is expected due to excitation of magnons with increasing temperature (see Sec. 2.2.1). However, in some samples a positive slope $\mathrm{d}R/\mathrm{d}T$and $\mathrm{d}(\Delta G)/\mathrm{d}T$ is observed with a well established explanation or model missing, see Ref. [110] and references therein. First, one has to consider that the electron transport in MTJs consists of a spin-dependent and spin-independent component. Therefore, the total conductance G_tot can be written as:

$$G_\mathrm{tot} = G_\mathrm{SD} + G_\mathrm{SI}.$$

That means, the resistance curves consists of spin-dependent and spin-independent contributions while ΔG excludes spin-independent contributions. They are independent from the magnetization state (P

Table 4.7: Parameters obtained from the temperature fit of ΔG in Fig. 4.27.

Junction (T_CFA, $d_\mathrm{b\text{-}CoFe}$)	C (K^{-1}) (smearing)	α ($\mathrm{K}^{-1.5}$)	P
400°C, 0.0 nm	$(1.19 \pm 0.06) \times 10^{-3}$ (2.1%)	$(2.12 \pm 0.05) \times 10^{-6}$	0.86
500°C, 0.0 nm	$(2.85 \pm 0.04) \times 10^{-3}$ (13.3%)	$(4.38 \pm 0.09) \times 10^{-6}$	0.79
500°C, 0.5 nm	$(2.16 \pm 0.01) \times 10^{-3}$ (7.4%)	$(2.70 \pm 0.01) \times 10^{-6}$	0.90

Figure 4.28: Resistance [(a),(c),(e)] temperature curves of three different MTJs as shown in the graphs; ΔG [(b),(d),(f)] curves are calculated from the respective resistance curves.

and AP) of the MTJ. Hence, they cancel out in ΔG. The temperature curves of the second MTJ in Fig. 4.28c and d suggest a positive spin-independent contribution because $d(\Delta G)/dT < 0$. Thus, the spin-dependent contribution temperature slope is solely negative and because $dR/dT > 0$, only the spin-independent contribution can be the origin of the positive slope. The slope of the resistance of the third sample (Fig. 4.28e) is negative. Contrarily, the conductance shows a positive slope which means that, opposite to the second MTJ, a positive spin-dependent contribution is observed in this sample. Consequently, spin-dependent and spin-independent contributions can be observed in these MTJs leading to positive slopes in ΔG and resistance curves, respectively.
Considering positive resistance slope, Hu *et al.* showed the same behavior in Co_2MnSi-based and $Co_2(Mn,Fe)Si$-based MTJs [111]. They argued that the positive slope is observed for samples with close to half-metallic electrodes with high spin polarization. However, this seems to be a too simplistic picture. Comparing the R_P slopes of CFA/$MgAl_2O_4$/CoFe MTJs in Fig. 4.6 with different barrier thicknesses shows a reduced slope (turning from positive to negative with increasing barrier thickness). For an MTJ with the highest TMR, the slope is negative while a positive slope is observed for an MTJ with a thin barrier having slightly reduced TMR. It appears that the slope depends more on the interface or barrier condition (i.e. oxidation state or thickness) rather than the spin polarization of the CFA or CoFe. Especially the interface seems to be the crucial criteria considering the change in resistance slope after CoFe insertion, see Fig. 4.8(b). It should be noted that a positive slope in resistance is usually observed in metals. Therefore, interactions of the tunneling electrons with phonon should be considered additionally to magnon excitation. The competition of both leads to a positive or negative slope, respectively.

4.2.5 TEM and EDS Characterization

In order to understand the observed high TMR ratio in the MTJ with $T_{CFA} = 550°C$ and $d_{b\text{-}CoFe} = 0.5$ nm, nanostructure analysis using STEM were carried out. An ADF-STEM image along the CFA[110] ‖ $MgAl_2O_4$[100] direction is shown in Fig. 4.29 (a). The fast Fourier transform (FFT) filtering image of CFA(440) atomic planes is also shown in Fig. 4.29 (b). Epitaxial growth with (001) orientation of the layers from the bottom- to the top-CFA and a perfect lattice-matched $MgAl_2O_4$ interface were confirmed by the images.
Fig. 4.30 (a) and (b) show the EDS elemental maps and corresponding profiles of each used element, respectively. It is seen that the Al content of the top-CFA and bottom-CFA is lower with respect to the nominal composition (25%). The high annealing temperature would cause interdiffusion of Al into the $MgAl_2O_4$ and CoFe buffer. Additionally, at the bottom $MgAl_2O_4$ interface, the Fe (Al) content increases (decreases), suggesting that the inserted-CoFe layer contains a smaller amount of Al.

