D2.4 Report on the best materials

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MAGWIRE

Magnetic Nanowires for High Density Non Volatile Memories

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Dissemination level

PU	☒	Public
PP	☐	Restricted to other programme participants (including the Commission Services)
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CO	☐	Confidential, only of the members of the Consortium (including the Commission Services)

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1. Introduction

In order to address the problems faced by Hard Disk Drive (HDD) and Flash memories, the basic requirement for the storage track concept is to control via a CMOS driver the dynamics of large arrays of Domain Walls (DWs) to be moved synchronously under current along a nanoscale wire made of high quality magnetic **materials** with lateral widths below 32 nm (Figure 1). Precise prerequisites for such technology include control of DW nucleation (**writing**) at one position of the track, stable pinning (**storing)** of the walls at regularly spaced traps, synchronous **shifting** of the walls under current, and **reading** of the walls and domains at another position of the wire. Thus, as for the HDD technology, the storage track concept implies several building blocks that need to evolve successfully in parallel.

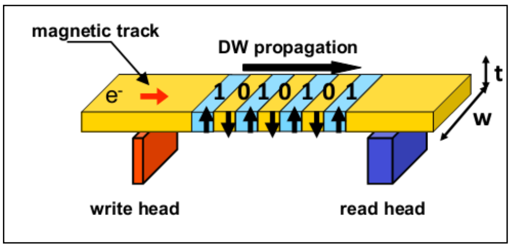

Figure 1. *The race track Memory concept*

Particularly, one important objective of the MAGWIRE project has been to develop materials with perpendicular magnetic anisotropy (PMA) that are compatible with the writing/storing/shifting/reading schemes. This is the most important task of Workpackage 2 (WP2).

As decided at month 12 (see D2.2), the best system to be further developed and investigated by WP2, is magnetic tunnel junctions based on CoFeB-MgO materials. This decision has been motivated by the favorable domain wall motion mechanism obtained in annealed Ta-CoFeB-MgO stack deposited on top of Si/SiO_2 substrates with Ta buffer layer. This choice has led to the proposition of a targeted demonstrator as indicated in Figure 2. The bottom CoFeB based layer (top CoFeB based layer) of the MTJ corresponds to the free layer (hard layer) respectively. The reading scheme is performed through Tunnel Magnetoresistance (TMR) measurement and the writing scheme uses spin transfer torque (STT) to create domain walls. The consortium also decided to use alternatively a writing scheme based on the generation of local Oe field using a current flowing in an electrode going onto the wire.

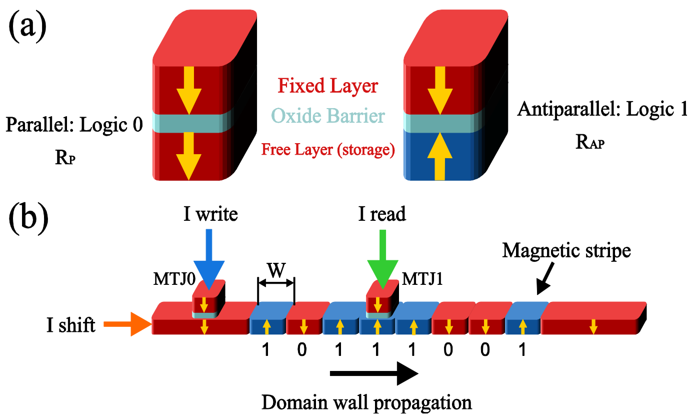

Figure 2*: Design of the prototype based on DW motion in CoFeB based MTJs (or spin valves) with PMA. A current perpendicular to plane is used for the writing and reading schemes.*

This document, namely the Deliverable D2.4 focuses on the development of CoFeB-MgO based material that will be used in the demonstrator. The material has been definitively validated at M18 through complementary measurements performed during the period M12-M18 :

- (1) High quality CoFeB-MgO materials with perpendicular anisotropy and ultra low propagation fields <10 Oe have been developed for different stochiometries;
- (2) Bottom and free CoFeB layers integrated in Magnetic Tunnel junctions have been developed with good TMR properties;
- (3) Magnetic anisotropy of CoFeB-MgO films can be controlled under ion irradiation for the storing scheme (see D3.4 for storing schemes);
- (4) CoFeB-MgO films grown on top of 8” CMOS wafers with different surface treatments have been developed for manufacturability issues; PMA has been confirmed on top of treated CMOS substrates, on large scale, and high PMA values has been measured, comparable to those obtained on top of standard Si/SiO2 substrates (see D2.3 for manufacturability issues).

