

CoFeB/MgO/CoFeB-based magnetic tunnel junctions for memory applications: optimization of the fabrication process and magnetic properties

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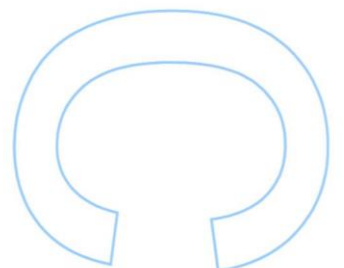
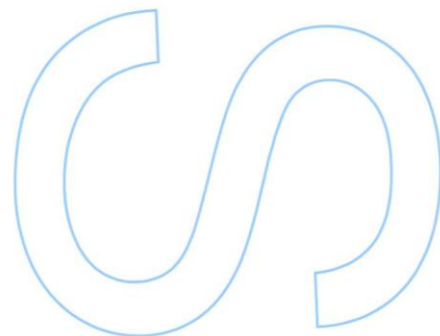
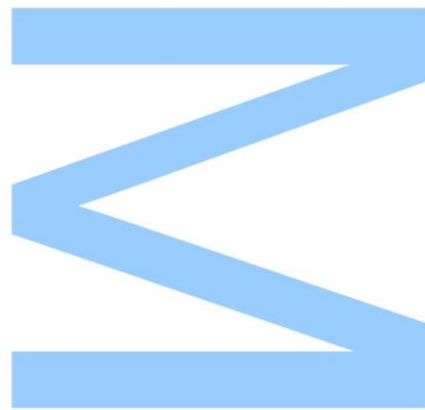
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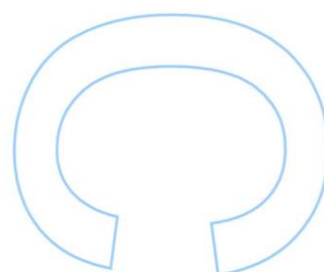
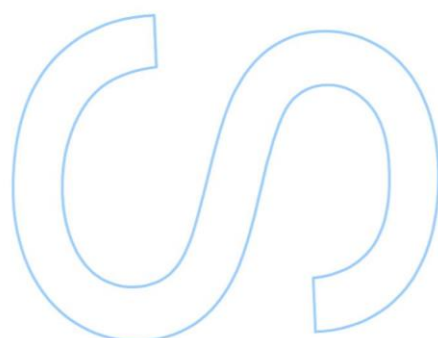
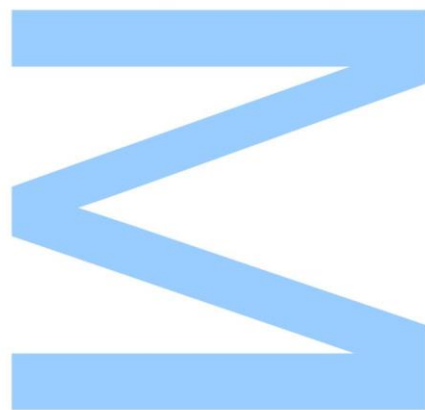




Todas as correções determinadas pelo júri, e só essas, foram efetuadas.

O Presidente do Júri,

Porto, ____/____/____



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Resumo

Nas últimas décadas, a área da Spintrônica tem recebido um interesse significativo que teve como resultado o desenvolvimento de nanoestruturas magnéticas com importantes aplicações na indústria eletrônica, nomeadamente a tão desejada *magnetic random-access memory* (MRAM). No contexto desta tese, a junção magnética de efeito túnel (MTJ) é a nanoestrutura em foco e, sem qualquer dúvida, é um dos mais importantes dispositivos magnéticos fabricados até hoje. A MTJ é constituída por duas camadas ferromagnéticas (FMs) separadas por uma barreira isoladora. A condução elétrica por efeito túnel é garantida pela deposição de uma barreira isoladora com uma espessura de alguns nanómetros ou até menos (abaixo dos 10 Å). A relevância da MTJ resulta da magnetoresistência por efeito túnel (TMR), que é definida como a dependência da resistência da MTJ, tendo em conta a sua configuração magnética. Apesar do efeito de TMR ter sido provado experimentalmente em 1975, o avanço mais importante só foi atingido em 2004, quando vários artigos científicos começaram a demonstrar experimentalmente valores de TMR acima dos 200% à temperatura ambiente. Particularmente, estes resultados foram atingidos para MTJs com uma barreira isoladora de MgO e camadas FMs de CoFeB. Tendo em conta os altos valores de TMR apresentados, estas MTJs apresentam-se como as melhores candidatas para aplicações. Atualmente, para aplicação em memórias, o foco prende-se na otimização das propriedades da MTJ, nomeadamente na diminuição da energia de operação e na otimização do processo de fabricação.

Em geral, este trabalho apresenta uma contribuição adicional para a otimização de MTJs com uma estrutura de CoFeB/MgO/CoFeB fabricadas com uma barreira de MgO ultra fina (~ 1 nm). O trabalho desenvolvido nesta tese resultou de uma parceria entre o Instituto de Física dos Materiais da Universidade do Porto (IFIMUP-IN) e o Laboratório Ibérico de Nanotecnologia (INL). As técnicas de deposição e caracterização foram implementadas nas instalações do INL, enquanto que parte das medições de transporte foram executadas no IFIMUP-IN. Especificamente, é proposto um novo processo de otimização que tem como objetivo diminuir a rugosidade da estrutura de multicamadas (*buffer*) que é depositada imediatamente abaixo da estrutura fundamental de CoFeB/MgO/CoFeB. Um processo de *etching* foi implementado na superfície do *buffer* antes da deposição completa da junção, usando a técnica de *ion beam milling*. Os resultados elétricos e morfológicos mostram uma influência direta entre a diminuição da rugosidade da superfície do *buffer* e o aumento dos valores TMR obtidos para as MTJs completas. Num segundo trabalho experimental, foi realizado um estudo sobre a dependência das propriedades magnéticas de ambas as camadas FMs de CoFeB tendo em conta a sua espessura. Este estudo teve como objetivo saber a espessura para a qual se obtém a transição para uma anisotropia magnética perpendicular (PMA) em ambas as camadas FMs. Os resultados magnéticos provam a obtenção de uma PMA separadamente para ambas as camadas FMs em estruturas distintas. Dependendo da posição da camada FM, a transição ocorreu para diferentes espessuras (1.0 nm para a camada FM de CoFeB abaixo e 1.4 nm para a camada FM de CoFeB acima da barreira de MgO), provando que a posição da camada FM tem uma influência direta nas suas propriedades magnéticas. Além disso, a comparação entre amostras com e sem *annealing* traduz

um melhoramento das propriedades magnéticas da camada FM após *annealing* à temperatura de 300 °C, nomeadamente pela diminuição da espessura da *dead layer* e pelo aumento da constante efetiva de anisotropia. O terceiro e último trabalho experimental foi implementado em MTJs de CoFeB/MgO/CoFeB com padrão litográfico. Medições elétricas foram efetuadas para diferentes valores de potencial constante aplicado. Em concordância com artigos científicos recentemente publicados, os resultados comprovam um efeito direto do potencial elétrico aplicado nas propriedades magnéticas das MTJs.

Abstract

Spintronics has received a significant interest in the last decades, resulting in the development of magnetic nanostructured devices with important applications in the electronics industry, namely the much desired magnetic random-access memory (MRAM). In the context of this thesis, the magnetic tunnel junction (MTJ) is the central nanostructure and, without any doubts, it is one of the most important nanostructured devices fabricated to date. The MTJ is defined as two ferromagnetic (FM) layers separated by a thin insulating barrier. To guarantee the electrical flowing by tunneling, the barrier is deposited with a few nanometers or even less (thickness below 10 Å). The MTJ is so relevant because it presents the tunnel magnetoresistance (TMR) effect, which can be defined as a dependence of the MTJ resistance on its magnetic configuration. Although the TMR effect has been experimentally demonstrated in 1975, the major breakthrough only happened in 2004, when many scientific articles started to report TMR ratios above 200% at room temperature for MTJs with an MgO insulating barrier and CoFeB FM layers, thus having the largest potential for applications. Nowadays, for memory applications, the focus concerns the optimization of the MTJ properties, namely by decreasing its operation energy and improving its fabrication process.

In general, this work provides an additional contribution towards the optimization of CoFeB/MgO/CoFeB-based MTJs with an ultra-thin MgO barrier (~ 1 nm). The work developed in this thesis resulted from a partnership between the *Instituto de Física dos Materiais da Universidade do Porto* (IFIMUP-IN) and the International Iberian Nanotechnology Laboratory (INL). Both deposition and characterization techniques were performed at INL facilities, while some of the transport measurements were performed at IFIMUP-IN. Specifically, a new optimization process is proposed to decrease the roughness of the buffer structure that is deposited below the fundamental CoFeB/MgO/CoFeB trilayer structure. The smoothing process was implemented in the buffer surface, before the deposition of the full MTJ stack, using the ion beam milling technique. The electrical and morphologic results show a direct influence of the roughness decrease on the improvement of the TMR ratio. In a second experimental study, the MTJ magnetic properties were studied by performing a thickness dependence study for both CoFeB FM layers. The objective was to know the thickness at which one obtains the transition for perpendicular magnetic anisotropy (PMA) in both FM layers. The magnetic results prove the achievement of PMA separately in both FM layers for different stack structures. Depending on the position of the FM layer, the transition occurred for different thicknesses (1.0 nm for the CoFeB layer below the MgO barrier and 1.4 nm for the CoFeB layer on top of the MgO barrier), thus proving the relevance of the FM layer position in the MTJ stack. Moreover, the comparison between annealed and as-deposited samples translates an improvement of the magnetic properties of the FM layer after annealing at 300 °C, namely by decreasing the thickness of the dead layer and increasing the effective anisotropy constant. The third and final experimental study was implemented in already patterned CoFeB/MgO/CoFeB-based MTJs. Electrical measurements were performed under different constant bias voltage values for both voltage polarities. In accordance with many scientific reported already published, the results prove a direct effect of the bias voltage in the MTJ magnetic properties.

Keywords: Magnetic tunnel junction, tunnel magnetoresistance, magnetic random-access memory, buffer structure, perpendicular magnetic anisotropy, bias voltage.

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List of abbreviations

- AF: Antiferromagnetic
- AFM: Atomic force microscopy
- CIPT: Current in-plane tunneling
- CMOS: Complementary metal - oxide - semiconductor
- DC: Direct current
- DOS: Density of states
- DRAM: Dynamic random-access memory
- E_F : Fermi level
- FM: Ferromagnetic
- FTM: Four-Target-Module
- H_C : Coercive field
- H_d : Demagnetizing field
- HDD: Hard disk drive
- H_{eff} : Effective magnetic field
- H_K : Anisotropy field
- HRTEM: High-resolution transmission electron microscopy
- I_{c0} : Threshold switching current
- IMA: In-plane magnetic anisotropy
- INL: International Iberian Laboratory of Nanotechnology
- K_{eff} : Effective anisotropy constant
- K_S : Surface crystalline anisotropy constant
- K_V : Volume crystalline anisotropy constant
- ME: Magnetoelectric
- M_{fixed} : Magnetization of the pinned layer
- M_{free} : Magnetization of the free layer
- MR: Magnetoresistive
- MRAM: Magnetoresistive random - access memory
- M_S : Saturation magnetization
- MTJ: Magnetic tunnel junction
- MTM: Multi-Target-Module
- P: Spin-polarization
- PMA: Perpendicular magnetic anisotropy
- PVD: Physical vapour deposition
- RA: Resistance-area product
- R_{AP} : Electrical resistance of the anti-parallel state
- RF: Radio frequency
- R_p : Electrical resistance of the parallel state
- SAF: Synthetic antiferromagnetic
- SPM: Superparamagnetic
- SPT: Spin-polarized tunneling
- SRAM: Static random-access memory
- STT: Spin transfer torque
- STT-MRAM: Spin transfer torque magnetoresistive random-access memory
- TMR: Tunnel magnetoresistance
- UHV: Ultra-high vacuum
- V_{bias} : Bias voltage
- VCMA: Voltage-control effect on the magnetic anisotropy
- VSM: Vibrating sample magnetometer
- Δ : Thermal stability factor
- ξ_n : Taylor expansion VCMA coefficients

Chapter 1

Magnetic tunnel junctions: an overview

This chapter presents an overview of the tunnel magnetoresistance (TMR) effect in magnetic tunnel junctions (MTJs). First, a theoretical description of the tunneling phenomenon in MTJs is presented, in parallel with an exposure of the main experimental results obtained for different fabrication materials. Then, a general stack structure for MTJs with in-plane magnetic anisotropy (IMA) is presented by specifying the function of each layer. Finally, one refers the main variables that affect directly the TMR ratio in MTJs, which is followed by the motivation to perform this thesis.

1.1 Tunnel magnetoresistance

The magnetic tunnel junction (MTJ) is one of the most important nanostructured devices in spintronics. The simplest MTJ structure consists in two ferromagnetic (FM) layers separated by an insulating barrier with a thickness in the order of 1 nm or even less. The electric current propagation is achieved by tunneling through the insulating barrier. The principle of operation is based on the TMR effect which can be defined as a dependence of the MTJ resistance on the angle between the magnetizations of the FM layers. The resistance is lower (larger) in the parallel (anti-parallel) configuration. In an equivalent way, the conductance increases from its lowest value (G_{AP}) in the anti-parallel configuration to its highest value (G_P) when the anti-parallel configuration is achieved. Moreover, the MTJ conductance can be defined as a function of the angle θ between the magnetizations of the FM layers [1]:

$$G(\theta) = \frac{1}{2}(G_P + G_{AP}) + \frac{1}{2}(G_P - G_{AP}) \cdot \cos \theta. \quad (1.1)$$

The TMR measurement is presented as a ratio that reflects the conductance difference between each configuration:

$$TMR = \frac{G_P - G_{AP}}{G_{AP}} = \frac{R_{AP} - R_P}{R_P}, \quad (1.2)$$

where R_P and R_{AP} represent the MTJ resistance in the parallel and anti-parallel configurations, respectively. The operation mode for an MTJ is very simple. One of the FM layers is defined as the reference/pinned layer that maintains its magnetic state. The other FM layer is defined as the free layer, which has a smaller coercive field. Figure 1.1 shows a TMR loop obtained for a CoFeB/ AlO_x /CoFeB – based MTJ (two CoFeB FM layers and an AlO_x insulating barrier). To guarantee its purpose for a specific external magnetic field range, the MTJ is constructed in order to rotate the magnetization of the free layer while maintaining the magnetization of the pinned layer unchanged.

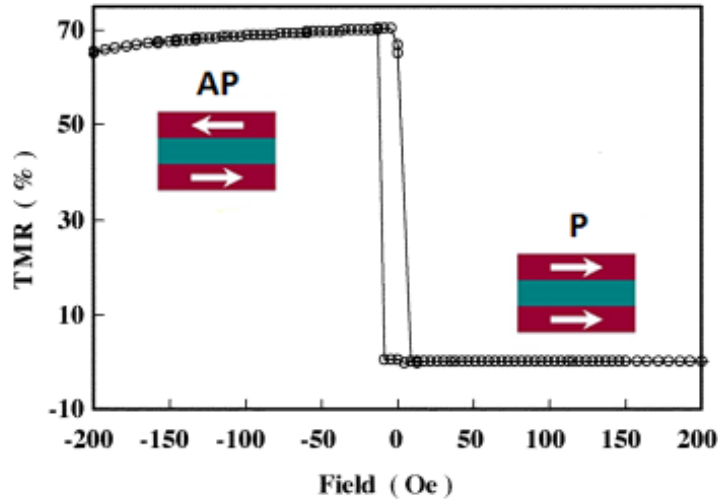


Figure 1.1: Example of a TMR ratio measured as a function of the in-plane external magnetic field for a CoFeB/AlO_x/CoFeB – based MTJ. The MTJ configuration is depicted by a trilayer structure where the magnetization of the top free FM layer rotates for the chosen magnetic field range (adapted from [2]).

MTJ applications go from advanced magnetic sensors, namely magnetoresistive (MR) reading heads for hard disk drives (HDDs), to the non-volatile magnetoresistive random-access memory (MRAM).

In the case of MR reading heads, an MTJ is used as a magnetic sensor. The low resistance-area (RA) product values required for applications reflect the low size of the sensor (area of the free layer) aiming to increase the disk recording density and the low resistance of the MTJ to overcome impedance matching problems in electronic circuits [3]. Decreasing the MTJ area directly increases its resistance, so the thickness of the insulating barrier should be equally decreased in order to cancel the resistance variation. Thus, the challenge for high density recording is to reduce the sensor size and, at the same time, maintain an acceptable TMR value. Nagamine *et al.* [4] obtained TMR values above 50% from MTJs with a crystalline MgO barrier and a RA product below $1 \Omega\mu\text{m}^2$, which could satisfy the requirements of reading heads for ultrahigh recording densities ($> 200 \text{ Gbit.in}^{-2}$).

Another important application is the use of MTJs as memory elements in MRAMs. Here, low RA products are equally mandatory for applications. Semiconductor-based memories, namely static random-access memory (SRAM) and dynamic random-access memory (DRAM), are volatile, which means that all the stored data vanishes when the power supply is shut down. In terms of speed, MRAM has reading and writing times comparable to the ones achieved by SRAM and DRAM (Table 1.1). Although Flash technology dominates the market of non-volatile devices, MRAMs have the potential to make Flash obsolete due to its larger writing speed and unlimited endurance (Table 1.1). Thus, MRAM can be considered as the “dream memory”, since it can replace the traditional RAM devices and work at the same time as an ultra-fast HDD due to its non-volatile nature.

	SRAM	eDRAM	DRAM	eFlash (NOR)	Flash (NAND)	FeRAM	PCM	STT-MRAM	RRAM
Endurance (cycles)	Unlimited	Unlimited	Unlimited	10⁵	10⁵	10 ¹⁴	10⁹	Unlimited	10⁹
Read/write access time (ns)	<1	1-2	30	10/10 ³	100/10 ⁶	30	10/100	2-30	1-100
Density	Low (six transistors)	Medium	Medium	Medium	High (multiple bits per cell)	Low (limited scalability)	High (multiple bits per cell)	Medium	High (multiple bits per cell)
Write power	Medium	Medium	Medium	High	High	Medium	Medium	Medium	Medium
Standby power	High	Medium	Medium	Low	Low	Low	Low	Low	Low
Other	Volatile	Volatile. Refresh power and time needed	Volatile. Refresh power and time needed	High voltage required	High voltage required	Destructive readout	Operating T < 125°C	Low read signal	Complex mechanism

Table 1.1: Comparison of the main features of existing and emerging memories. The disadvantages are marked in bold (adapted from [5]).

1.2 TMR theory

The first attempt to explain the physical phenomenon behind TMR was made by Jullière [6]. He related the TMR with the spin-polarized tunneling (SPT), whose principle is based in the different tunneling probability depending on the spin state of a given electron. Tedrow *et al.* [7] made one of the first experimental evidences of SPT by measuring the tunneling current between a ferromagnetic nickel film and a superconducting aluminum film. The results confirmed a spin-polarized current that translates the imbalance between the spin-up and spin-down electrons. Jullière's model relates the TMR with the spin-polarization (P) of each FM layer, where:

$$P_i = \frac{N_i^\uparrow - N_i^\downarrow}{N_i^\uparrow + N_i^\downarrow}. \quad (1.3)$$

The index i denotes the FM layer in question ($i = 1, 2$), while N_i refers to the density of states (DOS) at the Fermi level (E_F) for the majority-spin and minority-spin electrons. The model is based on the assumption that an electron maintains its spin state while tunneling, which means that a separation between the majority-spin and minority-spin propagation channels is made [8, 9]. In Fig. 1.2, electrons with a specific spin state from one FM layer (F1 in Fig. 1.2) will only tunnel to unfilled states of the same spin in the other FM layer (F2 in Fig. 1.2). Therefore, in the parallel configuration, the majority-spin (minority-spin) electrons tunnel to the majority-spin (minority-spin) states, while in the anti-parallel configuration, the majority-spin (minority-spin) electrons tunnel to the minority-spin (majority-spin) states. The second assumption in which the model is based states that the electric current for a particular spin state is proportional to the product of the effective DOS of the initial and final FM layers. Thus, in each configuration, the electric current tunneling through the junction is given by [6]:

$$I_P \propto N_1^\uparrow N_2^\uparrow + N_1^\downarrow N_2^\downarrow \quad (1.4)$$

and

$$I_{AP} \propto N_1^\uparrow N_2^\downarrow + N_1^\downarrow N_2^\uparrow, \quad (1.5)$$

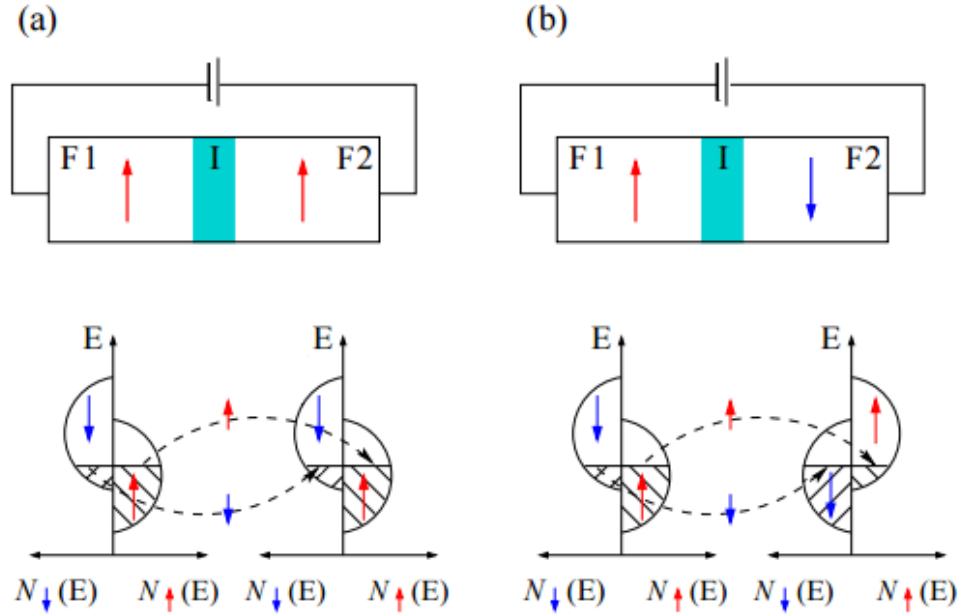


Figure 1.2: Schematic illustration of electron tunneling in an MTJ (FM/insulator/FM). (a) Magnetizations of the FM layers are parallel. (b) Magnetizations are anti-parallel (adapted from [10]).

where I_P (I_{AP}) is the tunneling current for the parallel (anti-parallel) configuration. Now, taking into account Eqs. (1.3) - (1.5), one can reach to the final Jullière's equation [6]:

$$TMR = \frac{2P_1P_2}{1 - P_1P_2}. \quad (1.6)$$

From Eq. (1.6), one can see that TMR depends only on the P of each FM layer. Thus, the improvement of the TMR is based on the research of FM materials that maximize P (values near one).