Fig. 4.31 (a)-(e) show the NBD patterns at five different positions around the $MgAl_2O_4$ barrier: (a) top-CFA, (b) $MgAl_2O_4$, (c) bottom-CFA, (d) near the $MgAl_2O_4$/top-CFA interface, and (e) near the inserted-CoFe/$MgAl_2O_4$ interface. From the patterns (a) and (c), a B2 order in both the bottom- and top-CFA layers is confirmed due to the superlattice reflections from {100} and {111} planes. It is also found that the top-CFA has a higher B2 order parameter; this may be due to the less Al depletion from the top-CFA by the interdiffusion. The strong B2 superlattice peaks are observed even at the $MgAl_2O_4$/top-CFA interface (Fig. 4.31 (d)). At the bottom interface (Fig. 4.31 (e)), however, only weak B2 peaks are observed. This is considered to be due to the low Al content in the inserted CoFe layer. Hence, the observed high TMR ratio is concluded to be mainly due to the high crystalline

Figure 4.29: (a) ADF-STEM image of the barrier region for an MTJ with $T_{\mathrm{CFA}} = 550°\mathrm{C}$ and $d_{\text{b-CoFe}} = 0.5$ nm; (b) FTT image of CFA(440) atomic planes.

Figure 4.30: (a) Elemental maps of each element for an MTJ with $T_{\mathrm{CFA}} = 550°\mathrm{C}$ and $d_{\text{b-CoFe}} = 0.5$ nm; (b) Corresponding element profile.

quality of the top-CFA interface. Furthermore, in the NBD pattern of the $MgAl_2O_4$ (Fig. 4.31 (b)), diffraction spots from the ordered spinel $MgAl_2O_4\{220\}$ planes are observed. In previous publications, it was suggested that the cation-disordered structure, i.e., the absence of {220} spots in the $MgAl_2O_4$ barrier, is the necessary condition to suppress the band-folding effect to observe high TMR ratios (e.g., >160% for Fe/$MgAl_2O_4$ (1 nm)/Fe) [40]. The band-folding occurs when the lattice size of the FM electrodes is smaller than that in the barrier, and it significantly reduces the effective spin polarization of the Δ_1 band in the case of $Co_{1-x}Fe_x(001)$ alloys [39]. The band-folding effect can occur even in the case of the B2-CFA/ordered-$MgAl_2O_4$, where $a_{\mathrm{CFA(B2)}} = 0.286$ nm is smaller than $a_{\mathrm{MgAl_2O_4}}/\sqrt{2} = 0.572$ nm (for 45° rotation). Nevertheless, if both the top- and bottom-FM electrodes adjoining the barrier are perfectly half-metallic, the band-folding would no longer reduce the spin polarization of the FM layers due to the absence of the bands for folding in the vicinity of the Fermi energy. Therefore, one can assume three different possibilities for the high TMR ratios observed in the CFA/(CoFe)/$MgAl_2O_4$/CFA MTJs can be found:

1. Bands get folded to the center of the Bioullin zone around E_F meaning that the observed TMR ratio is still low and by using a $L2_1$ ordered Heusler alloy the TMR ratio can be drastically observed.

Figure 4.31: NBD pattern of top-CFA (a), $MgAl_2O_4$ barrier (b), bottom-CFA (c), $MgAl_2O_4$/top-CFA interface (d), and inserted-CoFe/$MgAl_2O_4$ interface (e) for an MTJ with $T_{CFA} = 550°C$ and $d_{b\text{-}CoFe} = 0.5$ nm; respective reflection spots are labeled.

2. CFA is a perfect half-metal and therefore no minority bands exist around E_F; therefore, no bands get folded into the center.

3. CFA is a perfect half-metal except at the Γ-point; therefore, bands cannot get folded from the outside of the Brioullin zone to the center due to the half-metallicity but the observed TMR is still low because CFA is not a half-metal in tunneling direction.

The last two possibilities are similar as they differ only in the assumption of half-metallicity in tunneling direction. However, considering the still rather low TMR ratio as compared to other MTJs with Heusler electrodes and MgO barrier, number 2 can be excluded as a possibility. Number 1 seems one possibility as B2-CFA has a similar lattice constant as Fe or CoFe and no calculations have been done so far to investigate if band-folding takes place in the case of half-metals. Number 3 is another possibility when looking at band structure calculations of CFA in different directions. Fecher *et al.* calculated it and found a robust half-metallicity in CFA for all directions except Γ-X which strongly depends on the chosen calculation method and the strength of Coulomb interaction [112]. Excluding the Coulomb repulsion CFA is not half-metallic. In contrast, by increasing the Coulomb interaction the band gap opens in Γ-X for the minority states.