Section 2 describes in details the best achievements (points 1 and 2 above) of WP2 related to the development of CoFeB-MgO based structures that will be used in the demonstrator.

2. Properties of Ta-CoFeB-MgO stacks

We remember here that the strategy of the WP2 in the first 12 months of the project exploitation has been directed towards the development of CoFeB-based systems with both high PMA and showing DW motion at reduced propagation fields (<100 Oe) and with a low distribution of intrinsic pinning defects on large scales (200-300mm).

The developed films have to be compatible with tunnel junction for the writing and reading schemes, so the base structure must be **F1-CoFeB-MgO-CoFeB-F2,** where F1 and F2 can be a magnetic material or a non-magnetic metal or oxide. It is very important to note here that **PMA in CoFeB can be obtained only by interface anisotropy**, therefore the choice of F1 and F2 is very important. In order to be compatible with the design shown in Figure 2, F1-CoFeB must correspond to the free layer. **During the first year of the project, we have shown that the best free layer corresponds to Ta-CoFeB (see deliverable D2.2)**. Further structural characterizations and new structures have been developed from M12 to M18 as described below.

2.1. Structural characterizations

In order to refine the XRR/XRD study on single stacks previously reported in D2.2, *ad hoc* $Co_{60}Fe_{20}B_{20}$ based superlattices have been deposited, as listed in the following table (**Table I**). Particularly, the repetition of unit cells can give additional insight on the structural interfaces properties.

ID	BLANKET Substrates	layers stack [thickness in nm]
6560	2 x (1/2) therm. ox. 4" Si Wafer	/ 5 Ta/ [1.0 CoFeB/2 MgO] x 30 /5 Ta
6562	2 x (1/2) therm. ox. 4" Si Wafer	/ [5 Ta/ 1. 0 CoFeB/ 2 MgO] x 30 / 5 Ta
6567	2 x (1/2) therm. ox. 4" Si Wafer	/ [5 Ta/ 1.0 CoFeB] x 30 / 5 Ta
6568	2 x (1/2) therm. ox. 4" Si Wafer	[5 Ta/ 1. 0 CoFeB/ 2 MgO] x 30 / 5 Ta
6569	2 x (1/2) therm. ox. 4" Si Wafer	/ 5 Ta/[1 Ru/ 1.0 CoFeB] x 30 / 5 Ta

***Table I** – List of the samples investigated by XRR/XRD*

Depending on the sample, only 2 layers, or the complete trilayered stack, have been replicated for 30 repetitions, with the aim to focus the investigation on a specific interface and layer coupling. By studying simplified stacks, and considering the results obtained for each stack, a clear evidence of the contribution from each layer/material can be inferred by considering the respective XRD patterns. The information extracted with this methodology would help in complementing, better clarifying and sustaining the results obtained on single stack, reported in deliverable D2.2 at month 12. In addition to the samples listed in **Table I**, specific TEM investigations have been addressed to a detailed study of Ta/CoFeB/MgO/Ta single stacks.

All the stacks and superlattices were characterized before and after the annealing at 300°C for 2h. The superlattices analysis allowed distinguishing the contribution to the diffraction pattern from the different layered stacks. **Figure 3** summarizes the results obtained on superlattices mimicking the stacks including Ru or Ta as buffer layer. The main difference is due to the different degree of crystallinity of the layers, which is poor when Ru is included, while is more pronounced when Ta layer inserted in the stacks.

Among the observed features, it is of relevance to note that in structure with Ru, CoFeB (110) and MgO (200) reflections are only observed, while in structures including Ta, the CoFeB (200) and MgO (220) reflections are also observed. Further, a contribution from Ta (211) is also observed; despite the main Ta orientation seems to be Ta (110). As a consequence, in superlattices including Ta as buffer layer, Ta(110) // MgO (220) in-plane and CoFeB (200) // MgO (200) out-of-plane relationship seems to co-exist. These relationships could be ultimately relevant in promoting/stabilizing the perpendicular magnetic anisotropy in CoFeB.