Taking into account the definition of Eq. (1.3), there are two limits to be mentioned: when the electrode material is non-magnetic ($P = 0$) and when the DOS of the FM layer is fully spin-polarized ($|P| = 1$). For the intended goal, half-metal materials are good choices, due to their capacity to (in the ideal situation) act as conductors for electrons with a specific spin state and as insulators for electrons with the opposite spin state. Some results were reported with half-metals used as electrodes that show TMR values above 500 % at low temperature [11, 12], but low TMR values near room temperature (12 % at 270 K [11] and 67 % at 300 K [12]). Thus, half-metals cannot be presented as good solutions for applications.

About the insulating barrier, some experiments have proved its influence on the obtained TMR values [13, 14]. Specifically, de Teresa *et al.* [13] showed that a Co/I/La_{0.7}Sr_{0.3}MnO₃ MTJ ($I = \text{SrTiO}_3, \text{Al}_2\text{O}_3$ or Ce_{0.69}La_{0.31}O_{1.845}) presented different P values for the Co FM layer, depending on the insulating barrier used. Further theoretical work [15, 16, 17] showed that the interface (directly related with the crystalline structure of the barrier) between the FM layer and the barrier plays an important role in the coupling between the Bloch states in the FM layer and the evanescent states in the barrier. Thus, different polarization values obtained for the same FM electrode can be translated as different Bloch states that couple through the barrier (the main aspects regarding Bloch states are presented in section 1.3.1).

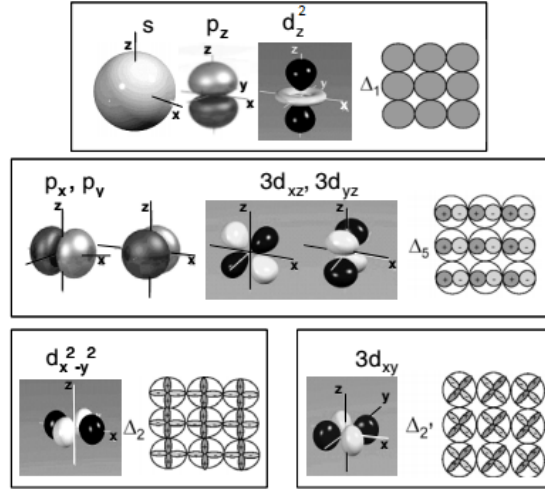


Figure 1.3: Relevant atomic orbitals for 3d metals organized by symmetry groups. Orbitals from the same symmetry group have equal xy components [19].

1.3 Different types of tunneling

1.3.1 Electronic wavefunctions

In single-crystal systems, electrons are described by Bloch wavefunctions which have the form [18]:

$$\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r}), \quad (1.7)$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. This theoretical introduction is extremely relevant, because for a specific Bloch state in one of the electrodes, the tunneling probability depends mainly on the rate of decay of its wavefunction in the barrier. The spatial shape of an atomic orbital gives information about its symmetry and depends on the electronic state of the associated electron. Thus, one can organize the atomic orbitals into symmetry groups. For a specific group, all the atomic orbitals have the same modulation regarding the component in the plane (xy plane in Fig. 1.3) perpendicular to the propagation direction (z direction in Fig. 1.3) or, in other words, the component in the plane parallel to the electrode/insulator interface. The reason for this selection is related to the direct influence of the xy oscillations on the rate of decay that a Bloch state experiences while tunneling [19]. Thus, as depicted in Fig. 1.3, one can identify the Δ_1 (s, p_z and d_z^2), Δ_5 (p_x , p_y , p_z , d_{xz} and d_{yz}), Δ_2 ($d_{x^2-y^2}$) and Δ_2' (d_{xy}) symmetries.

1.3.2 Incoherent tunneling through an amorphous barrier

When the insulating barrier is amorphous, there is no crystallographic symmetry on its structure. This means that Bloch states with various symmetries can couple with evanescent states, so for each symmetry, one can associate a non-zero tunneling probability. This tunneling process can be referred to as incoherent tunneling. Tunneling through an amorphous aluminum oxide (AlO_x) barrier is illustrated in Fig. 1.4(a), where the top Fe(001) layer is a 3d FM electrode.

According to Ref. [20], in 3d FM metals and alloys, Bloch states with Δ_1 symmetry usually have a large positive P at E_F , while Bloch states with Δ_2 and Δ_5 symmetries usually have a smaller positive or even negative P . The Jullière's model admits the same tunneling probability for all the Bloch states in the electrode

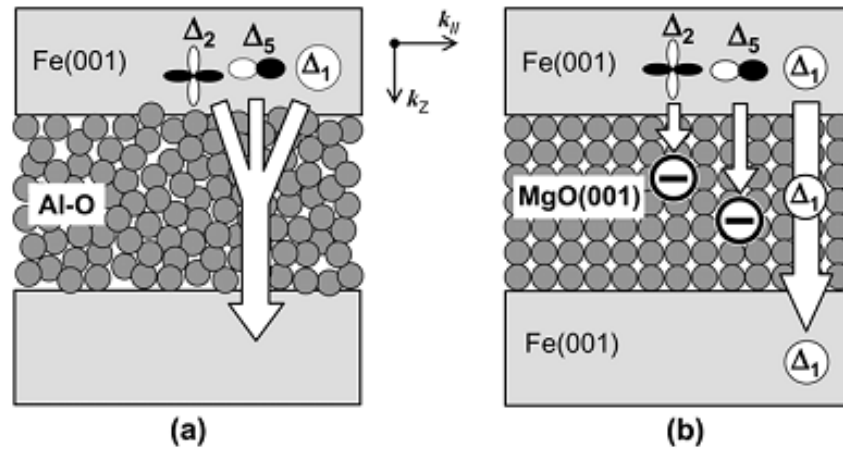


Figure 1.4: Schematic representations of electron tunneling through (a) an amorphous AlO_x barrier and (b) a crystalline $\text{MgO}(001)$ barrier [25].

(full incoherent tunneling). This assumption arises from an incorrect definition of P . In fact as defined in Eq. (1.3), P is negative for Co and Ni, while experimental results show that P is positive for the same materials when combined with an AlO_x barrier [21]. This discrepancy indicates that the tunneling probability for a Bloch state depends on its symmetry. Thus, it is easy to conclude that tunneling through an AlO_x barrier is not completely incoherent but an intermediate process between the former and coherent tunneling. The positive values of P obtained for 3d FM electrodes are the consequence of the higher tunneling probability for the Δ_1 Bloch states [22, 23]. From the smaller contribution of other Bloch states for the tunneling, results a decrease of P (values below 0.5 for standard 3d FM metals and alloys [21]). Thus, maximum TMR is achieved by coupling only the highly spin-polarized Δ_1 Bloch states in a process where a coherent tunneling and a maximum P value are present.

Experimentally, amorphous AlO_x was widely used as an insulating barrier and TMR values have been increased up to 80% [24] at room temperature, which is insufficient to compete with MTJs whose operation is based in a coherent tunneling mechanism.

1.3.3 Coherent tunneling through a crystalline barrier

The coherent tunneling process is the responsible for the largest TMR values obtained in MTJs [26]. Figure 1.4(b) shows an epitaxial Fe/MgO/Fe MTJ with a crystalline $\text{MgO}(001)$ barrier. Due to its crystalline structure, the MgO barrier can select the Bloch states from the FM electrode whose symmetries can couple with the evanescent states.

Butler [27] made the calculation of the transmission probability for the different Bloch states that can couple in the MgO barrier. The calculation was made for wavefunctions with $k_{||} = 0$ that are transmitted from the electrode/barrier interface, where $k_{||}$ is the component of the wavevector in the plane parallel to the same interface. Figure 1.5 shows the calculation results of the decay that each symmetry experiences while tunneling for the parallel and anti-parallel configurations of a Fe/MgO/Fe MTJ. The MgO barrier allows the coupling of Δ_1 , Δ_2 , Δ_2' and Δ_5 symmetries.

For the parallel configuration, in the majority-spin channel [Fig. 1.5(a)], the Δ_1 states are the only that show a small decay. In the minority-spin channel [Fig. 1.5(b)], one can see the absence of the Δ_1 states, while all the other symmetries suffer an extremely large decay. Thus, in the parallel alignment, most of the current is a consequence of the tunneling of electrons in Δ_1 symmetry states.

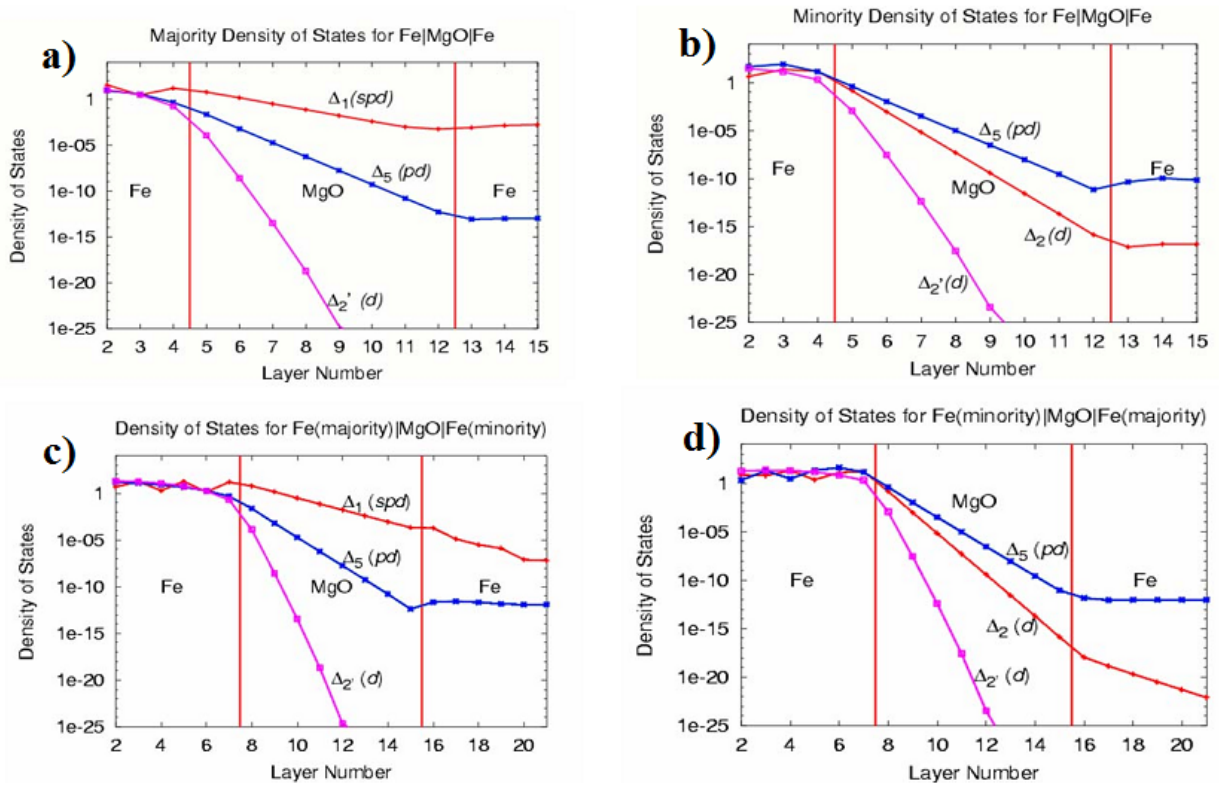


Figure 1.5: Tunneling DOS ($k_{\parallel} = 0$) for the possible coupling symmetries across an epitaxial Fe/MgO/Fe MTJ. Contributions to the tunneling current in the parallel configuration - (a) and (b). In the same way, (c) and (d) show the contributions in the anti-parallel configuration (adapted from [27]).

For the anti-parallel configuration, the decay behaviour for the Δ_2 , Δ_2' and Δ_5 symmetries is almost unchanged when compared with the parallel configuration. In the ($\downarrow\uparrow$) channel [Fig. 1.5(d)] there is no Δ_1 states coupling, so the conductance will be small. In the ($\uparrow\downarrow$) channel [Fig. 1.5(c)], the Δ_1 states suffer a low decay in the barrier, but their contribution to the current will be very small because the wavefunction continues to decay, even when it reaches the second FM electrode. The results allow to conclude that a much higher conductance is obtained in the parallel configuration where the electrons in Δ_1 states dominate tunneling. Thus, the main advantage of the MgO barrier in MTJs is the creation of a highly spin-polarized current associated with the coherent tunneling of specific Bloch symmetries.

Since the first theoretical prediction of high TMR values in Fe/MgO/Fe MTJs [28], MgO-based MTJs have been intensively studied [26, 29, 30]. In particular, MTJs with CoFeB FM electrodes present results up to 600% at room temperature [26]. The work of Djayaprawira *et al.* [30] gives important clues about the physical reasons for the high TMR results in CoFeB/MgO/CoFeB-based MTJs. Figure 1.6 shows cross-sections for MgO-based MTJs with different FM electrodes. In Fig. 1.6(a), for CoFe electrodes, the MgO barrier presents an indistinct crystalline structure and both electrode/barrier interfaces are not smooth. Both crystalline structure and interface smoothness are improved when the electrodes are changed [Fig. 1.6(b)]. One important characteristic of CoFeB is its amorphous shape after deposition. This feature has two main advantages [30]. The first one is the inexistence of any mismatch problem during the deposition of the MgO barrier. The second one is related with the annealing process. In general, after the deposition, the MTJ is annealed and the CoFeB electrodes crystallize according to the crystalline structure of the barrier. Said in

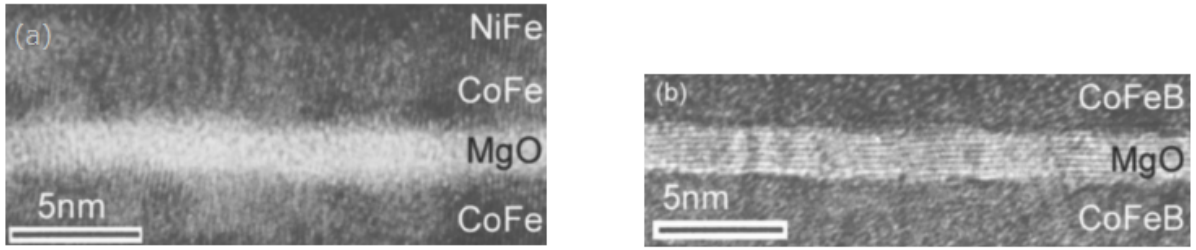


Figure 1.6: HRTEM images of the cross-section of (a) CoFe/MgO/CoFe and (b) CoFeB/MgO/CoFeB MTJs (adapted from [30]).

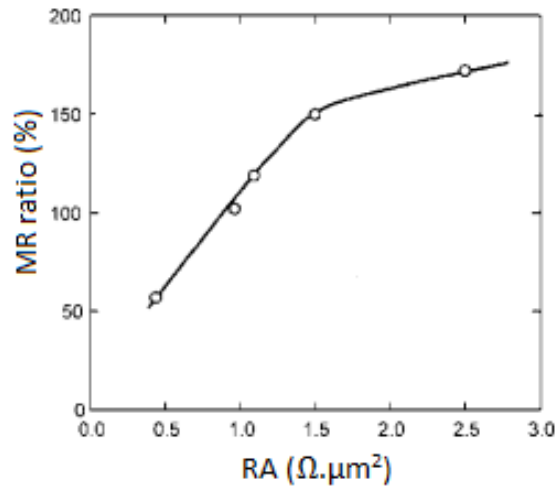


Figure 1.7: TMR at room temperature for CoFeB/MgO/CoFeB MTJs as a function of the RA product (adapted from [4]).

an equivalent way, the MgO barrier acts like a template for the electrodes crystallization, which is essential for the coherent tunneling of Δ_1 states. In Fig. 1.7, experimental results show the typical behaviour for TMR as a function of the RA product in CoFeB/MgO/CoFeB-based MTJs. For higher RA values (increasing the thickness of the insulating barrier), TMR tends to saturate, which proves the majority tunneling of highly spin-polarized Δ_1 states. As the thickness of the barrier decreases, in a theoretical perspective, other symmetries but Δ_1 start tunneling, decreasing the spin-polarization and the TMR ratio. In an experimental perspective, the TMR ratio decrease can also be associated with the barrier degradation or its amorphous shape for ultra-thin thicknesses ($t_{\text{MgO}} \leq 3$ monoatomic layers [31]).

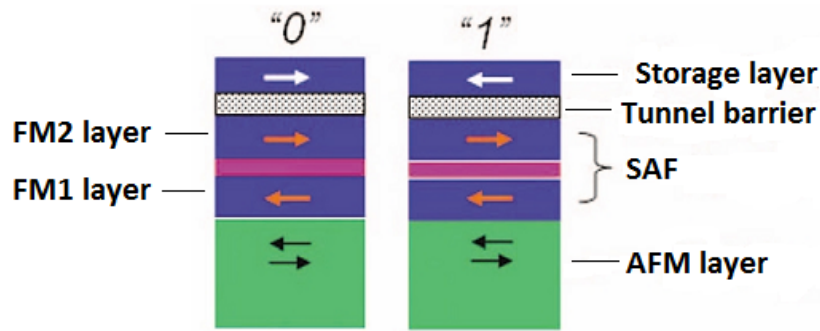


Figure 1.8: Conventional memory element using a specific MTJ stacking. The stored information (bit "0" or "1") is directly related to the magnetization of the free (storage) layer (adapted from [1]).

1.4 Basic MTJ structures

Until now, the exposure made about the MTJ stack was restricted to the fundamental FM/I/FM configuration. However, for practical applications, the MTJ structure must be much more complex to guarantee its functionality. An important issue is to find the best configuration to obtain a FM pinned layer. Between MTJs with in-plane magnetic anisotropy (IMA) and perpendicular magnetic anisotropy (PMA), one can find some differences on the stack structure. More information about typical MTJs structures with PMA is given elsewhere (see section 2.2.2).

Figure 1.8 shows a typical structure for an IMA MTJ, used as a memory element. Starting from the bottom (the buffer structure is not shown in Fig. 1.8), the MTJ is composed by an antiferromagnetic (AF) layer, a synthetic antiferromagnetic (SAF) structure, a tunnel barrier and a FM free layer (to finish the junction, a capping structure must be added). The AF layer is used to create an exchange bias interaction with the first FM layer (FM1 in Fig. 1.8) that constitutes the SAF structure. The trilayer FM1/non-magnetic/FM2 SAF structure creates an antiferromagnetic coupling (based in an RKKY interaction between the two FM layers and mediated by the thickness of the non-magnetic layer) that maintains the FM2 layer pinned. There are two main reasons for using a SAF structure instead of just an AF layer in direct contact with the pinned FM layer [25]. First, the exchange bias interaction is larger when a SAF structure is used. Second, there is an attenuation of the dipolar interaction between the free and pinned FM layers. The immediate consequence of the dipolar interaction is the shift on the magnetic field domain of the hysteresis loop obtained from the electrical measurements.

1.5 TMR dependency variables

1.5.1 Temperature dependence

At this point, it is clear that any experimental result about TMR values cannot be described without saying specifically what was the temperature at which it was obtained. This means that the TMR values obtained for an MTJ are strongly dependent on the temperature. In particular, the magnitude of TMR decreases with increasing temperature. Figure 1.9 shows the TMR dependence for two MTJs with AlO_x and MgO barriers. The results show that the decrease of the TMR with increasing temperature results almost completely from the decrease of the resistance in the anti-parallel configuration (R_{AP}), while R_P is almost independent on the temperature.

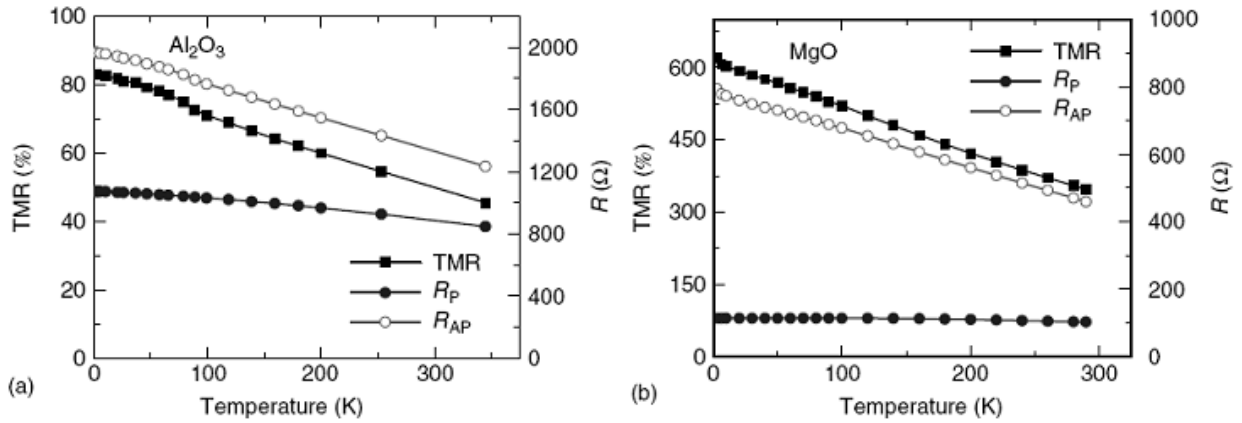


Figure 1.9: Temperature dependence of TMR for (a) Ta/IrMn/CoFe/AlO_x/CoFe and (b) Ta/IrMn/CoFe/MgO/CoFe MTJs (adapted from [33]).