4.2.6 Summary

This section has shown that an ordered spinel MTJ can exhibit large TMR ratios using half-metallic electrodes with prefect lattice matching. The CFA electrodes used in the present MTJs may not still be perfectly spin-polarized since (i) B2-CFA is predicted to be not a perfect half-metal [60] and (ii) the CoFe insertion, which can reduce the effective spin polarization, is needed to obtain a sharp interface at the bottom-CFA/$MgAl_2O_4$. Therefore, the compositional tuning of the Heusler layer [113, 112, 114, 115] and the further modification of the barrier/Heusler interface states [116, 117, 118, 119, 120]

may lead to much higher TMR ratios above the here observed 342% using an $MgAl_2O_4$-based MTJ. The non-perfect half-metallicity and the absence of the band-folding effect are not conflicting with each other. The latter one needs half-metallicity at the edges of the Brioullin zone in all directions except k_z (directions of electron tunneling). Although the band structure in k_z direction might not be 100% spin polarized, the band-folding effect might not occur because of the absence of foldable bands around the Fermi energy at the edges of the Brioullin zone. This is supported by band structure calculations by Fecher *et al.* [121] which showed that the Γ-X direction has the smallest band-gap and strongly depends on the Coulomb repulsion U. However, the other directions show a robust, wide band gap.

4.3 MTJs with a Li-substituted $MgAl_2O_4$ Barrier

As introduced in Sec. 2.4 doping and replacing of elements is a way of tuning physical parameters of $MgAl_2O_4$. This is necessary for future applications and the scale-down process of MRAM devices. Therefore, development of new barrier layers to further tune physical parameters, i.e. bandgap [122] and *RA* [123], has become a great interest.

The spinel group consists of a large variety of different oxides which makes it possible to choose one as a barrier based on the desired properties needed being only limited by the quality of the thin film one can achieve using sputtering. One example is $LiAl_5O_8$ which has the smallest lattice constant (0.791 nm [124]) of all spinel oxides and a 6.4% smaller lattice spacing than MgO. It has a very good lattice matching with $L1_0$ PMA materials, i.e MnGa (1.4% lattice mismatch with $LiAl_5O_8$) which makes it suitable for future spintronics applications. However, considering the Al_2O_3-$Li_{66.7}O_{33.3}$ phase diagram at low

Figure 4.32: (a) MTJ stack with post-annealing temperatures and layer thicknesses in nm; (b) Out-of-plane XRD measurement of the whole stack; stars mark Cu Kβ-reflections, etc.

temperatures (<1100°C) stable $LiAl_5O_8$ forms at a narrow composition range of about 7 at.% of Li content [125].

To form a stable spinel barrier and investigate the effect of Li substitution on the transport properties it is possible to use the known $MgAl_2O_4$ barrier and dope it with Li. Furthermore, the lattice constant of the compound can be tuned by Li^+ substitution due to the ions reduced atomic radius compare to Mg^{2+} [126]. The Li-Mg-Al-O compound was first investigated as a battery material showing a good stability of Li in the spinel structure [127, 128]. By adding Li^+ ions to $MgAl_2O_4$ they occupy octahedral sites while Al^{3+} ions move to tetrahedral sites resulting in a formula of $Li_xMg_{1-2x}Al_{2-x}O_4$ [129]. The RT conductivity of Li^+ ions in the compound is poor making it a promising barrier material [126]. Multilayers were fabricated on MgO(001) single-crystal substrates with a magnetron sputter at a base pressure of 4×10^{-7}. The stacking structure is similar for all junctions: Cr (40)/ Fe (30)/ Mg (0.45)/ $Li_{10}Al_{90}$ (1.05)/ oxidation/ Fe (6)/ IrMn (12)/ Ru-cap (20) (thickness in nm) (see 4.32(a)). The $Li_{10}Al_{90}$ layer was formed by post-plasma oxidation. All layers were in-situ annealed to improve their surface and crystalline structure. The post-annealing temperatures of the barrier and top-Fe electrode are fixed at 250°C. The bottom-Fe electrode (Cr-buffer) annealing temperature was 200°C (600°C). The actual compositions of $Li_{10}Al_{90}$ was determined by inductively coupled plasma analysis to be

Figure 4.33: (a) TMR curve at RT for a microfabricated MTJ; (b) Temperature dependence of TMR (left axis, red) and RA (right axis, black) of the same MTJ.

$Li_{11}Al_{89}$. The complete stack was *ex-situ* annealed in a 5 kOe strong magnetic field at 175°C along the MgO[110] ∥ Fe[100] direction.
Although no composition analysis has been done so far, it is possible to estimate the barrier composition using $Li_xMg_{1-2x}Al_{2-x}O_4$ [129]. Due to incorporation of Li^+ ions, the Al^{3+} ions content reduces to compensate for the ionic imbalance. Considering the 0.45 nm Mg insertion layer and 1.05 nm $Li_{11}Al_{89}$, the barrier composition is estimated to be $Li_{0.25}Mg_{0.72}Al_{2.03}O_4$.