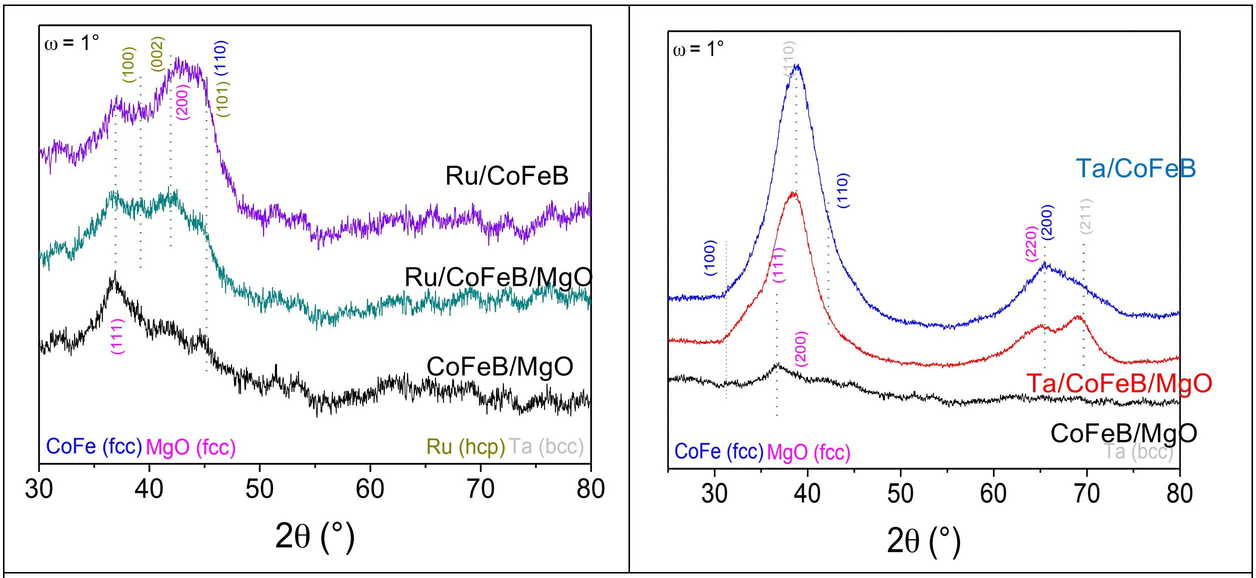

***Figure 3** – XRD patterns of annealed superlattices including Ru (left) or Ta (right) as buffer layer.*

With the aim to in-depth understanding the structure of thin CoFeB, MgO, and Ta layers and of their interfaces, **Transmission Eletcron Microscopy (TEM)** cross sections have been investigated considering the stack Si/SiO_2/Ta(5)/CoFeB(1)/MgO(2)/Ta(5) (nominal thickness in nm), before and after annealing at 300°C for 2h. Measurements have been taken using a JEOL 2200 FEG instrument (200 keV primary column) capable of a point resolution in High Resolution (HR) mode of 0.19 nm.

Figure 4 below shows TEM cross section of the stacks before (left) and after (right) annealing, with identification of the single layers and the direction of the ion milling used for the thin section preparation. XRR thickness (reported in D2.2) are confirmed, including the Ta_2O_5 layer forming due to Ta exposure to the air. Here it is worth to point out that the preparation process seems to partially affect the stack integrity. In particular, the thin CoFeB layer is heavily compromised, because of the adjacent Ta layers, which heavy atoms are forced inside CoFeB during the ion milling procedure. Further, being Ta highly absorbing (i.e. dark in the images), image contrast at Ta/CoFeB is difficult to achieve and impedes a clear identification of the interface.