Shang *et al.* [32] proposed a model to explain the TMR dependence on the temperature. In this model, the P behaviour is associated with that of the magnetization of a ferromagnet, where magnon excitations decrease the magnetization (the Bloch's law gives the magnetization of a ferromagnet at a given temperature). Thus, P of the tunneling electrons becomes:

$$P(T) = P(0)(1 - \alpha T^{3/2}), \quad (1.8)$$

where $P(0)$ is the spin-polarization at 0 K and α is a material dependent constant. Taking into account that variations of the resistance can be found in junctions with non-magnetic electrodes [32], the model includes two major factors to explain the TMR dependence. The first one is the spin-polarization variation with the temperature due to magnon excitations. The second is the realization that the variation of the TMR is not only a consequence of the magnetization of the FM electrodes, but also has a non-magnetic contribution (unpolarized conductance) that is temperature dependent, too.

1.5.2 Voltage dependence

The bias voltage dependence of TMR is another issue that should be taken into account. Figure 1.10 shows the TMR dependence for two MTJs with AlO_x and MgO insulating barriers. One sees that the TMR behaviour can be roughly described as even functions that reflect symmetric bias dependencies. In applications, this phenomenon is very important because it gives information about the stability and voltage functional range of the MTJ. In fact, one way to measure the quality of an MTJ is to calculate the voltage at which the TMR decreases to half of its value at zero bias [$\text{TMR}(V_{1/2}) = \text{TMR}(0)/2$] [34].

The physical explanation for this phenomenon is not clear yet. Just for reference, many studies have been performed that relate the bias voltage dependence with magnon excitations [35] or changes of the electronic band structure of the FM electrodes [36].

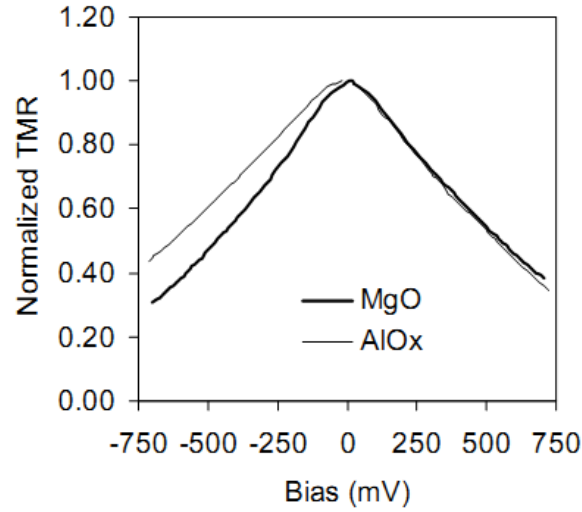


Figure 1.10: Normalized TMR bias dependence for Ta/PtMn/CoFe/Ru/CoFeB/I/CoFeB/Ta (I=AlO_x or MgO) MTJs [37].

1.6 Motivation

The present thesis embraces Spintronics which has already proved to be an area with a large potential for applications. For instance, MRAM is considered a revolutionary universal memory technology for the future. The word "future" should be noticed, because it proves that research must be done in the present, in order to reach the proposed objectives.

For memory applications, the insulating barrier must be extremely small [3] (~ 1 nm), which means that the roughness of the stack structure deposited below the insulating barrier plays an important role in defining the quality of the insulating barrier deposition. Many reports [38, 39, 40, 41, 42] have already studied the effect of different buffer structures in the magnetic and electrical properties of MTJs, but no study has been published on an optimization process aiming to decrease the roughness of MTJ buffer structures yet. Here, an optimization process of the buffer structure surface is performed (chapter 4) using the ion beam milling technique for CoFeB/MgO/CoFeB-based MTJs with an ultra-thin MgO barrier.

Another issue regarding the requirements for memory applications is the energy necessary to guarantee the functionality of the MTJ cell. It is well documented [43] that the induction of PMA in both FM layers decreases the necessary energy to switch the magnetization of the free layer. More recently, the bias voltage has already proved to have an effect in changing the magnetic properties of the FM layers [44]. Thus, this thesis aims to develop in parallel these two topics, by studying the conditions to have PMA in both FM layers (section 5.1) and performing a qualitative analysis of the effect of the bias voltage in CoFeB/MgO/CoFeB-based MTJs (section 5.2).

Chapter 2

Physics and applications in MTJs

Here, one provides a global overview of the main physical mechanisms used to achieve novel applications in MTJs. Specifically, the focus is made in three distinct topics: spin transfer torque (STT), MTJs with PMA and bias voltage effect in MTJs. For the STT effect and MTJs with PMA, after a theoretical introduction, arguments are given to show the advantages of combining both in the MTJ optimization. In the case of the bias voltage effect in MTJs, two different perspectives to understand this phenomenon are given. Finally, for both PMA optimization and bias voltage effect in MTJs, a literature review is made, in order to highlight the advances already achieved and the existing problems to solve.

2.1 Spin transfer torque effect in MTJs

2.1.1 Overview

The most obvious way to make a functional MTJ is by the application of an external magnetic field. The intensity range of the magnetic field is chosen to change the magnetization of one electrode (free layer), while maintaining the magnetization of the other electrode unchanged (fixed layer). This allows one to switch between the parallel and the anti-parallel configurations of the MTJ. Nevertheless, this is not the only operation method that can be applied in an MTJ.

As referred in section 1.2, an electric current is spin-polarized as it passes through the FM layers of the MTJ. Recovering the labelling of the last paragraph, the fixed layer has an unchanged magnetization ($\mathbf{M}_{\text{fixed}}$) while the magnetization of the other electrode ($\mathbf{M}_{\text{free}}$) is free to rotate. Consider the situation of Fig. 2.1, where $\mathbf{M}_{\text{fixed}}$ and $\mathbf{M}_{\text{free}}$ are not collinear. In the case of Fig. 2.1(a), the electrons become majority spin-polarized according to $\mathbf{M}_{\text{fixed}}$ while they propagate through the fixed layer. In the free layer, a similar phenomenon is going to occur: the electrons spin-polarization will align according to $\mathbf{M}_{\text{free}}$, so it will lose its transversal component (in the direction of the electrons propagation). From the conservation of the angular momentum, one concludes that the transversal spin component was transferred to the FM layer. This is the so-called spin transfer torque (STT) effect in which $\mathbf{M}_{\text{free}}$ "feels" a torque that tends to align the magnetizations of both FM layers. When the current direction is inverted [Fig. 2.1(b)], as the electrons propagate through the free layer, they become spin-polarized according to $\mathbf{M}_{\text{free}}$. In the interface between the barrier and the fixed layer, the electrons spin-polarized in the opposite direction of $\mathbf{M}_{\text{fixed}}$ will be in majority reflected back to the free layer (this is a consequence of the low density of states at the Fermi level that the fixed FM layer presents for electrons with that spin state). Thus, by STT effect, the reflected electrons will tend to rotate the magnetization of the free layer in the opposite direction of $\mathbf{M}_{\text{fixed}}$. At this point, it is clear that the direction of the electric current has an important role in defining if the spin torque promotes

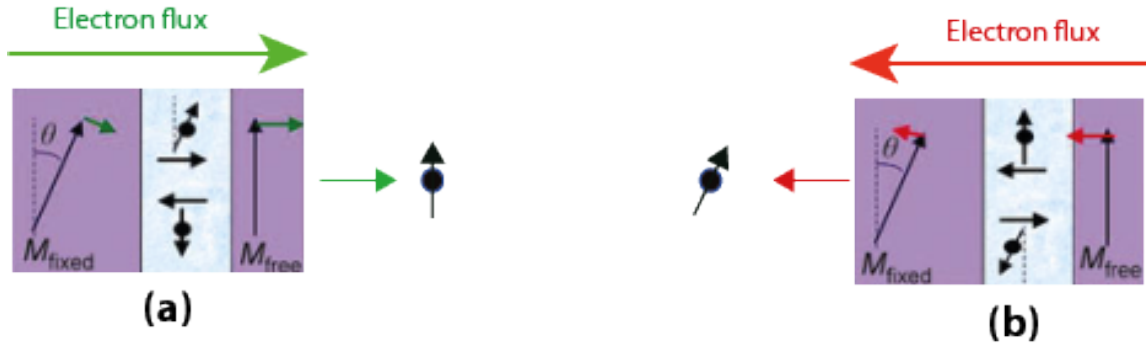


Figure 2.1: Illustration of the STT principle. (a) The electrons travel from the fixed to the free layer and favour the parallel configuration. (b) The electrons travel from the free to the fixed layer and favour the anti-parallel configuration. The green and red arrows inside the MTJ show the angular momentum transfer between the FM layers and the electrons (adapted from [46]).

the rotation of $\mathbf{M}_{\text{free}}$ towards (parallel configuration) or away (anti-parallel) from $\mathbf{M}_{\text{fixed}}$ [45]. This process allows to change the magnetization of the free layer based exclusively on the electric current that passes through the junction. Since $\mathbf{M}_{\text{fixed}}$ is pinned, this process does not admit any change in the magnetization of the fixed layer.

The angular momentum transfer between the spin-polarized current and the magnetization of the free layer is triggered by a torque whose equation is given by [47, 48, 49]:

$$\vec{\tau}_{STT} = \vec{\tau}_{\parallel} + \vec{\tau}_{\perp} = -a(\theta, J)\hat{M}_{\text{free}} \times (\hat{M}_{\text{free}} \times \hat{P}) + b(\theta, J)\hat{M}_{\text{free}} \times \hat{P}, \quad (2.1)$$

where $\mathbf{P}$ is the spin-polarization of the electric current. Taking into account the plane defined by $\mathbf{M}_{\text{free}}$ and $\mathbf{P}$, the first term on the right side of Eq. (2.1) [47] is the in-plane torque, where $a(\theta, J)$ (> 0) defines the amplitude of the torque, which depends on the angle θ between $\mathbf{M}_{\text{free}}$ and $\mathbf{P}$ and depends on the current density. The second term [48] refers to the out-of-plane torque, also called field-like torque, since it acts like an external applied magnetic field whose direction is the same of $\mathbf{P}$. In Eq. (2.1), $\hat{M}_{\text{free}}$ and $\hat{P}$ are unit vectors in the direction of $\mathbf{M}_{\text{free}}$ and $\mathbf{P}$, respectively.

The STT effect has a direct effect in changing the magnetization dynamics of the free layer. The total understanding of the $\mathbf{M}_{\text{free}}$ precessional motion can only be achieved by inserting the STT effect in the Landau-Lifshitz-Gilbert (LLG) equation. In that way, the equation becomes:

$$\frac{d\vec{M}_{\text{free}}}{dt} = -\gamma\mu_0\vec{M}_{\text{free}} \times \vec{H}_{\text{eff}} + \frac{\alpha}{M_S}\vec{M}_{\text{free}} \times \frac{d\vec{M}_{\text{free}}}{dt} + \vec{\tau}_{STT}. \quad (2.2)$$

The first term on the right side of Eq. (2.2) represents the torque exerted by the effective magnetic field ($\mathbf{H}_{\text{eff}}$) on $\mathbf{M}_{\text{free}}$, where γ is the gyromagnetic ratio and μ_0 is the magnetic permeability in vacuum. $\mathbf{H}_{\text{eff}}$ is defined as the sum of all the internal and external magnetic fields which have a direct effect on $\mathbf{M}_{\text{free}}$. Due to thermal fluctuations, there is a misalignment between the magnetization and the effective field which results in the precession of the magnetization around the effective field [valid if one forgets the other terms from Eq. (2.2)]. In real cases, the magnetization loses energy while precessing. The second term in Eq. (2.2) represents the damping torque that tends to rotate the magnetization (spiral movement whose objective is to minimize the energy of the magnetic system) towards the direction of the effective field, where α is the damping coefficient and M_S is the saturation magnetization of the free FM layer.

Experimental results in MgO MTJs show that the in-plane torque is larger than the field-like torque ($|\vec{\tau}_{\perp}| = 0.3|\vec{\tau}_{\parallel}|$ [50]). Thus, the analysis can be simplified by considering only the in-plane STT. It was

already seen that the STT effect depends, not only on the magnitude of the current density, but also on its direction. Figure 2.2(a) illustrates this concept in which, depending on the current direction, STT can reinforce or counter the damping by changing its direction. For instance, when one wants to switch the magnetization, the current is applied in order to oppose the directions of STT and damping torque. In that case, the final result depends on the magnitude of the current. If the current is below the critical value for switching, STT opposes the damping but it is weaker in magnitude, so STT decreases the effective damping torque but it cannot counter the damping motion that tends to align the magnetization with the effective field [Fig. 2.2(b)]. The same behaviour would happen if the direction of the current is changed (in that case, STT would increase the effective damping torque). If one increases the current below the critical value, STT can overcome the damping torque, increasing the angle between the magnetization and the effective field. Nevertheless, STT and the damping torque are angular dependent, so a possible dynamics equilibrium can be achieved for a certain angle. In that case, the energy gained from STT is balanced by the energy lost from damping, so that a precessional motion is achieved [Fig. 2.2(c)]. If the magnitude of the current applied is above the critical current, the STT magnitude is sufficient to tilt the magnetization for switching [Fig. 2.2(d)].

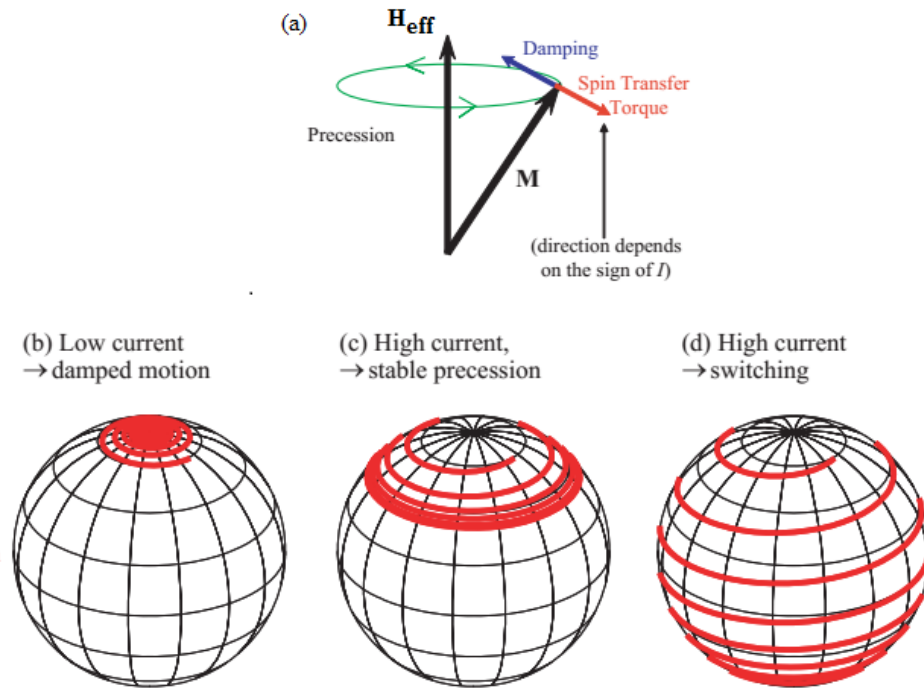


Figure 2.2: (a) Direction of the damping and STT vectors. The torque exerted by the effective field is not shown, but the consequent precession is depicted. If the current is applied in order to switch the magnetization (STT vector opposite to the damping torque) three distinct behaviours are possible to appear depending on the magnitude of the current: (b) damped oscillation, (c) stable precession and (d) switching (adapted from [51]).

2.1.2 Applications: STT-MRAM

One of the main practical results of the STT effect is the STT magnetoresistive random-access memory (STT-MRAM), which relies on an entirely current-based write mechanism, where the electric current is the only responsible for switching the magnetization of the free layer. Figure 2.3 shows the configuration of a STT-MRAM bit cell. In addition to the MTJ, a transistor, two parallel bit lines and a word line complete the memory cell. In a memory array, to select a specific bit cell for reading/writing, a bias voltage is applied between bit lines. The word line is connected to the gate of the transistor and, when selected, allows the conduction between bit lines. In a memory array, bit lines are perpendicular to the word lines, so the selection of a memory cell is made by the intersection between a bit and a word line. In the reading process, the current measurement allows to know the magnetic state of the MTJ, while in the writing process, a larger current with a specific direction changes the magnetic state of the free layer.

Energy efficiency is one of the main problems for the STT-MRAM, because large electric current densities must be used for switching ($J \sim 10^6 \text{ A/cm}^2$ [52]). By experimental research, the lowest switching energy achieved for STT-MRAM devices is in the order of $\sim 10^2 \text{ fJ}$ [53, 54]. On the other hand, a complementary metal-oxide-semiconductor (CMOS) transistor consumes $\sim 1 \text{ fJ}$ per operation [55], which is roughly one hundred times less when compared with the MTJ consumption to operate. Even with a great effort, MTJs cannot be an alternative yet. Thus, new approaches have been presented to reduce the switching current, including MTJs with PMA and the effect of the bias voltage.

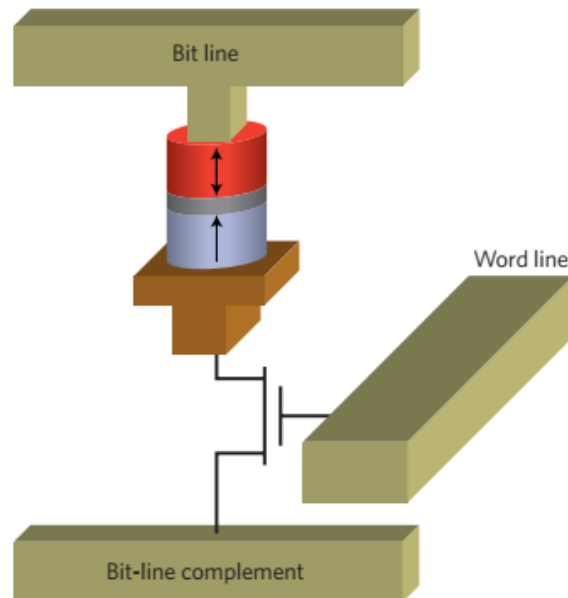


Figure 2.3: Illustration of a STT-MRAM bit cell. Both FM layers have PMA and the red layer stores the information of the bit ("0" or "1" depending on the magnetization direction). Together, the bit and word lines select the desired memory cell [56].

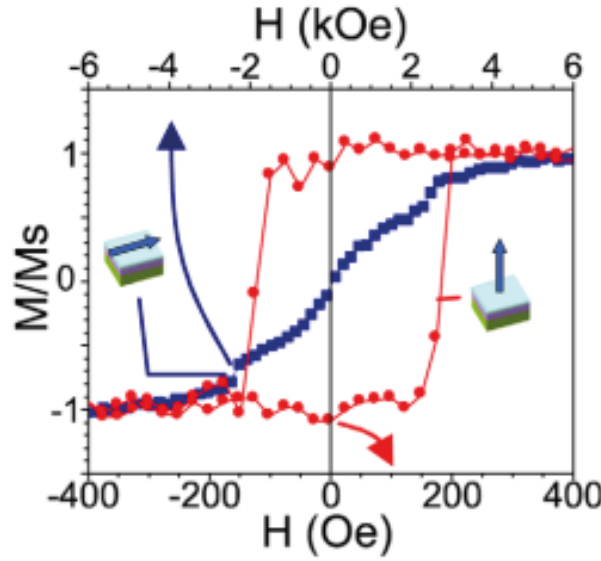


Figure 2.4: VSM measurements obtained for a 0.84 nm CoFeB FM layer. The red (blue) curve represents the data obtained when the external field is applied out-of-plane (in-plane) (adapted from [57]).

2.2 MTJs with perpendicular magnetic anisotropy

2.2.1 Magnetic anisotropy

In the case of thin films, a FM layer presents a magnetization with a direction that depends on its magnetic anisotropy. The latter is the sum of the crystalline and shape contributions.

The crystalline contribution is a direct consequence of the link between the crystallographic structure of the material and the electron orbitals. From this relation and taking into account FM materials presenting uniaxial magnetic anisotropy, results a preferential spatial direction (easy axis) at which the magnetic moments tend to align. Experimentally, it is straightforward to know the orientation of the easy axis by magnetic measurements in thin films. Figure 2.4 shows magnetic results for a 0.84 nm CoFeB FM layer. A hysteresis loop is visible when the external field is out-of-plane (red curve). These results allow to conclude that the FM layer has an in-plane hard axis represented by a blue curve with a linear behaviour between saturation edges.

The shape of the FM material influences directly the shape anisotropy contribution. If the material has a spherical shape, no preferential direction would result from the shape contribution. However, in the case of thin films, due to their dimensions (thickness much smaller than the sectional dimensions), this contribution is very important. For a finite FM sample, a stray field is created outside the sample as a consequence of its magnetization (Fig. 2.5). At the same time, a demagnetizing field is created inside the sample that tends to counteract its intrinsic magnetization. Taking as a reference the coordinates defined in Fig. 2.5, when the magnetization is in-plane ($+\hat{x}$ direction), the sample will induce a demagnetizing field in the $-\hat{x}$ direction. A similar analysis can be performed in the case of perpendicular magnetization, from which results a demagnetizing field in the $-\hat{z}$ direction. For a ferromagnet with an ellipsoidal shape, the demagnetizing field is given by [58]:

$$\mathbf{H}_d = -N\mathbf{M}_s, \quad (2.3)$$

where N is the demagnetizing tensor with unit trace, which is diagonalized in the Cartesian basis. If one approximates the free layer to a flat plate, the tensor becomes $N_{xx} \approx N_{yy} \ll N_{zz} \approx 1$, where the z direction

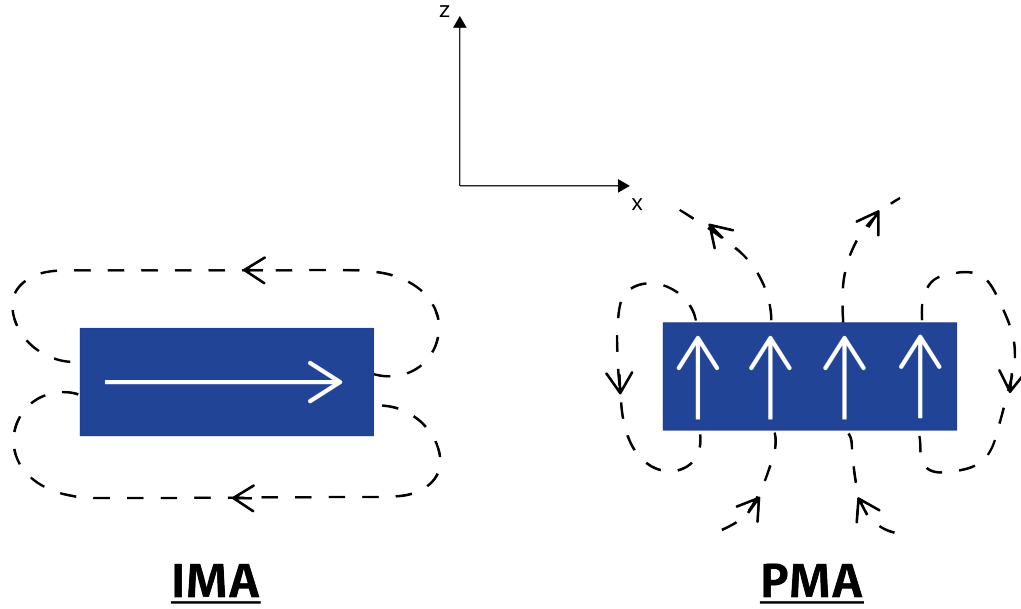


Figure 2.5: Lateral view of a thin film with IMA and PMA. The grey lines represent the stray field created by the magnetization of the sample.

is defined out-of-plane (see Fig. 2.5). These results show that H_d is very strong in the out-of-plane direction. Finally, for a finite sample, the demagnetizing field must be included in the general equation of the magnetic flux density [59]:

$$\vec{B} = \mu_0(\vec{H}_a + \vec{M} + \vec{H}_d), \quad (2.4)$$

where $\vec{H}_a$ the applied magnetic field, $\vec{M}$ the magnetization of the sample and $\vec{H}_d$ is the demagnetizing field, whose intensity depends directly on the shape of the FM sample.