4.3.1 MTJ Stack XRD characterization

The out-of-plane XRD pattern of a whole MTJ stack with the structure described in the experimental section is shown in Fig. 4.32(b). Note that the intensity is logarithmic. Stars are marking peaks due to Cu Kβ-radiation. IrMn(002), Cr(002) and Fe(002) (peak originates mainly from the 30 nm thick bottom-Fe) lattice reflections could be observed. All layers show epitaxial growth on the MgO single crystal. The ultrathin Li-Mg-Al-O barrier layer cannot be detected due to its weak reflection intensity. The lattice constants of Cr and Fe were calculated to be 0.2885 (0.2884) nm and 0.2852 (0.2866) nm (number in brackets are theoretical values), respectively, showing only small deviation for Fe from its theoretical value.

4.3.2 MTJ Transport Characteristics

In Fig. 4.33 the RT TMR ratio (a) and the temperature dependence of R_P, R_{AP} and TMR ratio (b) for a microfabricated junction is shown. The RT TMR ratio (RA) of the junction was measured to be 110% (583 $\Omega \cdot \mu m^2$). Compared to a similar junction with Fe electrodes and a plasma-oxidized $MgAl2O_4$ barrier with the same thickness, TMR and RA is lower here [42]. Especially, RA seems to reduce 2-3 times after Li-doping. The temperature dependence in Fig. 4.33(b) shows an increase of TMR ratio and R_{AP} with decreasing temperature. The TMR ratio at 3 K is 174%. Interestingly, R_P has a positive temperature slope which was observed in other MTJs with a $MgAl_2O_4$ barrier (see sections above). This leads to an 8% decrease of R_P at 3 K relative to the RT value. The reason for this behavior is still unclear. The large TMR and slight change of R_P with temperature suggest the

Figure 4.34: (a) Conductance spectra (dI/dV) of the MTJ in P and AP state at RT (dashed, black) and 3 K (solid, blue); Arrow indicates quantum oscillations; (b) Enlarged differential conductance curve of the P state at 3 K; (c) TMR vs. bias voltage at RT and 3 K.

existence of coherent tunneling channels in this MTJ with a Li-Mg-Al-O barrier.

For further clarification of the coherent tunnel effect in this junction conductance spectra, dI/dV vs. bias voltage, in the P and AP state was obtained and is presented in Fig. 4.34(a) for RT and 3 K. The spectra was calculated from the $I-V$ curve and obtained up to 0.6 V which was close to the breakdown of the junctions ($\approx$ 0.7 V). The AP curve at RT is featureless with a v-like shape similar to other MTJs with an $MgAl_2O_4$ barrier [42]. At 3 K the bias voltage shows the strong zero-bias anomaly. The P curve shows minima at 0.24 V (-0.15 V). The minima at negative bias voltage is not well developed hinting to underoxidation of the barrier [42]. As a result, the top and bottom interfaces are different resulting from the Mg insertion and oxidation leading to asymmetric spectra. If the low breakdown voltage originates from the underoxidation or the movement of Li inside the barrier cannot be clarified at the moment. An earlier paper has shown a poor RT conductivity of Li-Mg-Al-O, hence, a poor mobility of Li ions [129]. However, the P conductance curve at 3 K shows oscillation at the negative voltage branch of the spectra. Considering that for negative bias voltages electrons get injected from the bottom, it might be due to the creation of a quantum well in Fe between Cr and the barrier [130]. This is possible because Cr acts as a barrier for Δ_1-electrons [131]. In this case, in the P state a Δ_1 spin-polarized tunneling current flows through the barrier and gets reflected at the Fe/Cr interface. Thereafter, the current gets deflected at the Fe/barrier interface and so on creating a standing wave. The oscillations are proof of a high quality bottom Fe electrode. The high frequency results from the thickness of 30 nm of the Fe layer.

Figure 4.35: Quantum oscillation of the differential conductance (left) and conductance (right) for negative bias voltages.

Table 4.8: Interval distance ΔV for the number of oscillation marked in the left figure.

Number of Oscillation	ΔV
1	2.1 meV
2	2.8 meV
3	2.8 meV
4	2.9 meV
5	2.8 meV
6	3.5 meV
7	3.5 meV
8	3.6 meV
9	3.5 meV
10	4.2 meV

Figure 4.36: d_{Fe} vs bias voltage showing PAM calculation as lines for (a) $\phi_L = \phi_R$ and (b) $\phi_L \neq \phi_R$ for modes n = 40-50; markers are the measured peak positions and arrows indicate mismatch with the model.