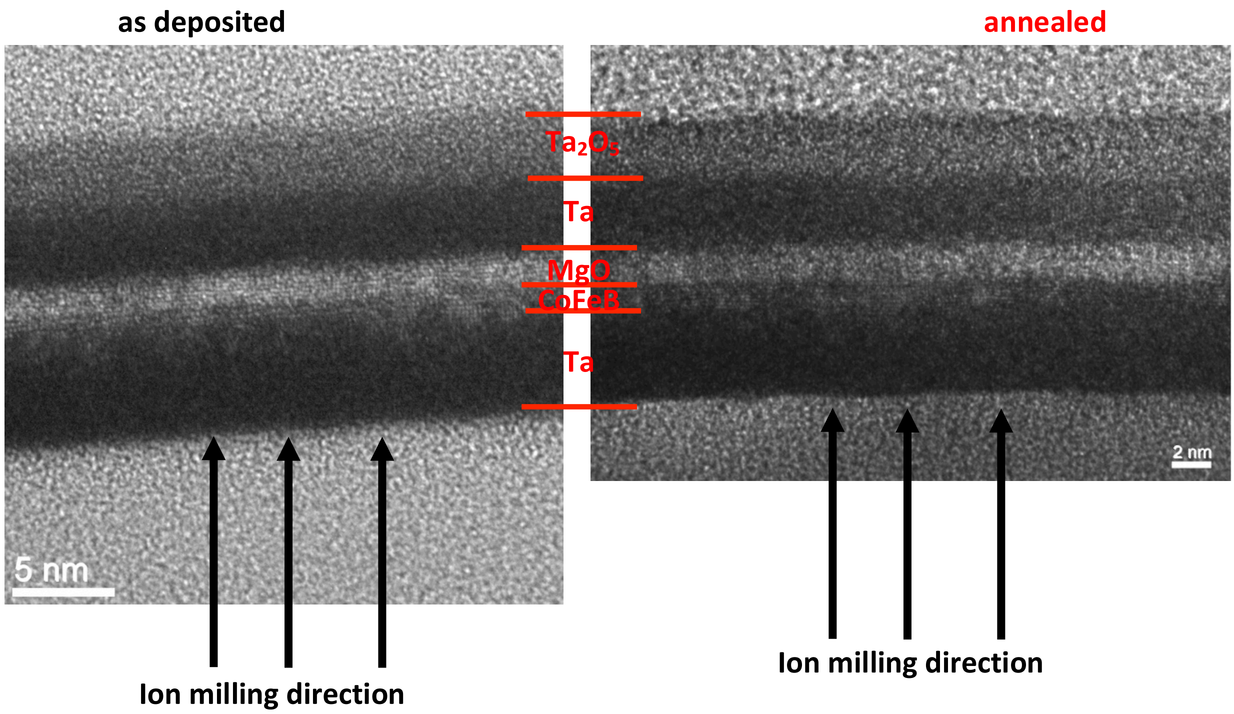

***Figure 4** – TEM cross section of Ta(5)/CoFeB(1)/MgO(2)/Ta(5) stack, before and after annealing.*

More in detail, when considering the sample before annealing, the difficult identification of the CoFeB layer is visible in the HR-TEM image in **Figure 5a**. Nevertheless, by sampling the intensity profile along the sample thickness of many HR-TEM sections is possible to identify a region of the sample, around 1nm thick, where a systematic increase of the intensity is revealed, which well corresponds to the CoFeB layer. **Figure 5a** shows the intensity profile taken along the region inside the box drawn in **Figure 5b** and the dashed red lines indicate the correspondent region associated with CoFeB layer in the intensity profile and in the cross section image.

A similar result is visible when considering the annealed sample, which intensity profile and HR-TEM are shown in **Figure 5c and 5d**, respectively. Again, the intensity profile taken along the region indicated by the solid red line drawn in the HR-TEM image evidences a modulation in the intensity profile in correspondence to the area in the image where CoFeB layer is expected (marked with green dashed lines).