2.2.2 Origin of PMA in the FM layers

The effective anisotropy constant (K_{eff}) is the energy per unit volume required to align the magnetization of the FM layer along the hard axis. Thus, K_{eff} defines the easy axis and is given in cgs units by [49]:

$$K_{eff} = \frac{M_S H_{eff}}{2} = K_V - 2\pi M_S^2 + \frac{2K_S}{t}, \quad (2.5)$$

where M_S is the saturation magnetization, H_{eff} the effective anisotropy field, K_V the volume crystalline anisotropy constant, $(-2\pi M_S^2)$ the shape anisotropy contribution, K_S the surface crystalline anisotropy constant and t the thickness of the FM layer. Here, one admits that the FM layer is sandwiched between two layers and the contributions of the bottom and top interfaces for K_{eff} are equal ($K_{S1} + K_{S2} = 2K_S$), which is not necessarily true if, for example, one considers layers of different materials under and above the FM layer. From Eq. (2.5), it is clear that the decrease of the FM layer thickness is followed by an increase of the interface contribution for K_{eff} . As an example, Fig. 2.6 depicts the $t \cdot K_{eff}(t)$ dependence for a Co thin layer in the case of Co/Pd multilayers. These experimental results show that $(K_V - 2\pi M_S^2)$ is negative, whose consequence is the negative slope obtained. At a critical thickness (t_{cr}), the change of sign for K_{eff} represents a transition of the easy axis. For $K_{eff} > 0$ the interface anisotropy contribution is dominant, so the easy axis becomes out-of-plane. Thus, to obtain PMA, one has to increase the $2K_S/t$ term. Experimentally, this can be achieved by decreasing the thickness of the magnetic layer and/or choosing the right materials for the

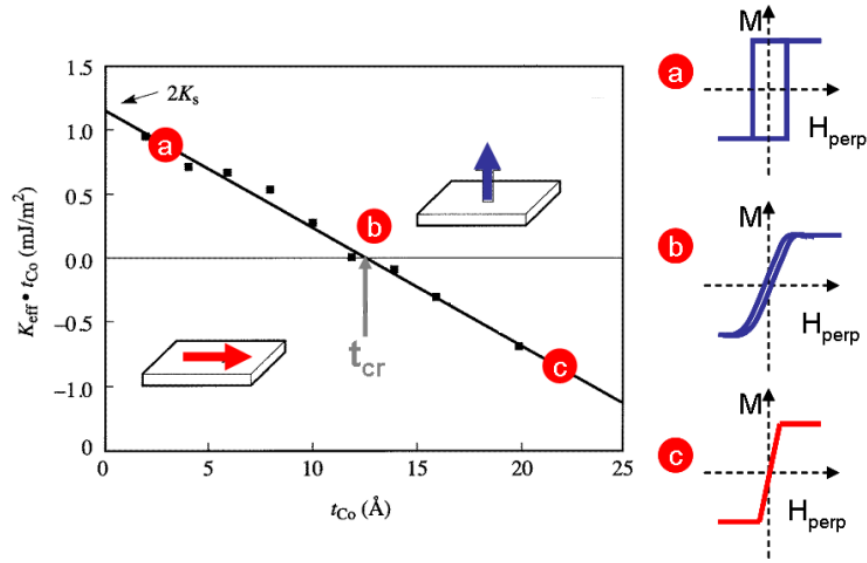


Figure 2.6: Dependence of $K_{\text{eff}} \cdot t$ on the thickness of the Co thin layer for Co/Pd multilayers: (a) out-of-plane magnetization; (b) critical thickness; (c) in-plane magnetization. In the $M(H)$ graphs, the magnetic field (H_{perp}) is applied in the direction perpendicular to the plane of the film (adapted from [60]).

interfaces, in order to increase K_s .

The optimization of PMA in MTJs is still an issue to be solve and many stack structures are currently being studied. Nevertheless, PMA was successfully induced in CoFeB/MgO/CoFeB-based MTJs (structure depicted in Fig. 2.7) with a TMR value around 120% [38]. More recently, the elements composition of CoFeB proved to have a direct effect in the interfacial anisotropy energy. In fact, it was observed that the boron composition $[(\text{Co}_{0.25}\text{Fe}_{0.75})_{100-x}\text{B}_x]$ can change K_{eff} and the TMR ratio [61]. Another important factor for PMA optimization is the buffer and capping layers. As an example, returning to Fig. 2.7, a Ta(5)/Ru(10)/Ta(5) (nominal thickness in nanometers) stack is used as the buffer structure below the bottom FM layer and a Ta(5)/Ru(5) stack as the capping structure above the top FM layer. As already referred, it must be noted that this is not the only MTJ structure studied. Thus, many studies have been performed with different types of materials, namely Nb [62] as capping layer, Hf [40] and Mo [39] as buffer layers and W [41] as both. These materials aim to replace Ta, the most widely used material but still with some problems for applications. As referred in section 1.3.3, an annealing process is essential for the crystallization of the CoFeB electrodes and the obtainment of a high TMR. The diffusion of Ta into the FM layers during annealing is an effect widely observed [26, 63, 64] which is dependent on the annealing temperature and affects not only the TMR ratio [26], but also the strength of PMA [39, 63]. This is particularly relevant for STT-MRAM applications in which MTJs are embedded with CMOS technology. In this case, MTJs must support a final 400 °C annealing process in order to be considered a compatible embedded technology [56, 65]. Moreover, the FM layers necessary to obtain PMA are very thin, in the order of 1 nm [$t_{\text{CoFeB}} = 1.3$ nm in Fig. 2.7 using Ta as buffer and capping layers], which is near to a superparamagnetic (SPM) behaviour [39, 62]. Thus, by choosing other materials as buffer and capping structures, one attempts to increase the maximum thickness at which PMA is achieved in CoFeB FM layers [39, 40].

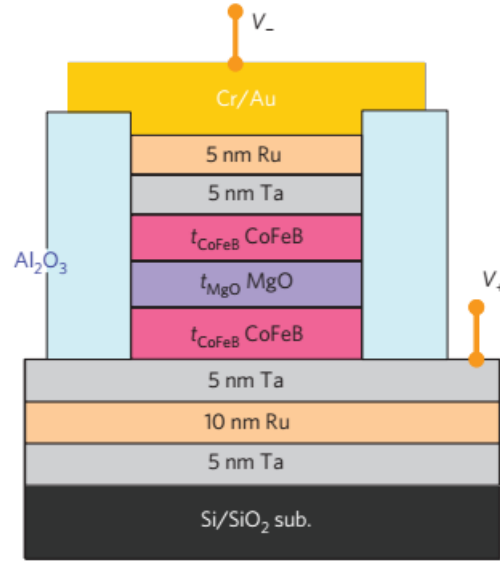


Figure 2.7: Example of an MTJ stack where PMA was successfully achieved for $t_{\text{CoFeB}} = 1.3$ nm (adapted from [38]).

2.3 STT switching in MTJs

The comparison between MTJs with IMA and PMA arises from the need to create a high performance MTJ that can be incorporated as a memory cell in an STT-MRAM. In this way, the basic requirement is a low threshold switching current. For a FM layer with IMA, the same is given by [66]:

$$I_{c0}^i = \left(\frac{\alpha \gamma e}{\mu_B g} \right) (\mu_0 M_S V) \left(H_{eff}^{\parallel} + \frac{H_d^z}{2} \right). \quad (2.6)$$

In the case of a FM layer with PMA, the threshold switching current is given by [66]:

$$I_{c0}^p = \left(\frac{\alpha \gamma e}{\mu_B g} \right) (\mu_0 M_S V) H_{eff}^{\perp}, \quad (2.7)$$

where α is the damping coefficient, γ the gyromagnetic constant, e the charge of the electron, μ_B the Bohr magneton, g the spin transfer torque efficiency which depends on P and on the angle between the magnetizations of both FM layers, μ_0 the magnetic permeability of vacuum, M_S the saturation magnetization and V the volume of the FM layer. The in-plane and out-of-plane effective anisotropy fields are referred as $H_{eff}^{\parallel}$ and $H_{eff}^{\perp}$, respectively, while H_d^z describes the demagnetizing field in the out-of-plane direction. From Eqs. (2.6) and (2.7), one can see the major advantage of the STT effect. Being $I_{c0} \propto V$, the reduction of the MTJ size is naturally followed by a decrease of I_{c0} . This is a big breakthrough compared with the conventional magnetic field writing process; in the latter, the magnetic field that changes the magnetization of the free layer is created by electric currents and it is inversely proportional to the junction size [67]; this means that there is a limit in the reduction of the junction size below which the magnetic field necessary for operation is unaffordable.

At the same time, a high thermal stability is indispensable to obtain an MTJ stable to thermal fluctuations. Generally, the thermal stability factor is defined as:

$$\Delta = \frac{E}{k_B T}, \quad (2.8)$$

where k_B is the Boltzmann constant and E the energy required for switching ($E = K_{\text{eff}}V$, where K_{eff} is the effective anisotropy constant of the free layer). According to Ref. [67], a thermal stability factor larger than 40 is required for a memory cell with an information retention of ten years. For a FM layer with IMA and PMA, the thermal stability is given by:

$$\Delta = \left(\frac{\mu_0 M_S V}{2k_B T} \right) H_{\text{eff}}^{\parallel} \quad (2.9)$$

and

$$\Delta = \left(\frac{\mu_0 M_S V}{2k_B T} \right) H_{\text{eff}}^{\perp} \quad (2.10)$$

respectively. From Eqs. (2.9) and (2.10), one sees that reducing the volume of the free layer decreases not only I_{c0} but also Δ .

As referred in section 2.2.1, H_d is directly related with the shape anisotropy, which is relevant in a thin film with a width much larger than the thickness. From these conditions, results a high H_d^z that increases directly the switching current in the in-plane configuration [see Eq. (2.6)]. Moreover, although increasing the switching current, H_d^z does not contribute to the thermal stability in the same configuration [see Eq. (2.9)]. In the PMA configuration, both I_{c0} and Δ are dependent on $H_{\text{eff}}^{\perp}$ that, taking into account Eq. (2.5), is given by:

$$H_{\text{eff}}^{\perp} = \frac{4K_S}{M_S t} - 4\pi M_S, \quad (2.11)$$

where K_V was neglected, because of the low thickness of the FM layer [40]. To achieve PMA, the surface crystalline anisotropy contribution must overcome the shape anisotropy that tends to maintain the magnetization in-plane, so $H_{\text{eff}}^{\perp} > 0$. The main breakthrough that must be emphasized in Eq. (2.11) is the possibility to cancel the demagnetizing field in the out-of-plane direction ($4\pi M_S$ in cgs units), thus obtaining a small $H_{\text{eff}}^{\perp}$ and decreasing I_{c0} in the PMA configuration. Nevertheless, a low $H_{\text{eff}}^{\perp}$ automatically decreases Δ , so the approach being followed to obtain highly scalable STT-MRAMs is to use PMA materials to reduce I_{c0} , taking into account that Δ should be high enough to guarantee their endurance.

2.4 Voltage-controlled magnetic anisotropy in MTJs

For memory applications, due to the need of decreasing the functional energy of MTJs, the voltage-control effect on the magnetic anisotropy (VCMA) became a hot topic in the last years [68, 69]. VCMA resulted from the realization that the intensity and the sign of the bias voltage can directly affect the magnetic properties of the FM layers. In MTJs with PMA, the goal is to control the magnetic anisotropy by VCMA. From the growing interest in this topic resulted many reports that tried to enhance VCMA for different material systems measured by magneto-optical Kerr [70], anomalous Hall [71] effects and FM resonance [72, 73]. Moreover, MTJs switching was successfully achieved using voltage pulses, with the objective to prove their potential as memory devices [44, 74, 75, 76]. Wang *et al.* [44] reported their experimental results in MTJs with PMA, where CoFeB/MgO/CoFeB is the active trilayer structure. The different TMR curves in Fig. 2.8(a) show the direct influence of the bias voltage in the coercive field (H_c) of both FM layers: H_c depends on the intensity and sign of the bias voltage (for negative values, the increase of the bias voltage intensity decreases H_c for the soft layer and increases the same for the hard layer). The different behaviours observed for the soft and hard layers can be used to construct a new switching method. Figure 2.8(b) shows this possibility, where a constant magnetic field is applied (dotted lines) to shift the magnetization state from the origin. When a negative voltage pulse is applied, the H_c of the soft (hard) layer is going to decrease (increase). This process induces a change in the magnetization of the soft layer that is maintained after the

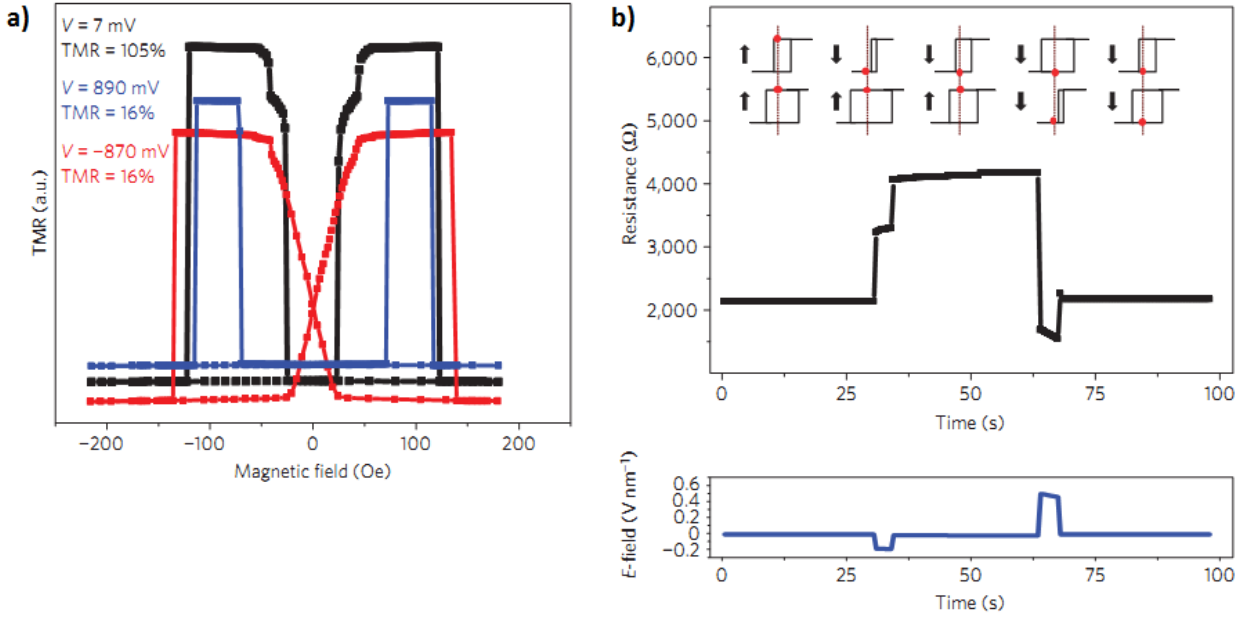


Figure 2.8: (a) TMR curves under different bias voltages for a CoFeB/MgO/CoFeB MTJ. (b) Manipulation of the MTJ resistance by an electric field. The upper graph shows the response of the resistance to the applied electric field shown in the lower graph. In the upper graph, the dotted lines represent the external magnetic field applied; the red circles and the black arrows represent the magnetic state of each FM layer (both figures adapted from [44]).

application of the pulse [see Fig. 2.8(b)]. If one then applies a positive voltage pulse, the inverse behaviour occurs: now, the switching of the magnetization state is observed in the hard layer and the resistance of the MTJ returns back to its initial value.

The physical explanation for the VCMA is not clear, yet. Even so, Fig. 2.9 can give a simple understanding of the phenomenon. Taking into account only the fundamental trilayer structure, the MTJ is fabricated with PMA in both FM layers (square loop at $V = 0$ V). For a positive (negative) potential, there is an accumulation (depletion) of electrons in the interface between the free FM layer (blue) and the insulating barrier, which results in a reduction (enhancement) of PMA. In fact, for $V = +1$ V, the reduction of PMA results in an effective change of the easy axis (there is no hysteresis for the red curve). A deeper analysis is possible by taking into account not only the electrons distribution in the interfaces, but also their spin distribution (see section 2.4.1).

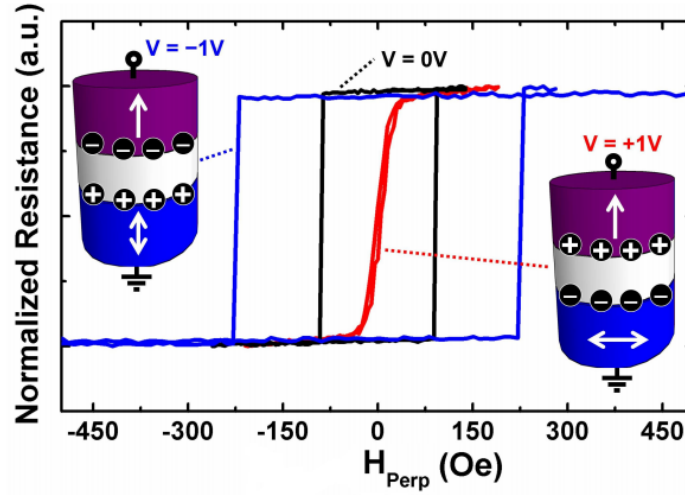


Figure 2.9: Measurements of the normalized resistance as a function of the perpendicular applied field in a $80 \times 80 \text{ nm}^2$ CoFeB/MgO/CoFeB-based MTJ. Different values of the applied voltage were used in order to see the perpendicular anisotropy changes in the electrical measurements (adapted from [77]).

2.4.1 Spin-dependent screening

Generally, the magnetoelectric (ME) effect is the production of an electric polarization (magnetization) with the application of a magnetic (electric) field in a given material. In the present case, the ability to produce a magnetization by applying an electric field is the wanted phenomenon. The application of a bias voltage in an MTJ creates an electric field in the dielectric region (insulating layer). The electrodes are FM metals, so the electric field cannot penetrate into the bulk. Thus, any ME effect that could take place in the electrodes is confined to the metal surface. In principle, this fact is a limitation on the effect that the electric field might present. Nevertheless, FM layers in MTJs have thicknesses in the order of nanometers, which improves the surface contribution to the magnetic properties presented by the FM layers (see section 2.2.2). The application of an electric field (E) in the MTJ creates a surface charge density $\sigma = \epsilon_0 \epsilon_r E$ (ϵ_r is the relative permittivity of the insulating layer) in each FM layer. According to Ref. [78], for a FM metal, the screening charge is spin-dependent, so that electrons with a spin-up state are going to have a different surface charge distribution when compared with the spin-down electrons, inducing a surface magnetization. From Duan *et al.* [79] theoretical calculations in FM metal thin films, resulted a linear dependence of the induced magnetization M_{surf} on E :

$$\mu_B M_{\text{surf}} = \alpha_s E, \quad (2.12)$$

where α_s denotes the surface magnetoelectric coefficient (in SI units, it is measured in Tm^2V^{-1}). Figure 2.10 shows the difference between the electron charge density for a disturbed ($E \neq 0$) and undisturbed ($E = 0$) Fe(001) thin film along the direction perpendicular to the same (z direction); the density variation is calculated for majority and minority spin electrons and the electric field is applied in the z direction. It is visible that the surface charge density is strongly spin-polarized, due to the different results for minority and majority spin electrons near the surface of the metal. It is the spin imbalance of the screening charges that induces a surface magnetization. Far from the metal surface, the charge density variation is negligible, which proves the limitation of the ME effect to the surface.

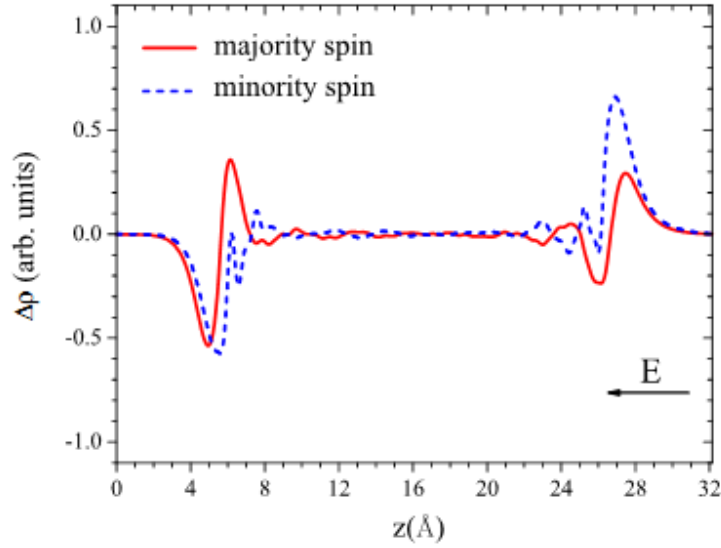


Figure 2.10: Induced xy-averaged electron charge densities $\Delta\rho = \rho(E) - \rho(0)$ along the z direction normal to the Fe film plane for majority and minority spin electrons. The direction of the applied electric field is pointed with a vector [79].