The differential conductance curve of the P state is shown in Fig. 4.34(b). The graph is enlarged to show the possible observed quantum oscillations. As can be seen the oscillations extends even to the positive bias voltage site. For comparison the conductance and differential conductance curve are plotted in Fig. 4.35 for negative bias voltages. Oscillations are visible from zero bias voltage. The dips of both curves match above 0.15 V with a average distance of 35 meV. The interval distances are shown in Table 4.8. Considering the model below, the change in interval distance should origin from a change in the electron waves' phase. As can be seen the distances increases by 7 meV in a step like manner with increasing bias voltage. For a better analysis, the phase accumulation model (PAM) is used [132]. The model simply assumes a electron in a potential box resembling the quantum well. The electron wave has to obey the quantization condition:

$$2k_{\perp}d - \phi_L - \phi_R - \phi_{int} = 2\pi n, \tag{4.2}$$

with $k_\perp = \sqrt{2m^*(E - E_L)}/\hbar$ being the wave vector in the direction perpendicular to the well wall of thickness d. m^* is the effective mass of the Δ_1 majority electrons in Fe. ϕ_L and ϕ_R are the phase differences occurring on the left (L) and right (R) boundary. It is empirically found to be:

$$\phi_\gamma = 2\arcsin(\sqrt{(E - E_{\gamma,D})/(E_{\gamma,U} - E_{\gamma,D})} - \pi). \tag{4.3}$$

γ=(L,R) and E_D and E_U are the energies of the lower and upper edge of the barrier band gap, respectively. From previous calculations E_D = -1.0 (-3.0) eV and E_U = 3.9 (0.9) eV for $MgAl_2O_4$ [130] (Cr) [133] majority Δ_1-band is taken. ϕ_{int} is a possible additional phase shift at the interface due to interface roughness, chemical disorder, impurities, etc. [130]. In Fig. 4.36 d_{Fe} vs bias voltage is plotted. The PAM calculations are shown represented by the lines taking $\phi_{int} = 0$. The markers represent the measured oscillation peak values. In (a) $\phi_L = \phi_R$ is assumed using the values for $MgAl_2O_4$ which represents two similar interfaces and (b) assumes two different interfaces for the $MgAl_2O_4$ and Cr interface. The theory matches the measurement better in the case of assuming two different interfaces. The arrows indicate a strong deviation of the theory from the measured values. For (b) the values below about 120 meV do not match the calculation due to the step like decrease of the interval distance.

The TMR ratio in Fig. 4.34(c) shows also asymmetry for the TMR at RT and 3 K. The corresponding V_{half} could not be measured due to the breakdown of the junction at lower voltages. Therefore, V_{half} was estimated to be -0.9 (1.1) V for negative (positive) bias voltage at RT and -0.5 (0.9) V. The values are larger for positive bias voltage as observed in other MTJs with a similar fabrication process [42]. Here again the asymmetry comes from the difference in bottom and top interface due to the oxidation process and the Mg insertion. Further investigations are needed to clarify the Li distribution and oxidation state and the low temperature behavior. The bias voltage curves suggest that further improvement of the junction is necessary, i.e. tuning the oxidation condition and Li concentration.

4.3.3 Summary

A new type of barrier can be fabricated by substituting Mg with Li in a $MgAl_2O_4$ barrier. The barrier can be fabricated by a $Mg/Li_{11}Al_{89}$ bilayer and post-oxidation. XRD measurements of a sputtered MTJ showed epitaxial growth of all layers on a MgO substrates indicating that the barrier might be epitaxial, too. Transport measurements of a microfabricated MTJ showed a TMR of 110% (173%) at Rt (3 K). Differential conductance spectra showed two local minima in the P state which are expected to be an indication for coherent tunneling across the barrier. Interestingly, at 3 K quantum oscillations were found for negative bias voltages which hints to a potential well in Fe. Waves are expected to get reflected at the Fe/Cr and MgO/Fe interface creating oscillations. The oscillations were fitted with the phase accumulation model and showed good agreement when two different interfaces are assumed for plotting. V_{half} were found to be -0.9 (1.1) V for negative (positive) bias voltages.

The results show that a new type of barrier which shows coherent tunneling properties can be created by substituting Li with Mg in a spinel barrier. This creates quaternary barrier which enables us to expand the already large group of spinels.