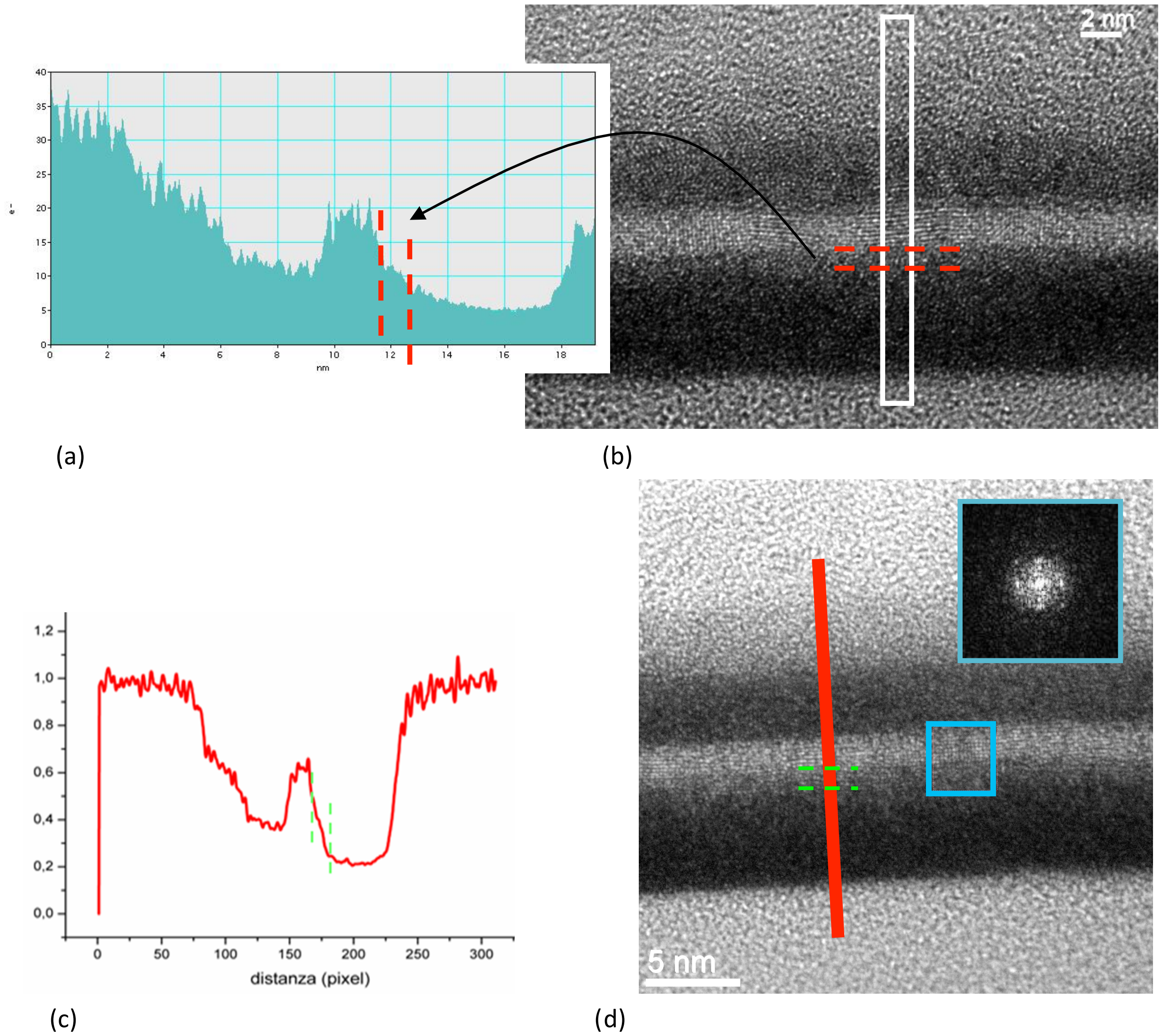

***Figure 5** – HR-TEM cross section (right) and intensity profile (left) of Ta/CoFeB/MgO/Ta stacks before (a,b) and after (c,d) annealing.*

When considering the electron diffraction patterns, the results are similar for samples before and after annealing, within the technical limits mentioned previously. Considering the sample before annealing (**Figure 6a**), and focusing on the MgO layer, namely in the region marked by the square with green borders, a cubic crystalline structure is evident. At high magnification (**Figure 6b**), bright spot belonging to **MgO (002)** direction are well identified, enabling the calculation of a **spacing d = 0.21 nm**. Further, when looking at the dark region corresponding to the Ta (bottom) layer and, in particular, focusing on the region identified by the square with red borders, despite the poor image contrast, it is possible to discriminate a certain degree of crystalline ordering within an amorphous environment. It should be here recalled that Ta amorphization may be induced by the ion milling during the preparation of the thin section. Nonetheless, when looking at high magnification (**Figure 6c**) spots and rings with enhanced intensity corresponding to **Ta (110)** direction can be detected, giving a spacing **d=0.233 nm**.