2.4.2 Macroscopic model

Using a simple single-domain macroscopic model, one can describe the VCMA effect. Consider a very common configuration in MTJs of a FM CoFeB thin film sandwiched between a MgO insulating barrier (on the top) and a Ta metallic thin film (on the bottom). In this case, the FM layer presents an effective magnetic anisotropy constant in cgs units given by [40, 80]:

$$K_{eff} = \frac{M_S H_{eff}}{2} = (K_V - 2\pi M_S^2) + \frac{K_S^{Ta} + K_S^{MgO}}{t}, \quad (2.13)$$

where M_S is the saturation magnetization, H_{eff} the effective anisotropy field, K_V the volume crystalline anisotropy constant, K_S^{Ta} and K_S^{MgO} the surface anisotropy constants in the Ta/CoFeB and CoFeB/MgO interfaces, respectively and t the CoFeB layer thickness. Due to the low thickness of the FM layer, the volume crystalline contribution is negligible [40] and the voltage-dependent $K_{eff}(V)$ can be approximated to [68]:

$$K_{eff}(V) \approx \frac{K_S(V)}{t} - 2\pi M_S^2, \quad (2.14)$$

with

$$K_S(V) = K_S^{Ta} + K_S^{MgO}(V). \quad (2.15)$$

The second term on the right side of Eq. (2.14) is the shape anisotropy contribution and it is a consequence of the demagnetizing field in the direction perpendicular to the film plane. Now, Eq. (2.14) indicates the voltage dependence of the anisotropy constant, which reflects the surface charge density change in the CoFeB/MgO interface and the voltage dependence of the surface anisotropy constant in the same interface [Eq. (2.15)]. The voltage contribution to the anisotropy change can be synthesized as [77]:

$$K_S(V) = K_S(V=0) - \sum_n \xi_n \left(\frac{V}{d} \right)^n, \quad (2.16)$$

where a_n are the VCMA coefficients in the Taylor expansion over the external applied electric field $E_{\text{ext}} = V/d$ (V is the electric potential applied across the MTJ and d is the dielectric layer thickness). Due to the fact that many experimental results show a linear dependence of VCMA on the electric field [39, 71, 72, 81, 82], Eq. (2.16) can be simplified to:

$$K_S(V) = K_S(V = 0) - \xi \frac{V}{d}, \quad (2.17)$$

where ξ [typically presented in fJ/(V.m)] is the linear VCMA coefficient that gives information about the strength and the sign of the VCMA effect.

For Ta/CoFeB/MgO-based MTJs, experimental results show values of ξ in the range of 25-50 fJ/(V.m) [71, 44, 83]. A simple calculation can be made to prove how small these values are. Based on the results of Ref. [83], Ta/CoFeB/MgO-based MTJs present a surface anisotropy constant of 1.46 erg/cm² and a VCMA coefficient of 32 fJ/(V.m) at room temperature. If one applies an electric field of 1 V/nm, the variation of the surface anisotropy constant will be roughly 2% of its initial value. Moreover, the values of the applied voltage are limited by the breakdown voltage of the insulating barrier. Beyond Ta/CoFeB/MgO-based MTJs, other material stack configurations have been studied [82, 84, 85], with results showing a VCMA coefficient at least one order of magnitude larger. One of the reasons for the persistence in Ta/CoFeB/MgO-based MTJs is related with the best TMR values obtained at room temperature with this configuration [26]. Thus, finding a material stack configuration which presents at the same time high TMR values and large VCMA coefficients is a challenge for the future.

Chapter 3

Experimental techniques

This chapter presents a brief description of the fabrication and characterization techniques used in the experimental work. The first section describes all the experimental techniques used for the fabrication of the nanostructures studied in this thesis. The second section provides a general overview of the magnetic, electrical and morphologic characterization techniques used to quantify the properties of the nanostructures. All the experimental techniques described in this chapter were used at the INL facilities.

3.1 Fabrication techniques

In this thesis, all the studied samples were deposited by physical vapour deposition (PVD) systems. At INL, two fully computer controlled machines were used: the Singulus Timaris Four-Target-Module (FTM) and the Multi-Target-Module (MTM) sputtering tools. Moreover, a Nordiko 7500 ion beam milling tool was used for etching studies on the MTJ buffer structures.

3.1.1 Sputtering: basic concepts

Sputtering is a PVD technique that aims to deposit a specific material in a substrate by ions bombardment of a target constituted by the intended material. In a vacuum chamber, an inert gas (usually argon) is controllably introduced. The use of an inert gas is related with its low chemical reactivity. The inert gas is ionized by applying either a direct current (DC) or a radio frequency (RF) signal, creating a plasma. The target is the cathode, so the cations are accelerated towards it. By linear momentum transfer between the cations and the atoms from the target, the latter are ejected to condense on the substrate as a thin film. The RF sputtering is used to deposit insulating materials, so the build-up of charges in the target surface can be prevented. In the magnetron sputtering configuration, a magnetic field parallel to the target is used to trap (Lorentz force) the electrons in the plasma near the target (see Fig. 3.1). This leads to a probability increase of the gas ionization and consequently to an increase of the plasma density in the target region [86]. Thus, the magnetic field aims to enhance the bombardment of the target, in order to increase the deposition rate.

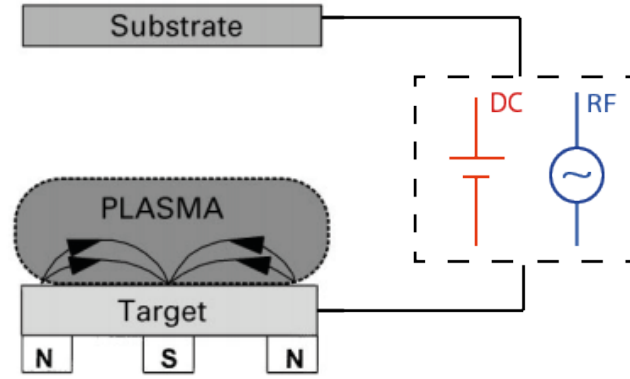


Figure 3.1: Illustration of the sputtering principle. The magnets are placed below the target. The power supply applies a DC or an RF signal, depending on the sputtering configuration and deposition material (adapted from [86]).

3.1.2 PVD systems

Singulus Timaris Multi-Target-Module sputtering tool The MTM sputtering tool is a PVD system by DC/RF magnetron sputtering. In the cleanroom of INL (see Fig. 3.2), this sputtering tool is constituted by a cassette module, a transport module, a soft-etch/oxidation module and a multi-target PVD module. The cassette module is used to introduce the wafers in the sputtering tool. The transport module allows to drive the wafer between modules. The soft-etch is a pre-clean module and it is used to clean the wafer before the deposition - by RF sputter etching, this module aims to remove any unwanted molecules (e.g. water, oxides) in the surface that could affect the deposition [87]. Moreover, the pre-clean module is combined with an oxidation module, which is used to oxidize metallic thin films. The oxidation can be performed using a plasma source to generate oxygen ions or exposing the thin film to pure oxygen at low pressure [87]. In the ultra-high vacuum (UHV) deposition chamber, there are 10 cathodes available for sputtering targets. This gives the possibility to perform multiple film stack deposition without breaking the UHV, since after the deposition of one layer, the sputtering target can be simply switched in order to deposit the next layer. The deposition goes as the substrate moves in a linear and cyclical path along the chamber (dynamic deposition), passing periodically below the stationary sputtering target (see Fig. 3.3). Therefore, an essential parameter to control the deposition rate is the linear velocity of the substrate (v_W), while the number of cycles (N_W) ultimately determines the total film thickness. For a specific power of the sputtering source (P_W), the final thickness t_W obtained for a deposited layer is given by:

$$t_W = t_R \left(\frac{N_W}{N_R} \right) \left(\frac{v_R}{v_W} \right) \left(\frac{P_W}{P_R} \right), \quad (3.1)$$

where t_R , N_R , v_R and P_R are the thickness, number of cycles, velocity and source power used in the calibration process of the sputtering tool, respectively. Appendix 6 gives a detailed overview about the deposition conditions used for all the materials and thicknesses used in this thesis. In the context of this thesis, all the nanostructures were deposited by using the MTM sputtering tool.



Figure 3.2: MTM sputtering tool used in this thesis. The images highlight the modules used for the stack depositions.

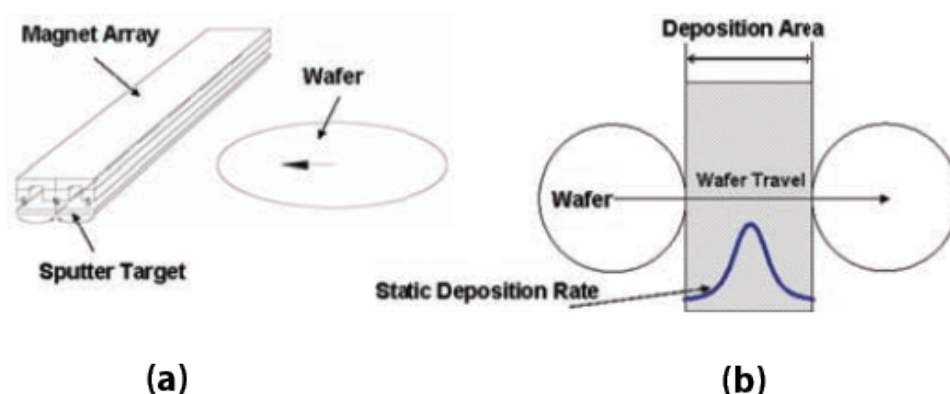


Figure 3.3: Representation of the dynamic deposition. (a) The wafer is moving towards the sputter target. (b) The deposition area is defined by the sputtering target position and the deposition rate presents a Gaussian profile (adapted from [88]).

Singulus Timaris Four-Target-Module sputtering tool Like MTM, the FTM sputtering tool is a PVD system by DC/RF magnetron sputtering. In the cleanroom of INL (see Fig. 3.4), this sputtering tool is constituted by a cassette, a transport and a soft-etch modules which are similar to the same modules described for the MTM sputtering tool (here, the pre-clean module is not combined with an oxidation module) and a four-target linear module. In the four-target linear module, an UHV chamber hosts the sputtering targets (up to four targets linearly disposed) and the substrate.

The FTM tool was used to deposit the first Al_2O_3 layer in all the 200 mm thermally oxidized silicon wafers used in this thesis. After this first step, the wafers were transported to the MTM tool, in order to deposit the desired stack structure.



Figure 3.4: FTM sputtering tool used in this thesis. The cassette module is not shown because is similar to the one presented in Fig. 3.2.

3.1.3 Ion beam milling

The ion beam milling is a dry etching technique and a purely physical process. In a general perspective, an ion beam (e.g. argon cations) is accelerated in a specific direction towards the surface of the sample. Like in sputtering, this process leads to the removal of atoms in the sample surface, but now the objective is only to remove material from the sample and no deposition aspects are considered.

In the context of this thesis, the ion beam milling was used to etch the surface of MTJ buffer structures, in order to study its effect on the growth of the final MTJ stack above buffer structures with different etching treatments.

At INL (see Fig. 3.5), the Nordiko 7500 ion milling tool is constituted by a cassette module, a transfer module and a working module which aggregates the ion beam source and the working chamber. The cassette and transfer modules are used to insert and drive the wafers between modules, respectively. The ion beam source [Fig. 3.6(a)] is responsible to generate and accelerate the ion beam towards the sample. The inert gas is inserted in a discharge chamber where, in the case of the Nordiko 7500 tool, an RF field



Figure 3.5: Nordiko 7500 tool used in this thesis.

produced by an RF source creates the plasma. A system of electrostatic grids is responsible for extracting the cations from the discharge chamber. Each grid is biased at a specific potential [Fig. 3.6(b)] in order to control the energy at which the cations leave the ion source. The grids are constituted by several apertures that collimate the exit beam. The working chamber is constituted by the neutralizers [Fig. 3.6(a)] (the Nordiko 7500 has two neutralizers) and the rotation table [not shown in Fig. 3.6(a)] where the sample is placed. Basically, a neutralizer is an electron source whose objective is to neutralize the cations by reaction with the emitted electrons. This step aims to prevent possible build-up of charges in the sample surface during the etching process. Finally, the rotation table allows to change the incidence angle between the sample surface and the ion beam. Moreover, it rotates the sample during etching to ensure a good uniformity to the process.

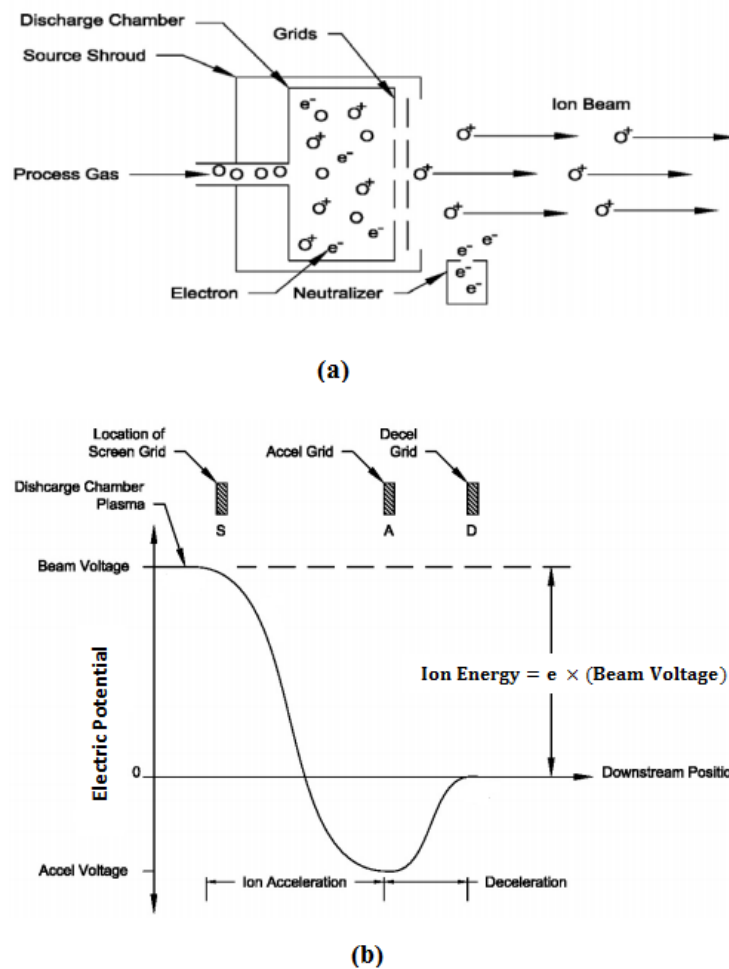


Figure 3.6: (a) A possible illustration of an ion beam source and respective neutralizer. (b) Acceleration process of the ion beam, represented by the electric potential felt by the cations as a function of their position in the grid system. The first grid (S) is positively biased ("Beam Voltage"). The second grid (A) is responsible for the cations acceleration and it is negatively biased ("Accel Voltage"). The third grid is maintained at ground potential and the cations leave the source with an energy that depends directly on "Beam Voltage" (adapted from [89]).

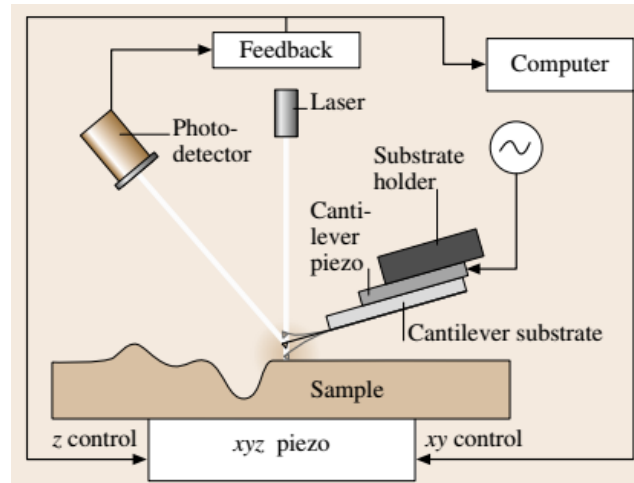


Figure 3.7: Illustration of the tapping mode combined with a laser/photodetector deflection sensor used for surface roughness measurements [91].

3.2 Characterization techniques

3.2.1 Atomic force microscopy

In order to verify the effects of the etching process in the buffer structures (see chapter 4), an atomic force microscopy (AFM) tool was used for surface characterization.

AFM is a scanning probe microscopy technique that uses a cantilever as the scanning probe and its principle is based on the interatomic forces between the cantilever and the atoms of the sample surface. The surface topography is mapped by measuring the cantilever deflection with a sensor, while the same is scanned over the sample. Thus, the surface topography reflects the force variation between the cantilever and the atoms from the sample.

In the context of this thesis, a Bruker Dimension Icon tool was used for topography measurements. In this tool, the deflection sensor is constituted by a laser and a photodetector (Fig. 3.7). A laser beam is directed to the free end region of the cantilever where it is reflected to the photodetector. The measurements were performed in the AFM tapping mode. In this mode, the cantilever is vibrating at a specific frequency and its oscillation barely touches the sample surface (Fig. 3.7). The objective of this procedure is to calculate the roughness of the buffer surface and to perform statistical analysis, so the fact that this mode does not present an atomic resolution [90] (it has a nanometric resolution) is not a problem.

3.2.2 Vibrating sample magnetometer

One of the objectives of this thesis is to fabricate MTJs with PMA in the two active FM layers (see section 5.1). Thus, magnetic measurements are mandatory to know the direction of the easy/hard axes of the FM layers. The vibrating sample magnetometer (VSM) was the tool used for magnetic measurements. Figure 3.8 shows a setup similar to the one used at INL. The sample is inserted in a region with a uniform magnetic field created by an electromagnet. The vibration unit maintains the sample in an oscillatory movement in the direction perpendicular to the external magnetic field. The vibration changes periodically the magnetic flux that passes through the nearby pickup coils, inducing an electromotive force (Faraday's law) in the same. Thus, the pickup coils collect the electrical signal used to measure the total magnetic moment of the sample as a function of the external magnetic field.

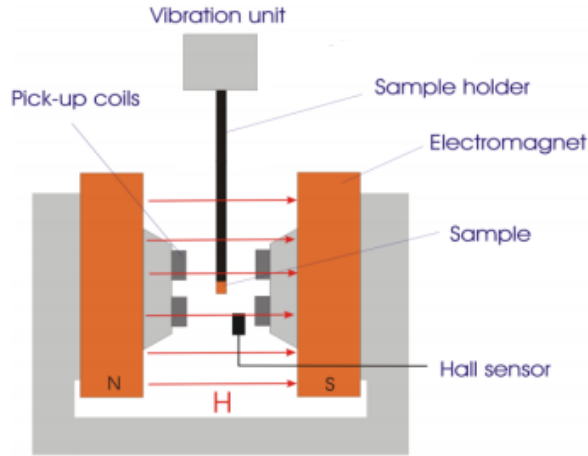


Figure 3.8: Schematic illustration of the VSM measurement setup (adapted from [92]).

3.2.3 Current in-plane tunneling method

The current in-plane tunneling (CIPT) method is a reliable and fast way to characterize MTJs in unpatterned wafers. Thus, MTJ characteristics can be known without the need of any process beyond deposition (e.g. lithography and etching processes). The technique is based in a series of four-point-probe measurements. An external magnetic field is applied to measure the resistance in both MTJ configurations and each resistance measurement is made at a different probe spacing. There are some important considerations regarding the range of the probe spacing. For a thin film, the resistance of a specific volume is given by:

$$R = \frac{\rho L}{Wt} = R_s \frac{L}{W}, \quad (3.2)$$

where L is the length, W the width, t the thickness, ρ the resistivity and R_s the sheet resistance of the material. In both FM layers, the resistance increases with the probe spacing ($R \propto L$). In the case of the insulating barrier, the raise of the probe spacing increases the section at which the electric current can tunnel between FM layers, so the resistance decreases [$R \propto (Wt)^{-1}$]. Below a certain probe spacing limit [Fig. 3.9(a)], the resistance of the top FM layer is much smaller than the resistance of the insulating barrier, so all the electric current flows through the top FM layer. Figure 3.9(b) shows the opposite limit at which the resistance of the insulating barrier is much smaller than the resistance of the FM layers, so that the current flows mainly through both FM layers in a parallel resistors configuration. In both limit situations, the TMR cannot be measured. In the case depicted in Fig. 3.9(a), for both MTJ configurations, the resistance measured does not change because the current flows only through the top FM layer. In Fig. 3.9(b), the contribution of the insulating barrier to the overall resistance of the junction is too small to see a significant resistance difference for different MTJ configurations. However, it is possible to measure TMR for an intermediate probe spacing, whose scale length is given by [93]:

$$\lambda = \sqrt{\frac{RA}{(R_T + R_B)}}, \quad (3.3)$$

being RA the resistance-area product of the MTJ and R_T and R_B the sheet resistance of the top and bottom FM layers, respectively.

The CIPT method was first proposed by Worledge *et al.* [93]. In that report, an analytical solution describing CIPT is derived, in which the resistance of the MTJ is given by:

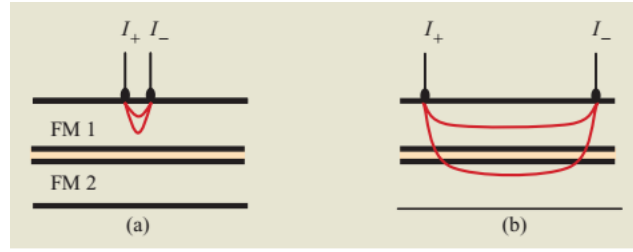


Figure 3.9: Illustration of CIPT measurements, representing the two probe spacing limits. (a) The probes are too close, so the current flows only through the top FM layer. (b) The large probe spacing creates a parallel current propagation through both FM layers [94].

$$R = \frac{R_T R_B}{R_T + R_B} \frac{1}{2\pi} \left[\frac{R_T}{R_B} \left[K_0 \left(\frac{a}{\lambda} \right) + K_0 \left(\frac{d}{\lambda} \right) - K_0 \left(\frac{b}{\lambda} \right) - K_0 \left(\frac{c}{\lambda} \right) \right] + \ln \left(\frac{bc}{ad} \right) \right], \quad (3.4)$$

where K_0 is the modified Bessel function of the second kind of zero order. Taking into account the four probes used in the measurements, a is the distance between I^+ and V^+ , b between I^+ and V^- , c between I^- and V^+ and d between I^- and V^- . Figure 3.10 shows CIPT experimental data obtained at INL. The CIPT tester has twelve cantilever electrodes with a variable spacing, down to 750 nm. The analytical solution of Eq. (3.4) is used to fit to the experimental data using TMR, RA, R_T , R_B and λ as fit parameters that characterize the MTJ.