5 Conclusion

In need of new materials and material combination for future MTJ applications, this thesis investigated the fabrication and characterization of MTJs with Co_2FeAl Heusler electrodes with an $MgAl_2O_4$ spinel barrier. Additionally, a new type of quaternary barrier was fabricated by Li-substitution of the $MgAl_2O_4$ spinel barrier. Of interest are high TMR ratios, a good bias voltage dependence and lattice matching at the electrode/barrier interfaces. Three different different MTJ stacks were investigated: (1) $Co_2FeAl/MgAl_2O_4/CoFe$; (2) $Co_2FeAl/MgAl_2O_4/Co_2FeAl$; (3) Fe/Li-Mg-Al-O/Fe. The results are as follows:

An $MgAl_2O_4$ could be grown on a Co_2FeAl electrode. Firstly, the transport properties of a $Co_2FeAl/MgAl_2O_4/CoFe$ MTJ was investigated. Using a wedge-shaped barrier to optimize its oxidation a TMR of 228% (398%) at RT (5 K) was found. To avoid oxidation of the Co_2FeAl, CoFe was inserted at the bottom interface. With insertion of 1 nm CoFe the TMR (RA) increased (reduced). The TMR was 280% (453%) at RT (5 K). Interestingly, the RA reduced ten times after insertion. The changes are most likely due to the protection of CFA interface from oxidation and a change of the interface electronic structure as was observed at in the differential conductance spectra. The TMR temperature dependencies were fitted using different models but proved to be difficult due to the positive R_P slope. The best results were obtained with a electron hopping model. The HAADF-STEM investigations proved the, theoretically expected, lattice matching i.e., no dislocations at the interfaces. Co_2FeAl is B2-ordered and the spinel barrier is cation-disordered.

Thereafter, the top-CoFe electrode was replaced with a Co_2FeAl electrode which should have a higher spin polarization. The top-Co_2FeAl electrode is growing epitaxial on top of the spinel barrier. Increasing the annealing temperature of the top-Co_2FeAl temperature showed a monotonic increase of TMR and RA. Insertion of CoFe at the bottom increased TMR slightly and reduced RA. Insertion at the top reduced TMR which indicates that this interface is not effected by overoxidation. The highest TMR of 342% (616%) at RT (5 K) was observed at an top-Co_2FeAl annealing temperature of 550°C and bottom CoFe insertion of 0.5 nm. A microstructure analysis showed perfect lattice matching and no diffusion of elements. Interestingly, the $MgAl_2O_4$ barrier is *cation-ordered* which is remarkable as previous MTJs with such a barrier were found to show low TMR ratios due to the band-folding effect. It seems possible to overcome the reduction of TMR by using highly spin-polarized Heusler alloys which have no foldable minority bands at the edge of the Brioullin zone.

Lastly, a Li-substituted spinel barrier was fabricated to show the possibility of creating new barriers. The Fe/Li-Mg-Al-O/Fe MTJ showed a relative high TMR of 110% (173%) at RT (3 K) with epitaxial electrodes. The barrier composition was estimated to be $Li_{0.25}Mg_{0.72}Al_{1.03}O_4$. The differential conductance curves showed two local minima which hints to coherent tunneling transport. Furthermore, quantum oscillations were observed at 3 K for negative bias voltages.

Figure 5.1: History of MTJs with Heusler electrodes and MgO or $MgAl_2O_4$ (MAO) barrier.

The results show that it is possible two use an $MgAl_2O_4$ in combination with Co_2FeAl Heusler electrodes. The stacks can be fabricated epitaxial with large TMR ratios exceeding 300%. Insertion of an element at the interface can improve TMR or *RA* drastically. The reason for this is still not completely understood. The most interesting result is that high TMR ratios can be obtained with a *cation-ordered* barrier. This is the first report of large TMR ratios in spinel-based MTJs with a *cation-ordered* barrier. The TMR ratio could be improved three times, see Fig. 5.1. Additionally, the here shown results are the highest measured TMR ratios in spinel-based MTJs. However, some MTJs with Heusler electrodes have higher TMR ratios above 400% in combination with an MgO barrier. Although, 1000% TMR ratio could not be measured. The results are promising to increase the ratio further by using $L2_1$-ordered Heusler alloys as electrodes.

This result suggest that the band-folding effect can be avoided when using Heusler electrodes. This is important for the future investigation of other spinel barriers that tend to be ordered at much lower temperatures than $MgAl_2O_4$. By combining new spinel materials with Heusler alloys giant TMR ratios can be expected. The investigation of the Li-substituted spinel barrier proves that the the spinel class is versatile and can even be broadened by adding a fourth element to a spinel barrier. This paves the way for new materials for the use as barrier in future MTJ structures.

A Microfabrication Process

The whole process consists of five total steps (see Fig.A.1):

a Making the MTJ pillar: Junctions are carved out with Ar^+-ion milling down to the bottom electrode and the removed material is filled up with SiO_2.

b Two free standing and two (to the junction) connected electrode structures are shaped out of the sample by milling down to the substrate.

c The bottom electrodes are fabricated by milling out the electrode structures and fill it with Ta and Au.

d SiO_2 pads are deposited between the free standing electrode structures and the junction to support the top electrode.

e The top electrode is fabricated by depositing Ta and Au. Before that a small area in the shape of the electrode is milled out of the top to remove any possible oxidized layers and improve connectivity to the underlayer.