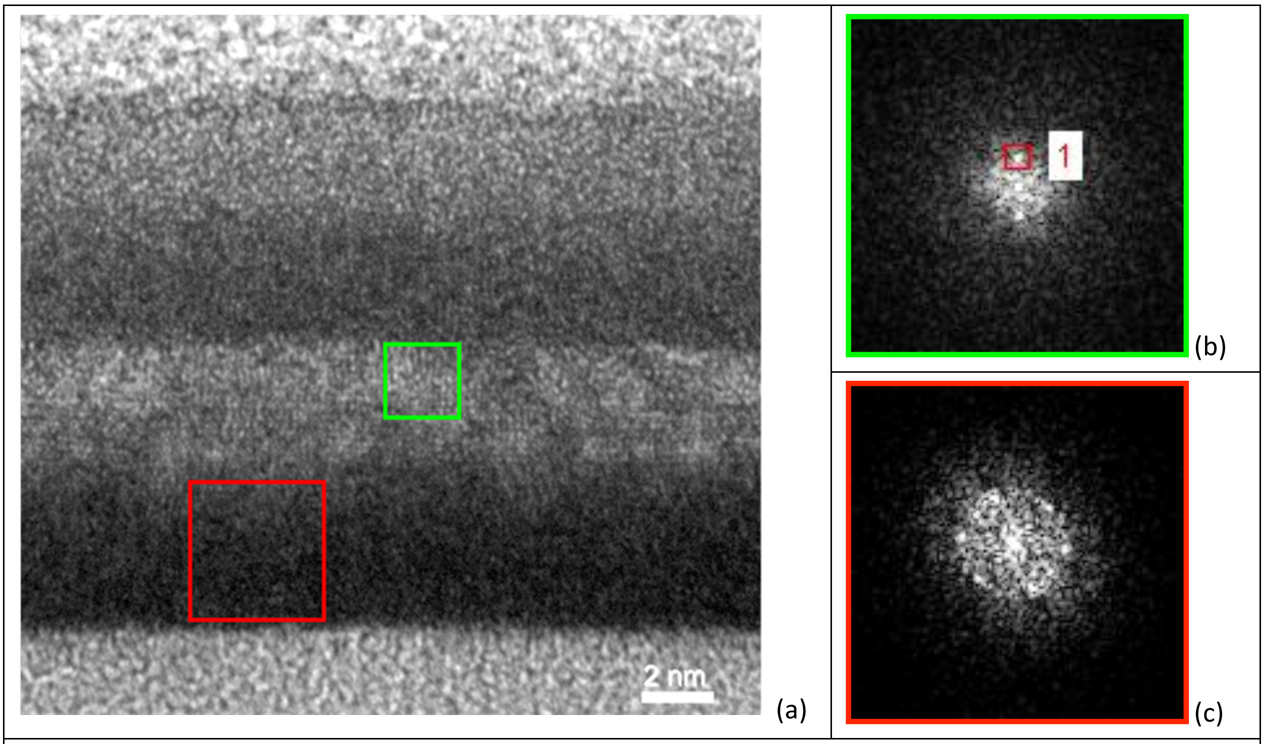

Figure 6 *– HR-TEM (a) cross section of Ta/CoFeB/MgO/Ta stack before annealing. Diffractograms from MgO (b) and Ta (c) of the regions identified by green and red boxes in (a), respectively.*

Despite a clear, direct, investigation of the CoFeB layer crystalline structure is difficult, due to the above mentioned limitations, a tentative structural analysis has been acquired focusing on the region where the modulation in the intensity profile is observed. The so calculated spacing are 0.21 along the (001) direction and 0.235 along the interface (i.e. (110) direction), values which are fully compatible with the spacing values calculated for MgO (002) and Ta (110) respectively. **Thus we can conclude that CoFeB, being a very thin layer, when crystallizes, accommodates the lattice parameters of the adjacent materials.**

Finally, it is worth mentioning that the results obtained from TEM structural analysis are in agreement with the findings from XRD analysis done on the same stacks (see D2.2) and on equivalent superlattices.