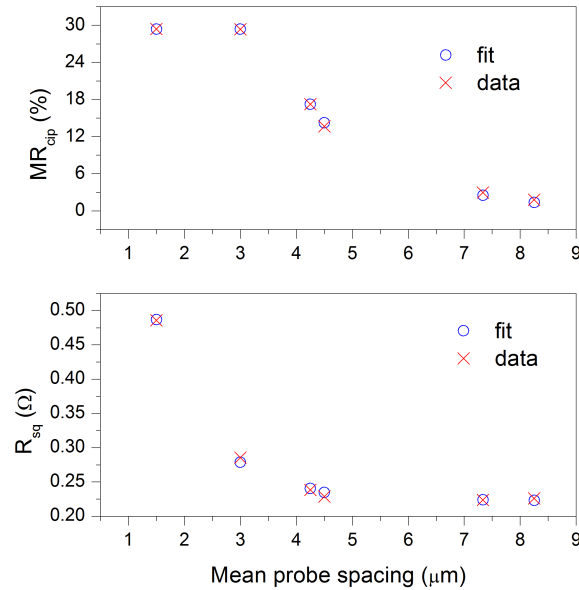


Figure 3.10: Experimental data obtained using the CIPT method and respective fit to the theory based on the analytical solution of Eq. (3.4). R_{sq} refers to the MTJ sheet resistance in the parallel configuration and MR_{cip} is the current in-plane magnetoresistance measured as a function of the probe spacing. In this specific measurement, the fit gives $RA = 1.63 \Omega \mu m^2$, $TMR = 98.04\%$, $R_T = 1.13 \Omega$, $R_B = 0.28 \Omega$ and $\lambda = 1.075 \mu m$.

Chapter 4

Optimization of the buffer structure in CoFeB/MgO/CoFeB-based MTJs

For memory applications, MTJs must have low RA product values ($\sim 1 \Omega\mu m^2$) [3], which is equivalent to say that the insulating barrier should be extremely thin (~ 1 nm). This means that every defect related with the roughness on the MTJ stack has a direct impact in the insulating barrier growth. Here, one describes the experimental procedure for the implementation of a smoothing process in a specific buffer structure. The morphologic and electrical results give important clues regarding the effect of the smoothing treatment in the optimization of the MTJ physical properties.

4.1 Roughness optimization

The buffer optimization here performed was an etching/smoothing process, whose objective was to decrease the roughness of the buffer surface. This process was performed at INL by ion beam milling, using the Nordiko 7500 tool.

The first parameter that must be known is the etching rate, which is essential to control the smoothing process. Thus, a $\text{Al}_2\text{O}_3(100)/\text{Ru}(400)$ stack (thickness in nanometers) was deposited by magnetron sputtering in a 200 mm thermally oxidized silicon wafer. The Al_2O_3 layer was deposited by RF magnetron sputtering in the FTM tool and has the objective to improve the insulation between the substrate and the

Forward Power (W)	Reflected Power (W)	Grid 1 Voltage (V)	Grid 1 Current (mA)	Grid 2 Voltage (V)	Grid 2 Current (mA)	Ar Flow (sccm)
350	13	602	232	-2381	-31	19.9

Table 4.1: Ion beam source parameters obtained during a smoothing process.

Parameters	Neutralizer 1	Neutralizer 2
Voltage (V)	25	309
Current (mA)	48	267
Ar Flow (sccm)	5.0	5.0

Table 4.2: Parameters obtained for the two neutralizers during a smoothing process.

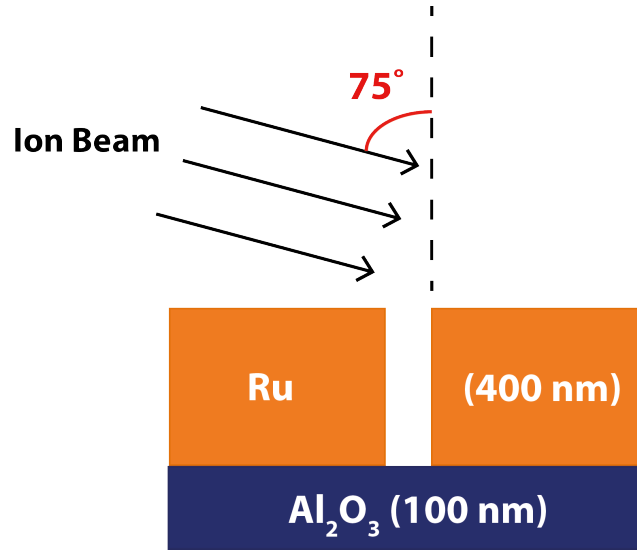


Figure 4.1: Illustration of the smoothing process. The step in the Ru layer represents the region where the lift-off was performed.

stack deposited above. After vacuum break, the Ru layer was deposited by DC magnetron sputtering in the MTM tool with a base pressure of 2×10^{-9} mbar (the main details about the deposition conditions used in this thesis are presented in appendix 6). One pretends to calculate the etching rate of the ion beam milling process in Ru, because the final buffer structure has a top Ru layer (see section 4.2). Before the Ru deposition, a mark was made with a permanent pen in the alumina surface. After the Ru deposition, a lift-off process removed the Ru deposited above the mark. Then, a profilometer (P-16+ surface profiler) was used to calculate the thickness of the Ru layer in the region of the lift-off. Moreover, a four-point-probe system (AIT CMT-SR2000N model) was used to measure the sheet resistance by choosing a map with 197 measuring points in the Ru surface. Thus, in the lift-off region, one has the thickness (t) of the step and the sheet resistance (R_s) given by the points of the map near the lift-off, so using the equation $\rho = R_s \cdot t$, one calculates the resistivity (ρ) of the Ru layer. Figure 4.1 depicts the smoothing process applied in the stack structure and Tables 4.1 and 4.2 show the parameters obtained for a performed smoothing process.

The wafer is placed in a rotation table at 30 rpm and the etching process is performed at an angle of 75° between the ion beam direction and the normal to the stack surface. In order to calculate the etching rate, a similar sheet resistance map was obtained after a smoothing process of 30 minutes. Using the resistivity value obtained above, one can transform the sheet resistance maps before and after the smoothing process into thickness maps (Fig. 4.2). The thickness removed at each point can then be calculated by subtracting the thicknesses in both maps. Finally, the etching rate is given by

$$ER = \frac{\Delta t_{av}}{t_{etch}} = 1.8 \pm 0.1 \text{ (nm/min)}, \quad (4.1)$$

where Δt_{av} is the average of the Ru thickness removed and t_{etch} the etching time (in this case, 30 minutes). At this point, it is possible to control the exact Ru thickness to be removed by choosing the right etching time.

After the calculation of the etching rate, seven samples with a $\text{Al}_2\text{O}_3(100)/\text{Ru}(400)$ stack were used to perform different smoothing times (samples similar to the one depicted in Fig. 4.1, but without the lift-off process). Figure 4.3 shows the AFM measurements (Gwyddion 2.44 software) obtained for different smoothing times, where the effect of the smoothing treatment in the polycrystalline surface is clearly visible.

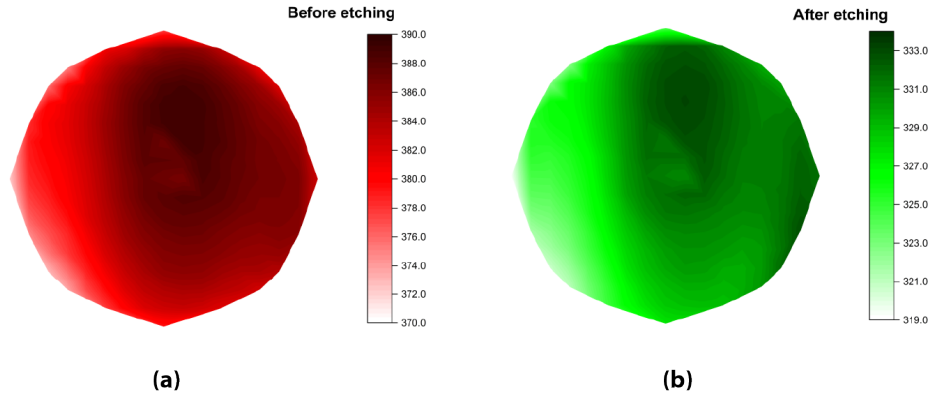


Figure 4.2: Thickness distribution of the Ru surface (a) before and (b) after the smoothing process.

Figure 4.4(a) shows the roughness of the Ru surface obtained from the AFM measurements as a function of the smoothing time. The roughness (σ) is defined as the average value of the absolute distances of the surface points from the mean plane, so:

$$\sigma = \left(\frac{1}{n} \sum_{i=1}^n (z_i - \mu)^2 \right)^{1/2}, \quad (4.2)$$

which is calculated from the height of all the n surface points measured. The mean plane μ is given by:

$$\mu = \frac{1}{n} \sum_{i=1}^n z_i. \quad (4.3)$$

The results show a direct effect of the smoothing process in decreasing the roughness of the Ru surface. For instance, an etching time of 15 minutes decreases the roughness for almost half of its initial value (from 1.95 to 1.02 nm). Nevertheless, the effect does not present a monotonous behaviour, proved by the increase of the surface roughness for etching periods larger than 15 minutes. Moreover, σ is not enough to make a complete evaluation of the surface quality. While the roughness gives a general perspective about the surface morphology, the peak-to-peak distance gives relevant information about the existence of surface defects, by comparing the order of magnitude between the latter and the roughness. Figure 4.4(b) depicts the peak-to-peak distance (d_{pp}) between the maximum and minimum points ($d_{pp} = z_{\max} - z_{\min}$) obtained from the AFM measurements. The behaviour is similar to the one observed for the surface roughness and both results in Fig. 4.4 translate an optimal etching time of around 15 minutes. In general, the peak-to-peak distance is roughly one order of magnitude larger than the surface roughness. Therefore, to improve the smoothness of the stack surface, one has to decrease the surface roughness to the minimum possible and, at the same time, guarantee a maximum approximation between the latter and the peak-to-peak distance to prevent surface defects.

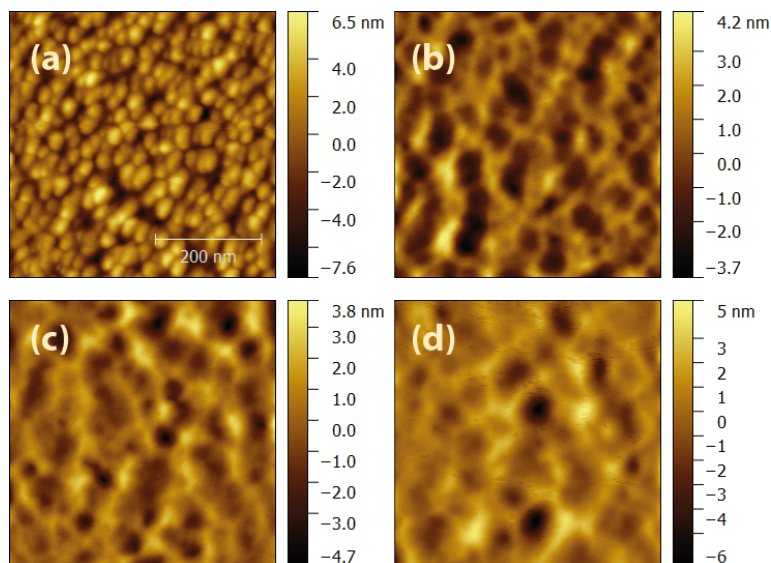


Figure 4.3: AFM measurements of the Ru surface in the $\text{Al}_2\text{O}_3(100)/\text{Ru}(400)$ stack, where smoothing treatments of (a) 0, (b) 10, (c) 20 and (d) 30 minutes were performed.

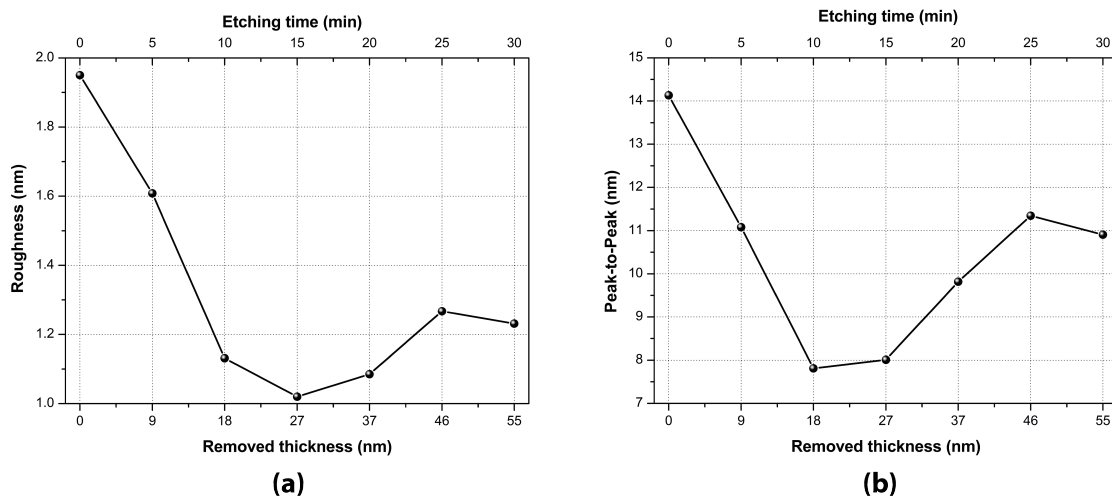


Figure 4.4: AFM results translated into normal distributions that represent the height distribution for each sample surface. The height is defined as the distance between the surface point and the mean plane, in the direction perpendicular to the sample surface.

4.2 Electrical results for MTJs with optimized buffer structures

After studying the effect of the etching process in a simple stack structure (see section 4.1), a more realistic study was performed. Thus, five $\text{Al}_2\text{O}_3(100)/\text{Ta}(5)/\text{CuN}(50)/\text{Ta}(5)/\text{CuN}(50)/\text{Ru}(20)$ buffer structures were deposited by magnetron sputtering in thermally oxidized silicon wafers. Once again, the Al_2O_3 was deposited by RF magnetron sputtering in the FTM tool, while all the remaining layers were deposited by DC magnetron sputtering in the MTM tool. Figure 4.5 shows histograms for the five buffers with different treatments, obtained from the AFM measurements (Fig. 4.6). Four of the buffers were annealed in vacuum for 2 hours at 330 °C and different etching times (different Ru thicknesses removed) were performed for three of the annealed samples. The histograms present a statistical analysis of the height distribution for each sample surface. The height (h_i) is defined as the distance between the surface point (z_i) and the mean plane [as defined in Eq. (4.3)], in the direction perpendicular to the sample surface, so $h_i = z_i - \bar{z}$. The results allow to conclude that the annealing alone does not improve the surface smoothness. In fact, the normal distribution for the annealed sample (red histogram in Fig. 4.5) is broader than the normal distribution for the as-deposited sample (blue histogram in Fig. 4.5), which is translated in an increase of the standard deviation. When the smoothing process is performed, there is a clear decrease of the standard deviation, which means that the number of points with a height near the mean plane increases.

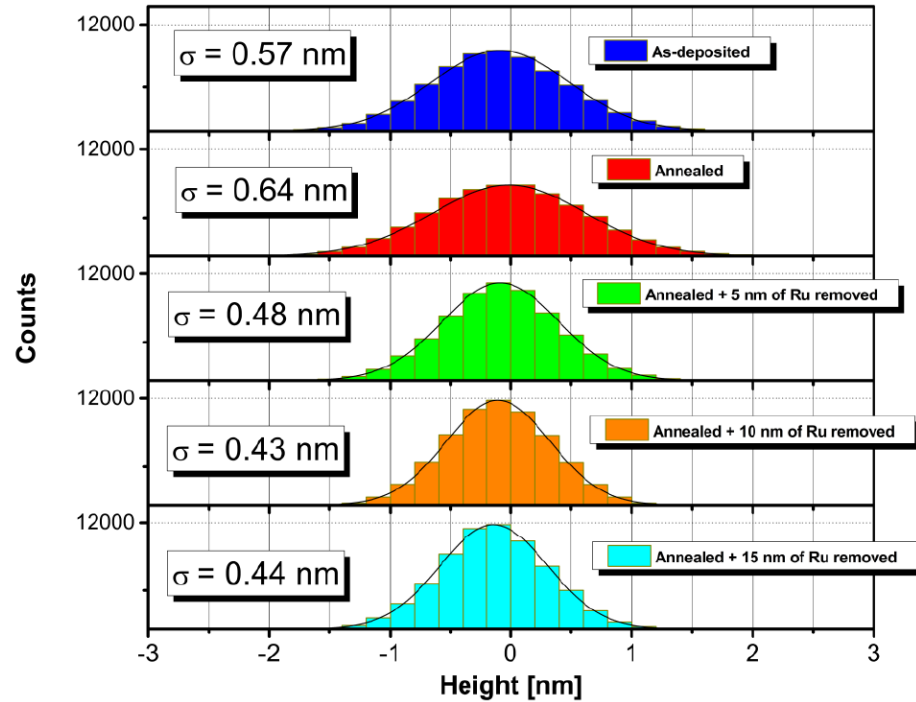


Figure 4.5: AFM results translated into normal distributions that represent the height distribution for each sample surface. The height is defined as the distance between the surface point and the mean plane, in the direction perpendicular to the sample surface.

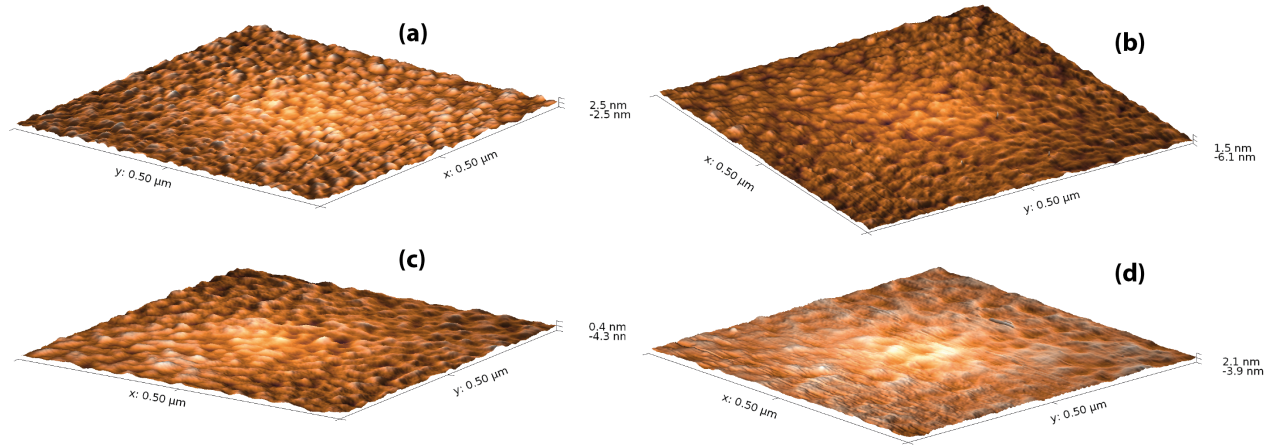


Figure 4.6: 3D images obtained from the AFM measurements. (a) Buffer as-deposited. (b) Buffer annealed without an etching process. Buffer annealed with an etching process performed in order to remove (c) 5 nm and (d) 15 nm of Ru.

In order to obtain the electrical measurements by CIPT, the same five buffer structures were used to deposit the final MTJ structures. Thus, above the existing buffer structure and after vacuum break, a Ta(5) / Ru(5) / PtMn(20) / CoFe₃₀(2) / Ru(0.85) / CoFe₄₀B₂₀(2.5) / MgO(2.0 Ωμm²) / CoFe₄₀B₂₀(2) / Ta(10) / CuN(30) / Ru(7) stack was deposited, as depicted in Fig. 4.7. In addition, a reference sample with a Al₂O₃(100) / Ta(5) / CuN(50) / Ta(5) / CuN(50) / Ta(5) / Ru(5) / PtMn(20) / CoFe₃₀(2) / Ru(0.85) / CoFe₄₀B₂₀(2.5) / MgO(2.0 Ωμm²) / CoFe₄₀B₂₀(2) / Ta(10) / CuN(30) / Ru(7) stack was deposited in order to acquire electrical results for an MTJ without vacuum break. All the metallic layers were deposited by DC magnetron sputtering in the MTM tool, while the Al₂O₃ and MgO insulating layers were deposited by RF magnetron sputtering in the FTM and MTM tools, respectively. After the final deposition, all samples were annealed in vacuum for 2 hours at 330 °C with an in-plane external magnetic field of 1 T.