Figure A.1: Top schematic of a sample for each step during microfabrication.The steps (a) to (e) are explained in the text. (f) shows a microscope image of a junction after the microfabrication.

In the following, the general procedures for photo lithography, milling and sputtering are described more into detail (The equipment used, are listed in the experimental section 3.3):

Photo lithography was mainly used for junctions without CoFe insertion due to high RA of these junctions. A negative resist was used with a spin coater (1000 rpm for 5 s & 5000 rpm for 45 s). After

coating the samples were baked at 100°C.
For the lithography a monochromatic mercury lamp was used. The exposure time was 90 s. Two different mask sizes, depending on the sample were used, with 22×22 junctions or 22×46 junctions corresponding to a sample size of 1×1 cm or 1×2 cm, respectively, with junction sizes ranging from 50 µm to 288 µm. The irradiated samples were developed for about 45-55 s with maD-533S developer.

Milling with Ar^+-ions was used at a rate of 5 ccm with a chamber pressure of about 4×10^{-4} Pa. The source was operated with a current of 40 mA and under a voltage of 250 V (steps 1 & 5) or 400 V (steps 2 & 4). The angle between the normal of substrate holder and the ion source is 5°, except for step 1 during which only the barrier was milled at an angle of 45° to ensure a cylindrical shape of the barrier as much as possible. The milling was stopped every seven minutes for one minute to avoid overheating of the sample.

Sputtering was done with an ULVAC sputter using a base pressure of 4×10^{-4} Pa. SiO_2, Ta and Au were sputtered under a Ar-pressure of 0.4 Pa and 175 W (SiO_2) and 70 W (Ta & Au). For the electrodes (step 3 & 5) 3 nm and 120 nm of Ta and Au, respectively, were sputtered. For step 4, pads of 120 nm SiO_2 were deposited.

B Multilayer Fabrication Routine

All samples were fabricated with an automated sputter. In the following the computer program and routine to fabricate a sample are shown. The computer program is shown in Fig. B.1. In the top panel all information (i.e., file name, run time, step name, etc.) about the running procedure is shown. In the bottom of the top panel the status (i.e., power, temperature, gas flow, ect.) of the actual cathode selected by the program is displayed. X and O mark 'not active' or 'active status'. The bottom panel is a live monitor for temperature, pressure, cathode power, etc.

Figure B.1: Screenshot of the program that controls the automated sputter.

One sputter procedure consists of several modules, called text-files (see TEXT LIST in Fig. B.1). Each module can be seen as one step in the sample fabrication, e.g., sputtering, annealing or oxidation. One procedure for a $Co_2FeAl/MgAl_2O_4/Co_2FeAl$ is shown below:

```
0,38
1,C:\Program Files\ProcessNT\suke,Stay_L1_30m.pag,1,1
2,C:\Program Files\ProcessNT\suke,L1_to_S1.pag,1,1
3,C:\Program Files\ProcessNT\Thomas\Barrier,NO4.pag,1,1
4,C:\Program Files\ProcessNT\suke,S1_to_A7.pag,1,1
5,C:\Program Files\ProcessNT\suke,A7_700C30m60m25mA9_30m.pag,1,1
```

```
6,C:\Program Files\ProcessNT\suke,A9_Cr_40nm_N.pag,1,1
7,C:\Program Files\ProcessNT\suke,A9_to_A6.pag,1,1
8,C:\Program Files\ProcessNT\Thomas,A6R_500s45020m60m10mA9_40m.pag,1,1
9,C:\Program Files\ProcessNT\Thomas,A9_to_A5.pag,1,1
10,C:\Program Files\ProcessNT\Thomas,A5_Co5Fe_start2.pag,1,1
11,C:\Program Files\ProcessNT\Thomas,A5_Co5Fe_5nm.pag,1,1
12,C:\Program Files\ProcessNT\Thomas,A5_to_A2.pag,1,1
13,C:\Program Files\ProcessNT\suke,A2_CFAm1_5nm.pag,1,1
14,C:\Program Files\ProcessNT\Thomas,A2_to_A5.pag,1,1
15,C:\Program Files\ProcessNT\Thomas,A5_Co5Fe_start2.pag,1,1
16,C:\Program Files\ProcessNT\Thomas,A5_Co5Fe_0.5nm.pag,1,1
17,C:\Program Files\ProcessNT\Thomas,A5_to_A2.pag,1,1
18,C:\Program Files\ProcessNT\Thomas,A2A9N_a300s175_20m15m10m00m.pag,1,1
19,C:\Program Files\ProcessNT\Thomas,A9_to_A3.pag,1,1
20,C:\Program Files\ProcessNT\suke,A3_Mg0.45nm0.1Pa3.pag,1,1
21,C:\Program Files\ProcessNT\suke,A3_to_S1.pag,1,1
22,C:\Program Files\ProcessNT\Thomas,S1_MgAl6_0.75nm_p3m.pag,1,1
23,C:\Program Files\ProcessNT\Thomas\Barrier,Ox_O17Ar3_O15s_5W.pag,1,1
24,C:\Program Files\ProcessNT\suke,S1_to_A2.pag,1,1
25,C:\Program Files\ProcessNT\suke,A2A9N_a250s125_15m15m05m00m.pag,1,1
26,C:\Program Files\ProcessNT\suke,A9_to_S1.pag,1,1
27,C:\Program Files\ProcessNT\suke\Barrier,Ox_natu_O17_13s_60s.pag,1,1
28,C:\Program Files\ProcessNT\Thomas,S1_to_A2.pag,1,1
29,C:\Program Files\ProcessNT\Thomas,A2_CFAm1_5nm.pag,1,1
30,C:\Program Files\ProcessNT\Thomas,A2A9N_a550s406_30m15m20m50m.pag,1,1
31,C:\Program Files\ProcessNT\Thomas,Stay_A9_10min.pag,3,1
32,C:\Program Files\ProcessNT\Thomas,A9_to_A5.pag,1,1
33,C:\Program Files\ProcessNT\Thomas,A5_Co5Fe_start2.pag,1,1
34,C:\Program Files\ProcessNT\Thomas,A5_Co5Fe_0.5nm.pag,1,1
35,C:\Program Files\ProcessNT\Thomas,A5_to_A6.pag,1,1
36,C:\Program Files\ProcessNT\Thomas,A6_IrMn12nm.pag,1,1
37,C:\Program Files\ProcessNT\Thomas,A6_to_S2.pag,1,1
38,C:\Program Files\ProcessNT\Thomas,S2_Ru_12nm.pag,1,1
```