Starting from the bottom, it is worth to refer the function of each layer in the MTJ depicted in Fig. 4.7. The Ta(5)/Ru(5) stack completes the buffer structure. The AF PtMn layer creates the exchange bias interaction with the CoFe₃₀ layer immediately above, in order to fix the magnetization direction of the latter. The CoFe₃₀(2)/Ru(0.85)/CoFe₄₀B₂₀(2.5) stack is the SAF structure, being the Ru thickness chosen for an AF configuration. In the fundamental CoFe₄₀B₂₀(2.5)/MgO/CoFe₄₀B₂₀(2) trilayer structure, the FM layers have in-plane magnetic anisotropy, which is clearly deduced from the thickness chosen for both. In this analysis, no objective regarding the induction of PMA in the FM layers is considered - the focus is only the relation between the electrical results and the buffer optimization process. The Ta(10)/CuN(30)/Ru(7) structure completes the stack as the capping structure. The choice of Ru as the last layer has a specific reason. After the deposition, the samples are air exposed, so the Ru layer will partially oxidize. The advantage relies on the fact that Ru-O is still conductive, which is a requirement for the layer in contact with the probes of the CIPT tester. The use of CuN in both capping and buffer structures also has the objective to fulfill the requirements for CIPT measurements. As already referred, the deposited MgO barrier has an ultra-thin thickness, which means that its RA product is extremely low ($\sim 1 \Omega \cdot \mu\text{m}^2$). In section 3.2.3, it is emphasized that an intermediate scale length for the probe spacing must be chosen, in order to perform a correct measurement of the electrical properties. From Eq. (3.3), if the RA product is very low, one has to guarantee that the sheet resistance of the bottom and top stacks are sufficiently low to obtain a proper scale length (in this case, not too low). Thus, CuN layers with a low resistivity are deposited in the buffer and capping

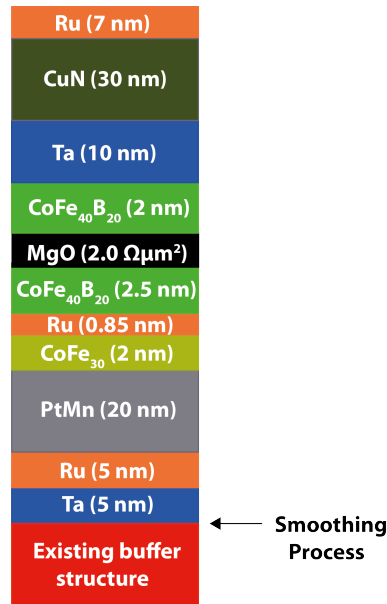


Figure 4.7: MTJ stack after the final deposition above the buffer structures.

stacks, aiming to decrease the sheet resistance of both structures.

Table 4.3 and Fig. 4.8 summarize the processes performed in the samples and present the respective final electrical results. The buffer annealing alone does not improve the buffer roughness and the TMR ratio (larger TMR ratio and lower roughness for sample "A" when compared with sample "B"), which sustains the conclusion already achieved from Fig. 4.5. Once again, the evolution of the roughness and peak-to-peak distance with the smoothing process does not present a monotonous behaviour, although their decrease from the initial values is evident. From the CIPT results, it is clear that the smoothing process improves the TMR ratio. For instance, a smoothing process of 10 nm of Ru removed (sample "D") almost doubles the TMR ratio (103.32%) by comparison with sample "B" (55.36%) which has an annealed buffer without any smoothing process. For a smoothing process of 15 nm of Ru removed (sample "E"), the TMR ratio starts to decrease from the results obtained for lower smoothing times. The original Ru layer was deposited with 20 nm, so this subtle TMR ratio decrease could denote the onset of the etching of the underneath CuN layer. In this situation, both Ru and CuN would be etched simultaneously. In principle, Ru and CuN have different etching rates, so that the smoothing process could never be uniform - in this case, an increase of the surface roughness is more likely than the opposite. Now, comparing the best result obtained for a sample with a smoothed buffer (103.32% for sample "D") and the result obtained for the reference sample (99.29%), it is clear that the improvement is still short from the one desired. In fact, the comparison between sample "A" and the reference sample proves that the vacuum break alone decreases the TMR ratio by almost half of the value obtained for the reference sample. Taking into account that the time spent for the fabrication of MTJs with a smoothed buffer is much larger than the one required for the deposition of MTJs without vacuum break, the electrical results must be further improved in order to consider the smoothing process a relevant mechanism.

Sample	Buffer annealing	Buffer smoothing	RA ($\Omega\mu\text{m}^2$)	TMR (%)	Buffer roughness (nm)	Peak-to-peak distance (nm)
Reference	-	No	1.75	99.29	-	-
A	No	No	1.54	56.71	0.57	4.3
B	Yes	No	1.48	55.36	0.64	7.7
C	Yes	Yes (5 nm of Ru)	1.70	92.25	0.48	3.4
D	Yes	Yes (10 nm of Ru)	1.71	103.32	0.43	3.3
E	Yes	Yes (15 nm of Ru)	1.70	89.91	0.44	3.9

Table 4.3: Overall results after the CIPT measurements. The "Reference" sample was deposited without vacuum break, in order to compare its results with the samples in which the smoothing process and/or vacuum break were performed.

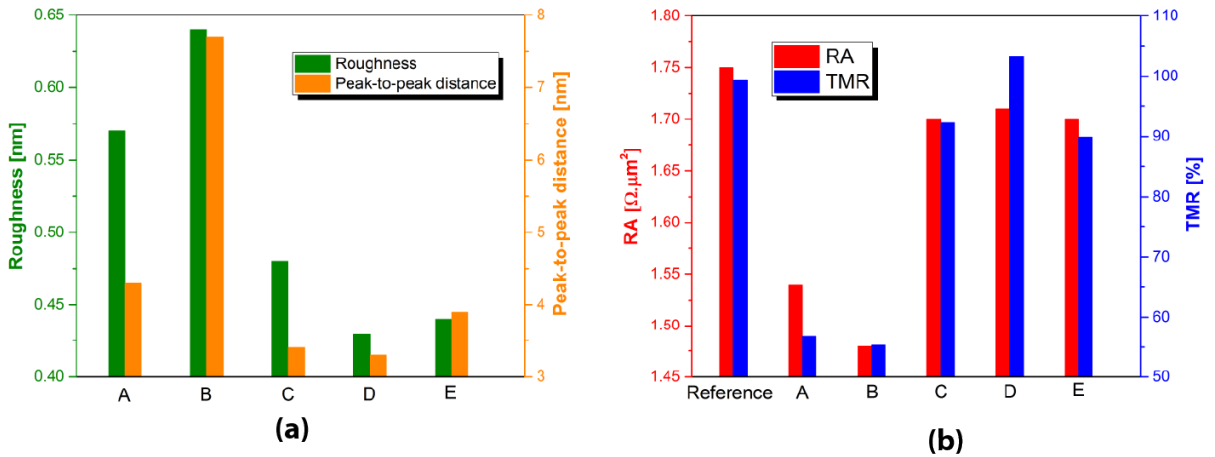


Figure 4.8: (a) Morphologic properties of the Ru surface in the samples as defined in Table 4.3. (b) Electrical properties obtained after the deposition of the full MTJ stack in the same buffer structures.

4.3 Conclusion

By ion beam milling, an optimization process (165° between the ion beam direction and the buffer surface) was performed to MTJ buffer structures, aiming to decrease the roughness of the Ru surface (top layer of the buffer stack). AFM measurements show a decrease of the Ru surface roughness with the increase of the etching time, although not presenting a monotonous behaviour. The CIPT measurements show a correlation between the decrease of the surface roughness and the improvement of the TMR ratio, indicating a direct effect of the smoothing treatment in the electrical properties of the MTJs. The results obtained for an MTJ without vacuum break and smoothing treatment ("Reference" sample with TMR = 99.29%) show a less than desired improvement of the electrical properties by the smoothing treatment, proved by the similar TMR ratio obtained for the best sample with the smoothing treatment (103.32%).

Chapter 5

Study of the magnetic properties in MTJ nanostructures

This chapter presents the most relevant experimental results obtained from the study of the magnetic properties of the two active FM layers in MTJs. Section 5.1 presents an IMA-PMA transition study, where magnetic results are presented for CoFeB/MgO, MgO/CoFeB and CoFeB/MgO/CoFeB-based nanostructures with different FM layer thicknesses. Moreover, magnetic results for nanostructures with and without an annealing treatment give information about the effect of the same in the magnetic properties of the nanostructures. Finally, section 5.2 gives a qualitative description of the bias voltage effect in the magnetic properties of nano-patterned CoFeB/MgO/CoFeB-based MTJs.

5.1 Optimization of PMA in the FM layers

As already referred in section 2.3, for MTJs with a switching process based on the STT effect, the critical current density can be decreased by inducing PMA in both FM layers [38]. Thus, in parallel with the experimental work performed in chapter 4, PMA was successfully achieved for the top and bottom FM layers in different stack structures. Specifically, the work relied on a thickness dependence study of the magnetic properties of both FM layers for annealed and as-deposited samples.

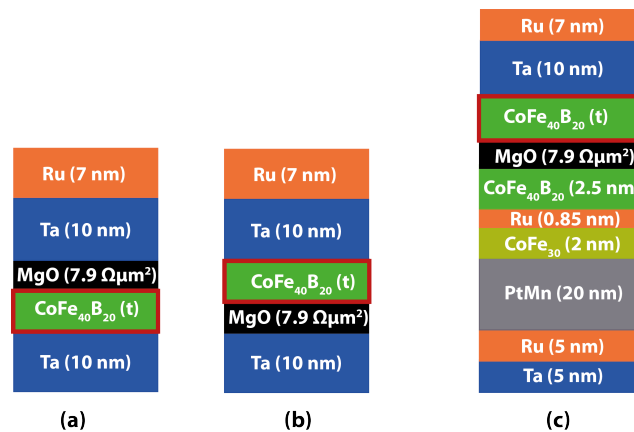


Figure 5.1: Stack structures used for the PMA optimization process in the (a) bottom and [(b) and (c)] top FM layers.

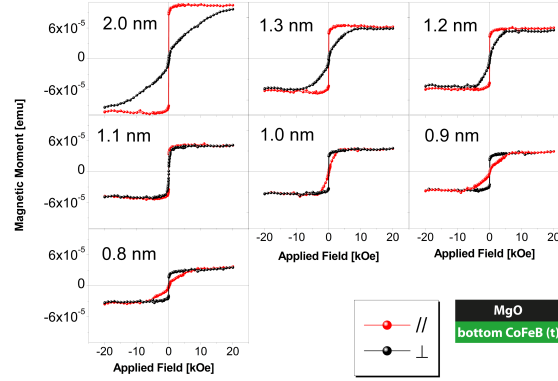


Figure 5.2: VSM results obtained for stack structures as depicted in Fig. 5.1(a). Each graph highlights the thickness of the FM layer and the results were obtained with in-plane (//) and out-of-plane (⊥) applied magnetic field.

5.1.1 Thickness dependence study

As the first step, two different stack structures [Figs. 5.1(a) and (b)] were deposited by magnetron sputtering in alumina oxidized substrates. In the MTM tool, all the metallic layers were deposited by DC and the MgO barrier by RF magnetron sputtering. The difference in the stack structures lies on the position of the FM layer regarding the insulating barrier. Here, the objective was to induce PMA separately in a bottom and top FM layer. For each stack, seven samples were deposited with FM layers presenting different thicknesses, ranging from 0.8 to 2.0 nm. The samples were annealed in vacuum for 1 hour at 300 °C with an in-plane applied magnetic field of 1 T. Knowing from the start that a thickness of 2.0 nm guarantees an IMA for the FM layers [39, 40, 62], the objective was to find the thickness at which the transition between IMA and PMA occurs.

Figure 5.2 shows the magnetic results obtained for the stack structure where the FM layer is below the insulating barrier [Fig. 5.1(a)]. Here, a clear IMA-PMA transition is achieved, which is proved by the amplified view depicted in Fig. 5.3, where PMA is achieved for a bottom FM layer with $t_{\text{CoFeB}} = 0.8$ nm and a coercive field of (39 ± 7) Oe. In fact, the transition already occurs for $t_{\text{CoFeB}} = 1.0$ nm, followed by a sudden increase of the coercive field (inset of Fig. 5.3) and it is maintained down to 0.8 nm. The coercive field (H_c) was calculated as the average of the positive (H^+) and negative (H^-) fields at which the sample is demagnetized, so $H_c = (H^+ + H^-)/2$.

In a similar way, Fig. 5.4 depicts the magnetic results obtained in VSM for the stack structure where the FM layer is above the insulating barrier [Fig. 5.1(b)]. For $t_{\text{CoFeB}} = 2.0$ nm, the FM layer presents an IMA as expected, but when the thickness starts to decrease, the transition for PMA does not occur. Figure 5.5 shows the VSM results for the sample with $t_{\text{CoFeB}} = 1.3$ nm, where an amplified view was performed in the origin. Both results (for in-plane and out-of-plane applied magnetic fields) show a negligible remanent magnetic moment at zero field, which proves the beginning of a SPM state for the FM layer. The SPM state is even clearer for smaller thicknesses, which is proved by the almost undistinguished behaviours for the two magnetic loops. The different results obtained for the two distinct stack structures prove that the position of the FM layer in the stack structure has a direct effect on its magnetic properties. This can be understood by looking to the thickness of the insulating barrier. The relation between the RA product and the MgO thickness is well known and given by [25]:

$$RA = B \cdot \exp(C \cdot t_{\text{MgO}}), \quad (5.1)$$

where B and C are fitting parameters. Using the parameters obtained from a previous work at INL [95], for a $RA = 7.9 \, \Omega \mu m^2$, one obtains a $t_{\text{MgO}} \sim 0.8 \, \text{nm}$, which makes it susceptible to defects that can affect directly the growth of the FM layer immediately above.

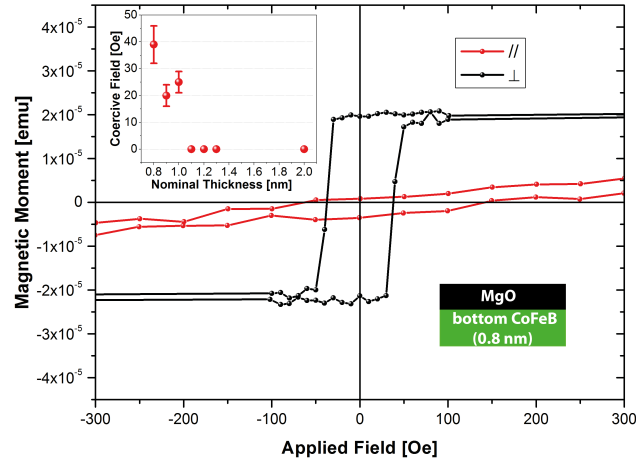


Figure 5.3: Magnetic results obtained for a bottom FM layer with $t_{\text{CoFeB}} = 0.8 \, \text{nm}$. The amplified view in the origin highlights the out-of-plane easy axis. The inset shows the coercive field of the FM layer obtained from the out-of-plane measurements as a function of the nominal thickness.

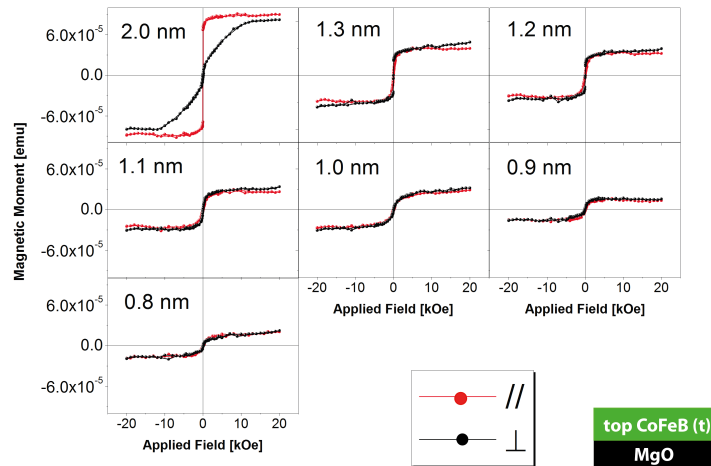


Figure 5.4: VSM results obtained for stack structures as depicted in Fig. 5.1(b). Each graph highlights the thickness of the FM layer and the results were obtained with in-plane (//) and out-of-plane ($\perp$) applied magnetic field.

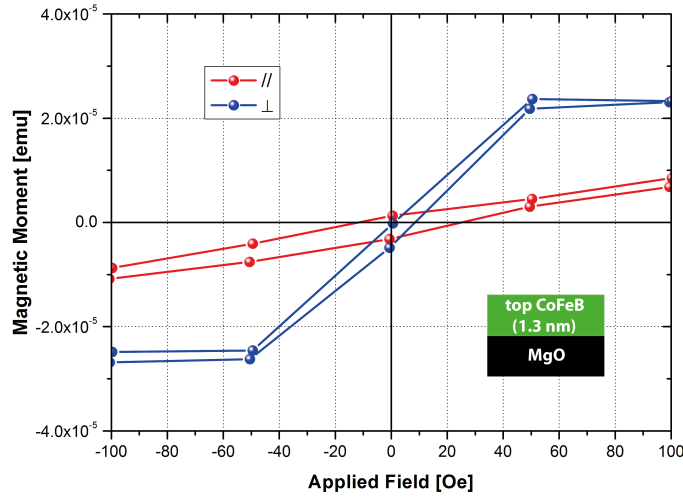


Figure 5.5: Magnetic results obtained for a top FM layer with $t_{\text{CoFeB}} = 1.3$ nm. The amplified view in the origin proves the negligible remanent magnetic moment at zero field.

After the failure of PMA on the top FM layer, a new approach was considered by choosing a more realistic stack structure. Thus, a $\text{Al}_2\text{O}_3(100)/\text{Ta}(5)/\text{Ru}(5)/\text{PtMn}(20)/\text{CoFe}_{30}(2)/\text{Ru}(0.85)/\text{CoFe}_{40}\text{B}_{20}(2.5)/\text{MgO}(7.9 \text{ } \Omega\mu\text{m}^2)/\text{CoFe}_{40}\text{B}_{20}(t)/\text{Ta}(10)/\text{CuN}(30)/\text{Ru}(7)$ stack structure was deposited by magnetron sputtering in alumina oxidized substrates [Fig. 5.1(c)]. The pinned FM layer has IMA and a thickness study was performed to the free FM layer. Thus, seven samples were deposited with a thickness of the free FM layer, ranging from 0.8 to 2.0 nm. Figure 5.6 shows the magnetic results obtained from VSM. For the in-plane applied field, the saturation of the magnetic moment is achieved in both directions, which translates a complete rotation of the three FM layers towards the direction of the applied field. In contrast with the previous results depicted in Fig. 5.4, an IMA-PMA transition is achieved. Figure 5.7 shows PMA obtained for a 1.3 and 1.4 nm FM layers with a coercive field of (13.3 ± 0.3) and (18.8 ± 0.6) Oe, respectively. For $t_{\text{CoFeB}} = 1.2$ nm, the remanent magnetic moment is negligible for both measurements, thus showing a similar behaviour as demonstrated in Fig. 5.5. Although obtained for a different stack structure, these results can be compared with the results obtained for a bottom FM layer (Fig. 5.2). It is observed that the IMA-PMA transition occurs for a different thickness (1.0 nm for a bottom and 1.4 nm for a top FM layer), depending on the position of the FM layer. Thus, the fabrication of MTJs with PMA in both FM layers must be optimized by choosing the proper thickness for a specific FM layer, taking into account its position in the MTJ structure.

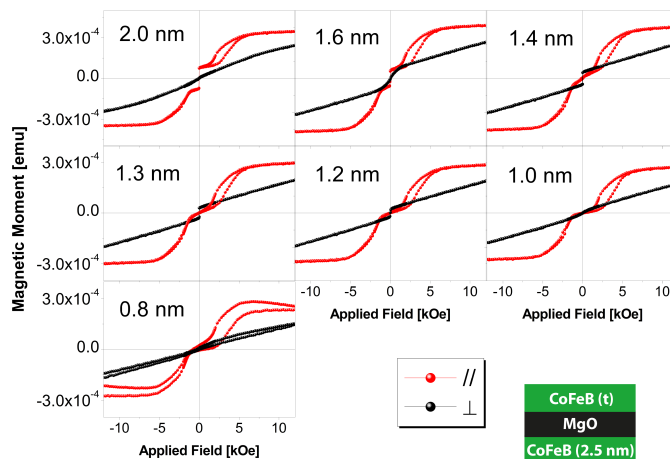


Figure 5.6: VSM results obtained for stack structures as depicted in Fig. 5.1(c). Each graph highlights the thickness of the FM layer and the results were obtained with in-plane (//) and out-of-plane ($\perp$) applied magnetic field.

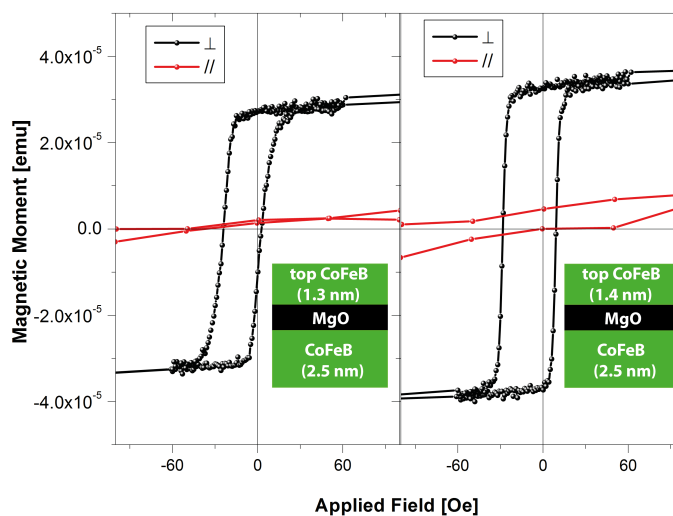


Figure 5.7: Amplified view for the magnetic results presented in Fig. 5.6 where PMA was achieved for the free FM layer.

5.1.2 Effect of the annealing treatment

In addition to the fourteen samples whose results were presented in Figs. 5.2 (CoFeB/MgO-based stack) and 5.4 (MgO/CoFeB-based stack), a similar group of fourteen samples was deposited at the same time. For these samples, the annealing process was not performed. Thus, one aims to study the effect of the annealing treatment on the magnetic properties of the FM layer. Specifically, two physical quantities are studied: the magnetic dead layer and the effective anisotropy constant. For the latter, the analysis was not performed for MgO/CoFeB-based nanostructures [Fig. 5.1(b)] because, as already referred in section 5.1.1, the IMA-PMA transition was not accomplished for the annealed samples (a similar behaviour was obtained for the as-deposited samples). Many reports present results that highlight significant changes of the MTJ properties in the annealing temperature range between 300 and 400 °C, namely a decrease of the TMR ratio [38] and K_{eff} [96, 97]. Thus, after the annealing performed at 300 °C in the CoFeB/MgO-based nanostructures, the same set of samples was used to perform a second annealing treatment at 330 °C for 1 hour with an in-plane applied magnetic field of 1 T.

The effective anisotropy constant is calculated from Eq. (2.13) where $K_{\text{eff}} = (M_S H_{\text{eff}})/2$. Both M_S and H_{eff} are obtained from the magnetic results. The intersection between both loops (with in-plane and out-of-plane applied magnetic fields) gives H_{eff} . In the case of M_S , it is mandatory to know the volume of the FM layer, in order to calculate M_S from the saturation magnetic moment obtained from the magnetic results. Figure 5.8 shows the saturation magnetic moment per unit area obtained for the as-deposited and annealed CoFeB/MgO-based nanostructures. A linear fit can be performed to the experimental data, based on [41]:

$$\frac{m_S}{A} = M_S \cdot (t - t_d), \quad (5.2)$$

where m_S is the saturation magnetic moment, A the area of the FM layer, M_S the saturation magnetization and $(t - t_d)$ the difference between the nominal thickness (t) and the thickness of the dead layer (t_d). The linear fit highlights the existence of a dead layer [98, 99] which does not contribute to the magnetization of the FM layer. For 300 °C, it is clear that the annealing treatment decreases the thickness of the dead layer

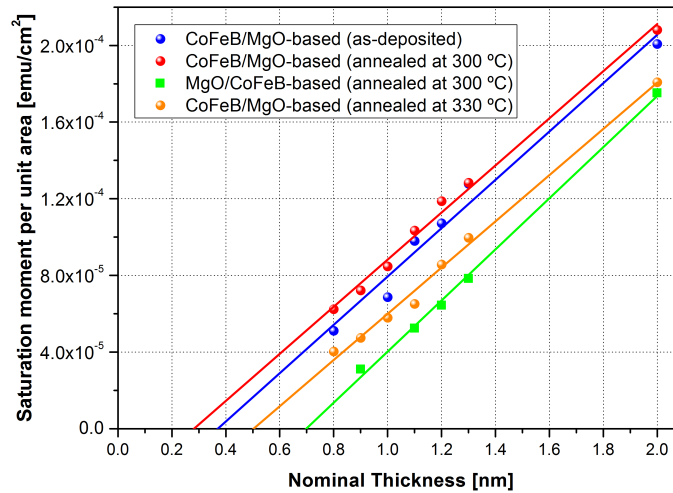


Figure 5.8: Saturation magnetic moment per unit area as a function of the nominal thickness of the FM layer. These results were obtained for the as-deposited (blue) and annealed (red at 300 °C and orange at 330 °C) CoFeB/MgO-based [Fig. 5.1(a)] and annealed (green) MgO/CoFeB-based [Fig. 5.1(b)] nanostructures.

- from (0.40 ± 0.08) nm to (0.28 ± 0.04) nm, which is a decrease of 30%. Although some reports [63, 64] suggest that an annealing treatment promotes the Ta diffusion through the CoFeB FM layer, these results show that the annealing conditions chosen in this case (300 °C for 1 hour) improve the CoFeB interfaces, which is translated by the decrease of the dead layer. Nevertheless, when the same samples are annealed at 330 °C, there is an increase of the dead layer to (0.50 ± 0.04) nm. In addition, Fig. 5.8 shows the saturation magnetic moment per unit area obtained for the annealed MgO/CoFeB-based nanostructures. From the linear fit, results a dead layer of (0.70 ± 0.04) nm, which is larger than any of the values obtained for the samples with a bottom FM layer. Taking into account that no IMA-PMA transition was achieved for the MgO/CoFeB-based samples, the existence of a thicker dead layer can possibly be one of the reasons for the transition absence. In fact, as discussed in section 2.2.2, PMA is a consequence of a surface effect that results from the increase of the surface anisotropy contribution as the thickness of the FM decreases [see Eq. (2.5)], so the increase of the dead layer can possibly be associated with a decrease of the surface crystalline anisotropy constant and a degradation of the MgO/CoFeB interface. Moreover, a larger dead layer increases the nominal thickness at which the transition for the SPM state occurs. This fact can explain why for a CoFeB/MgO-based sample, PMA is still present for a nominal thickness of 0.8 nm (Fig. 5.3) and for a MgO/CoFeB-based sample, the SPM state is already present for a nominal thickness of 1.3 nm (Fig. 5.5).

The volume of the FM layer is calculated by using the effective thickness, $t_{\text{eff}} = t - t_d$. Finally, Fig. 5.9 shows the $K_{\text{eff}} \cdot t_{\text{eff}}$ product as a function of the effective thickness, where the same comparison between as-deposited and annealed CoFeB/MgO-based samples is made. For both sets of samples, the IMA-PMA transition is accomplished, as proved by the sign change of the $K_{\text{eff}} \cdot t_{\text{eff}}$ product. Rewriting Eq. (2.13) results in:

$$K_{\text{eff}} \cdot t_{\text{eff}} = (K_V - 2\pi M_S^2) \cdot t_{\text{eff}} + (K_S^{\text{Ta}} + K_S^{\text{MgO}}). \quad (5.3)$$

The linear fit allows to conclude that the annealing treatment at 300 °C improves the magnetic properties of

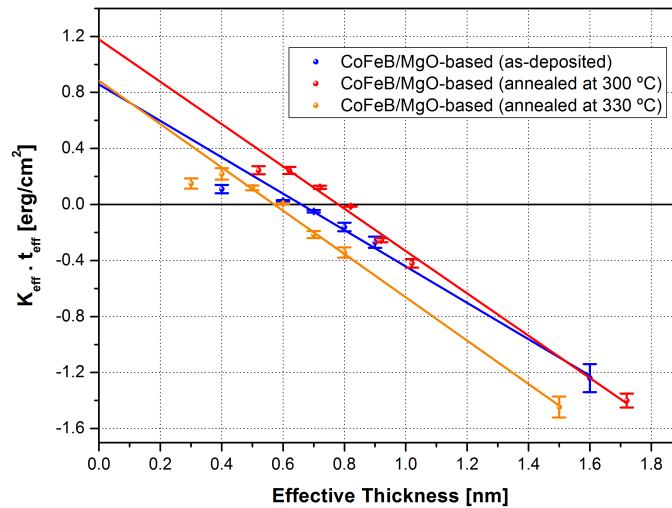


Figure 5.9: $K_{\text{eff}} \cdot t_{\text{CoFeB}}$ product as a function of the effective thickness of the FM layer. These results were obtained for the samples with the stack depicted in Fig. 5.1(a). K_{eff} refers to the effective anisotropy constant and t_{CoFeB} to the effective thickness of the FM layer.

the FM layer by increasing the surface crystalline anisotropy constant (here defined as the sum $K_S^{\text{Ta}} + K_S^{\text{MgO}}$), from $(0.85 \pm 0.05) \text{ erg/cm}^2$ to $(1.18 \pm 0.06) \text{ erg/cm}^2$. It should be noted that in all linear fits of Fig. 5.9, the numerical result obtained for the smallest effective thickness was not considered as a fitting point. In fact, the deviation from the linear fit presented for the same points is also present in similar reports [39, 40, 42, 62]. This sudden deviation towards a progressive decrease of K_{eff} is widely justified as a consequence of the onset of the SPM state that the FM layer starts to present [62]. Nevertheless, for the set of annealed samples, the increase of the coercive field verified for the smaller thicknesses (see inset of Fig. 5.3) proves that the SPM state is still not presented in the FM layer. The results obtained for an annealing treatment at 330°C allow to make a direct relation between the increase of the dead layer and the decrease of K_S [from $(1.18 \pm 0.06) \text{ erg/cm}^2$ at 300°C to $(0.88 \pm 0.03) \text{ erg/cm}^2$ at 330°C], thus supporting the assumption used above to justify the IMA-PMA transition absence in the MgO/CoFeB-based nanostructures.

5.1.3 Conclusion

For two similar stack structures, PMA was achieved (IMA-PMA transition for $t_{\text{CoFeB}} = 1.0 \text{ nm}$) for a bottom CoFeB FM layer [Fig. 5.1(a)], but not for a top FM layer [Fig. 5.1(b)], where a direct IMA-SPM transition is obtained for $t_{\text{CoFeB}} = 1.3 \text{ nm}$. The IMA-PMA transition was only obtained for a complete MTJ structure [Fig. 5.1(c)] for $t_{\text{CoFeB}} = 1.4 \text{ nm}$, proving that the PMA induction depends, not only on the FM layer thickness, but also on its position in the stack structure. Moreover, a comparison between as-deposited and annealed CoFeB/MgO-based stack structures [Fig. 5.1(a)] was performed. After annealing at 300°C , the magnetic results show a decrease of the magnetic dead layer and an increase of the surface crystalline anisotropy constant, thus favouring PMA for smaller thicknesses. For an annealing temperature of 330°C , a degradation of PMA is observed, thus showing a direct relation between the increase of the FM dead layer and the decrease of K_S .

5.2 Bias voltage effect study in MTJs

Here, following the discussion presented in section 2.4, a qualitative study of the bias voltage (V_{bias}) effect in CoFeB/MgO/CoFeB-based MTJs is performed. The samples used in this analysis were not fabricated for this purpose. Instead, the study was performed in patterned MTJs, previously fabricated in INL for Spin Hall Effect studies [100]. Specifically, $\text{Ta}(50) / \text{CoFe}_{40}\text{B}_{20}(1.2) / \text{MgO}(3.0 \text{ nm}) / \text{CoFe}_{40}\text{B}_{20}(2.2) / \text{Ru}(0.85) / \text{CoFe}_{30}(2) / \text{IrMn}(20) / \text{Ru}(45) / \text{Cu}(100) / \text{Ru}(30)$ elliptical shaped nanopillars were patterned by e-beam lithography, with areas ranging from $40 \times 60 \text{ nm}^2$ to $200 \times 600 \text{ nm}^2$. The stack structure was deposited with an inverted SAF structure, which means that the free FM layer is deposited below the insulating barrier.

The electrical measurements were obtained using the four-probe method in a semi-automatic probe

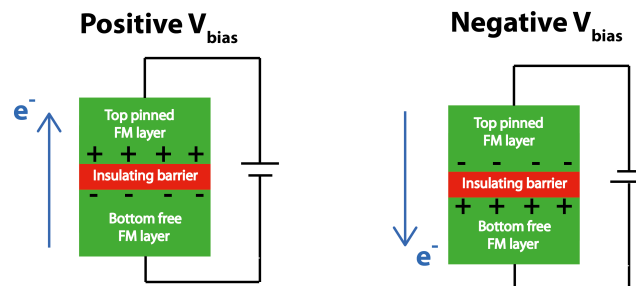


Figure 5.10: Illustration of the configuration used in the electrical measurements.

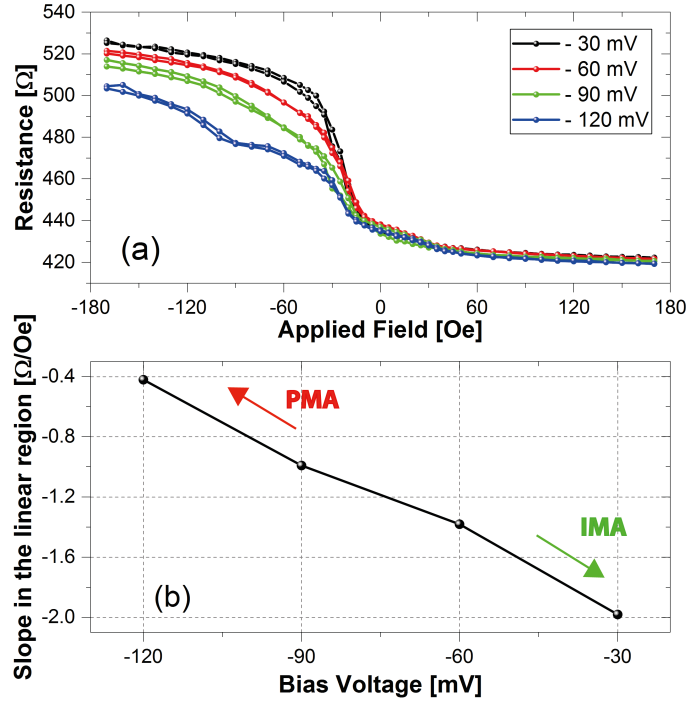


Figure 5.11: (a) Electrical measurements obtained for negative V_{bias} in a $50 \times 110 \text{ nm}^2$ MTJ. (b) Slope in the linear region obtained for different negative V_{bias} . The increase of the absolute value of V_{bias} is followed by a decrease of the absolute value of the R-H curve slope in the transition region, which favours PMA.

station with an in-plane applied magnetic field. As depicted in Fig. 5.10, a positive V_{bias} corresponds to the tunneling of electrons from the bottom to the top FM layer. In general, the R-H curves present two distinct behaviours, depending on the sign of V_{bias} . Figure 5.11(a) shows the electrical results obtained for a $50 \times 110 \text{ nm}^2$ MTJ, where negative V_{bias} were applied. For negative V_{bias} , the increase of its absolute value goes with an effective change of the R-H curve slope in the transition between anti-parallel (high resistance) and parallel (low resistance) magnetic states [Fig. 5.11(b)]. In other words, as one increases V_{bias} , it becomes more difficult to rotate the free FM layer - this fact translates a change of the easy axis away from the in-plane direction. In the configuration used, a negative V_{bias} corresponds to the depletion of electrons in the interface between the bottom FM layer and the MgO barrier (Fig. 5.10), so the depletion of electrons in the interface is directly related with an increase of the surface crystalline anisotropy constant, which favours PMA. This result is in complete accordance with scientific reports already published [44, 70, 101]. For positive V_{bias} [Fig. 5.12(a)], the results show a progressive appearance of an intermediate magnetic state, clear for $V_{\text{bias}} = 150 \text{ mV}$ in Fig. 5.12(b). This intermediate state is represented by a plateau that extends itself in an applied field domain of $\sim 30 \text{ Oe}$. Moreover, that domain includes the zero applied field, which proves that a $V_{\text{bias}} = 150 \text{ mV}$ induces an intermediate magnetic state by itself, without the requirement of an applied field. From Eq. (1.1), results an angle around 106° between magnetizations [see the trilayer structures of Fig. 5.12(b)]. Unlike other reports [44, 102], the range of V_{bias} used was very small, which can be justified by the small thickness of the MgO barrier ($\text{RA} = 3.0 \Omega \mu\text{m}^2$). In general, the breakdown of the insulating barrier was achieved for the range $150 \text{ mV} < |V_{\text{bias}}| < 200 \text{ mV}$.

The measurements were performed in a die with more than one thousand patterned MTJs. Thus, it is

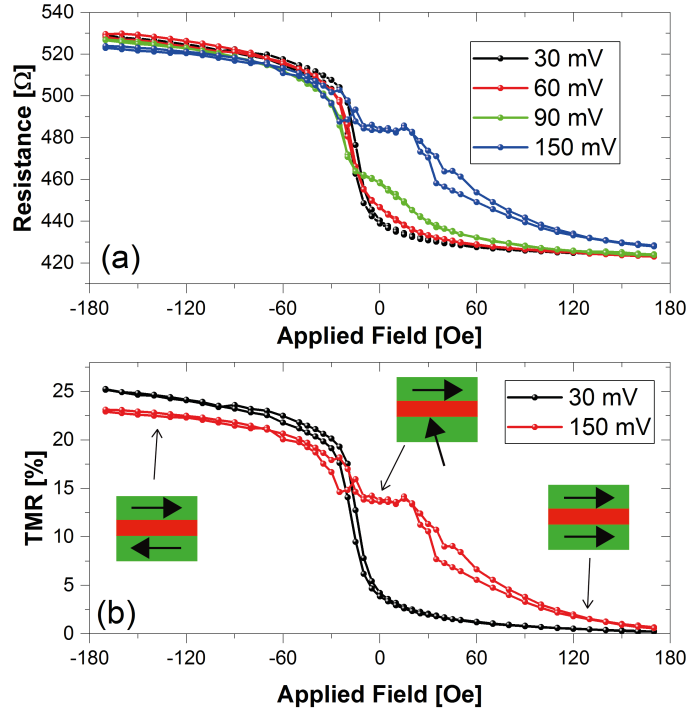


Figure 5.12: (a) Electrical measurements obtained for positive V_{bias} in a $50 \times 110 \text{ nm}^2$ MTJ. (b) Comparison between the electrical results obtained for two positive V_{bias} . The intermediate magnetic state is present for $V_{\text{bias}} = 150 \text{ mV}$. The trilayer structures illustrate the magnetic configuration of the CoFeB/MgO/CoFeB fundamental stack for the red loop. In the plateau region, the trilayer structure shows an angle of 106° between magnetizations.

worth to mention the reason why only results of one MTJ were presented. As already referred, the MTJs were patterned at nanometric scale, which is the same order of magnitude of the grains that constitute the polycrystalline unpatterned wafer. After the lithography process, one obtains individual nanopillars, each one constituted by a few grains. Being all grains different from each other, different nanopillars will present different characteristics. This effect is attenuated in MTJs patterned at micrometric scale, because the area of an individual nanopillar is much larger than the grain size of the polycrystalline unpatterned wafer. Although not shown, the electrical results obtained for other patterned MTJs of the die prove the heterogeneous physical behaviour of the different R-H curves. This is the main reason why the results presented in Figs. 5.11 and 5.12 could only be clearly obtained in one sample.

In summary, using the four-probe method, electrical measurements were performed in a patterned $50 \times 110 \text{ nm}^2$ MTJ under different V_{bias} for both polarities. For negative V_{bias} , a change of the easy axis of the free FM layer is clear from the change of the R-H curve slope in the transition between anti-parallel and parallel magnetic states. This behaviour translates a change of the easy axis towards out-of-plane (in Fig. 5.11 the magnetic field is applied in-plane). For positive V_{bias} , a clear intermediate magnetic state appears for $V_{\text{bias}} = 150 \text{ mV}$ near zero field, which proves its maintenance in the absence of applied field.

Chapter 6

Conclusion and future work

MTJs with a crystalline MgO barrier have already proven their superior performance for memory applications. Now, the main issue lies in decreasing the necessary energy to make each MTJ element functional, while maintaining a sufficiently large thermal stability. Moreover, for the deposition of a ultra-thin MgO barrier, it is mandatory to optimize the deposition of the MTJ stack, mainly by decreasing the roughness of the stack that is deposited below the insulating barrier. Without reaching these milestones, MTJs cannot be a viable alternative to CMOS structures [55]. In this thesis, three independent experimental studies were performed towards the optimization of the magnetic properties and fabrication of CoFeB/MgO/CoFeB-based MTJs.

Optimization of the buffer surface by ion beam milling The main novelty brought by this thesis was the roughness optimization process of the buffer surface. The smoothing process performed by ion beam milling proved to decrease the roughness of the Ru surface and improve the TMR ratio of the final MTJ. In the future, to clarify the effect of the smoothing process, one possibility is to perform the same process to an MTJ with a deposited MgO wedge. By CIPT measurements in different wafer positions, it is possible to obtain the TMR ratio as a function of the RA product which is a parameter that was not varied in the experimental work. Comparing the TMR(RA) curves for samples with and without smoothing treatment can give a more general view about the effect of the same.

Thickness dependence study towards PMA in both active FM layers. Following the advantages presented by MTJs with PMA in both FM layers, magnetic measurements were performed in CoFeB/MgO and MgO/CoFeB-based stack structures, where the thickness of the top/bottom FM layer was varied in a specific range. The results show a IMA-PMA transition for the bottom and a IMA-SPM transition for the top FM layer. The different results are justified by the effect of the ultra-thin MgO barrier on the growth of the FM layer above. As a future work and for a better insight, morphologic studies should be performed to the MgO barrier (e.g transmission electron microscopy), in order to verify the conclusion referred above. For a top FM layer, the IMA-PMA transition was only achieved in a full MTJ stack, but for a different thickness (1.4 nm) when compared with the transition for the bottom FM layer in the CoFeB/MgO-based stack (1.0 nm). Thus, the results prove that not only the thickness, but also the position of the FM layer play an important role in defining the magnetic properties. Moreover, the effect of the annealing treatment was quantified in the comparison between as-deposited and annealed CoFeB/MgO-based stack structures. For annealed samples (300 °C), the magnetic results show a decrease of 30% for the thickness of the dead layer and an increase of 39% for the surface crystalline anisotropy constant. To clarify the physical phenomenon behind such results, spectroscopy measurements (e.g energy dispersive spectroscopy) should be made in

the future. Depth profiles through the nanostructures are extremely helpful to highlight possible material diffusions between layers. The final step would be to fabricate and characterize an MTJ with PMA in both FM layers, taking into account the information obtained from the study of individual bottom and top FM layers.

Bias voltage effect. More recently, the effect of the bias voltage proved to be a possible way to reduce the switching energy by changing the magnetic properties of the free layer, namely reducing its coercive field. Thus, electrical measurements were performed in patterned MTJs at different V_{bias} . For negative V_{bias} , a clear change of the easy axis (towards out-of-plane) is visible as the absolute value of V_{bias} increases. For positive V_{bias} , an interesting intermediate magnetic state is induced for $V_{\text{bias}} = 150$ mV, with a near out-of-plane magnetization for the free FM layer.

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Appendix A

Deposition conditions

Material	Thickness (nm)	Number of cyclical paths	Velocity of the substrate (mm/s)	Power (kW)	Ar Flow (sccm)	N ₂ Flow (sccm)
Ta	5	2	95	1.1	300	0
	10	2	48	1.1	300	0
	50	8	38	1.1	300	0
Ru	0.85	1	219	0.6	300	0
	5	2	74	0.6	300	0
	7	2	53	0.6	300	0
	20	4	37	0.6	300	0
	45	8	33	0.6	300	0
	400	54	25	0.6	300	0
Cu	100	10	60	1.1	300	0
Al ₂ O ₃	100	75	20	1.5	200	0
CuN	30	2	93	3	270	30
	50	2	56	3	270	30
PtMn	20	4	24	0.35	600	0
IrMn	20	1	47	2.6	300	0
CoFe ₃₀	2	2	62	0.35	300	0
CoFe ₄₀ B ₂₀	0.8	2	161	0.4	300	0
	0.9	2	146	0.4	300	0
	1.0	2	131	0.4	300	0
	1.1	2	119	0.4	300	0
	1.2	2	109	0.4	300	0
	1.3	2	101	0.4	300	0
	1.4	2	94	0.4	300	0
	1.6	2	82	0.4	300	0
	2.0	2	66	0.4	300	0
	2.2	2	60	0.4	300	0
	2.5	2	53	0.4	300	0

Material	RA ($\Omega\mu\text{m}^2$)	Number of cyclical paths	Velocity of the substrate (mm/s)	Power (kW)	Ar Flow (sccm)
MgO	2.0	2	95	3	600
	3.0	2	90	3	600
	7.9	2	75	3	600