The total sequence consists of 38 pag-files with different purposes, i.e., moving to another position (Line 2), annealing (Line 5) or sputtering (Line 6).

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Publications

Journal Publications

- T. Scheike, H. Sukegawa, and S. Mitani, "Li-substituted $MgAl_2O_4$ barriers for spin-dependent coherent tunneling", Jpn. J. Appl. Phys., **55**, 110310 (2016).
- T. Scheike, H. Sukegawa, K. Inomata, T. Ohkubo, K. Hono, and S. Mitani, "Chemical ordering and large tunnel magnetoresistance in Co_2FeAl/ $MgAl_2O_4$/Co_2FeAl (001) junctions", Appl. Phys. Express **9**, 053004 (2016) (**selected spotlight**).
- T. Scheike, H. Sukegawa, T. Furubayashi, Z. Wen, K. Inomata, T. Ohkubo, K. Hono, and S. Mitani, "Lattice-matched magnetic tunnel junctions using a Heusler alloy Co_2FeAl and a cation-disordeed spinel Mg-Al-O barrier", Appl. Phys. Lett. **105**, 242407 (2014).

Patent

- 発明の名称：強磁性トンネル接合体、これを用いた磁気抵抗効果素子及びスピントロニクスデバイス並びに強磁性ンネル接合体の製造方法
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Conferences

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- T. Scheike, H. Sukegawa, and S. Mitani, "Lattice-matched magnetic tunnel junctions using a Heusler Co_2FeAl electrode and s spinel Mg-Al-O barrier", (**invited**) JSPS Core-to-Core Workshop on New-Concept Spintronic Devices, 13 November 2015, Sendai, Japan.
- T. Scheike, H. Sukegawa, T. Furubayashi, Z.C. Wen, K. Inomata, T. Ohkubo, K. Hono, and S. Mitani, "Temperature Dependence of Lattice-matched Co_2FeAl/Mg-Al-O/CoFe Magnetic Tunnel Junctions", 22nd International Colloquium on Magnetic Films and Surfaces, 14 Juli 2015, Krakow, Poland.

- T. Scheike, H. Sukegawa, T. Furubayashi, Z.C. Wen, K. Inomata, K. Hono, and S. Mitani, "Tunnel Magnetoresistance in lattice-matched epitaxial tunnel junctions with a Co_2FeAl Heusler alloy layer and an Mg-Al-O barrier", IEEE International Magnetics Conference, 7 Mai 2014, Dresden, Germany.

Domestic:

- T. Scheike, H. Sukegawa, K. Inomata, T. Ohkubo, K. Hono, and S. Mitani, "Lattice-matched Co_2FeAl/cation-ordered/Co_2FeAl Magnetic Tunnel Junctions with large Tunnel Magnetoresistance exceeding 300%", 2nd International ImPact Symposium, 30 September 2016, Tsukuba, Japan.
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