2.2 Magnetic properties of Ta-CoFeB-MgO stacks

We have investigated the magnetic properties of 3 different CoFeB compositions, namely $Co_{20}Fe_{60}B_{20}$, $Co_{40}Fe_{40}B_{20}$ and $Co_{60}Fe_{20}B_{20}$, in order to determine the best properties in terms of DW motion. The full structure consists of Ta(3nm)-CoFeB(1nm)-MgO(2nm)-Ta(3nm). In deliverable D2.2 at M12, only the composition $Co_{60}Fe_{20}B_{20}$ was included. Hysteresis loops are shown in **Figure 7** for both the as deposited state and after annealing at 300°C for 2 hours. Note that only the $Co_{40}Fe_{40}B_{20}$ composition shows perpendicular anisotropy without annealing (amorphous state). The presence of PMA after annealing is consistent with an increase of the CoFeB-MgO interface anisotropy due to the crystallization of the CoFeB layer in the bcc (001) phase. As measured by angular dependence, the typical effective field and uniaxial anisotropy values for the 3 different alloys are about H_k=100 mT and K_u=2-3. x 10^7 erg/cm^3 respectively, which is comparable to conventional Co/Pt and Co/Ni multilayers with PMA.

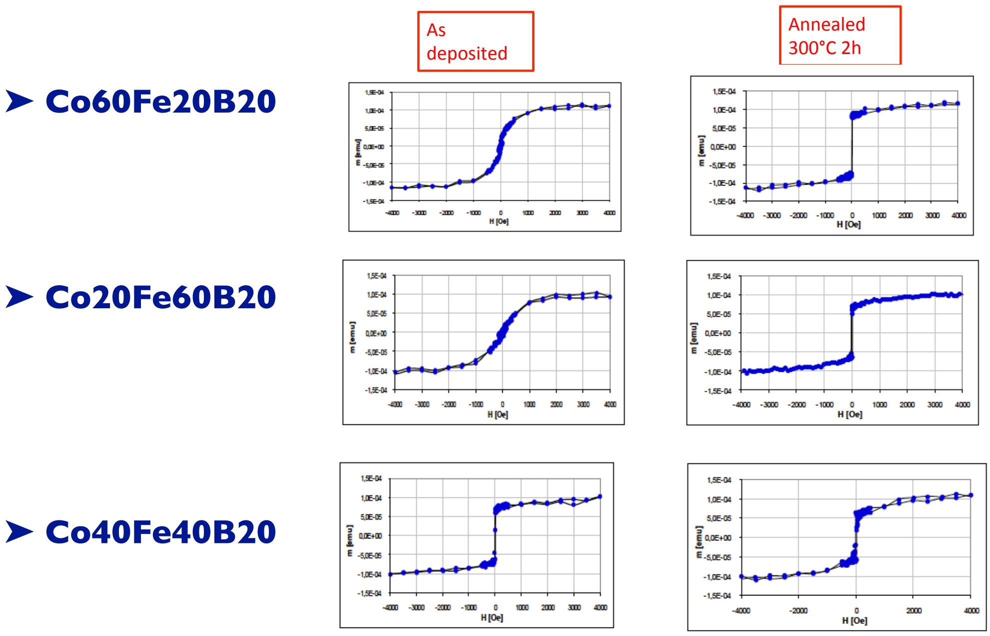

***Figure 7** : Hysteresis loops for 3 different CoFeB compositions in the as-deposited state and after annealing at 300°C for 2 hours. The magnetic structure consists in Ta-CoFeB(1nm)-MgO(2nm)-Ta*

We have studied the DW motion mechanism in each of these samples. Typical domain patterns are shown in Figure 8 at different range of magnetic fields (0.1, 0.6 and 1 mT). It is surprising to see that DWs can move at fields as low as 0.1 m. In this ultra low field regime, 360° DWs and domain jaggedness are present, which is consistent with a creep regime sensitive to the underlying pinning potential. **Around H=1 mT, a perfect circular shape is found consistent with a flow regime insensitive to the pinning potential. This field can be considered as the propagation field.**

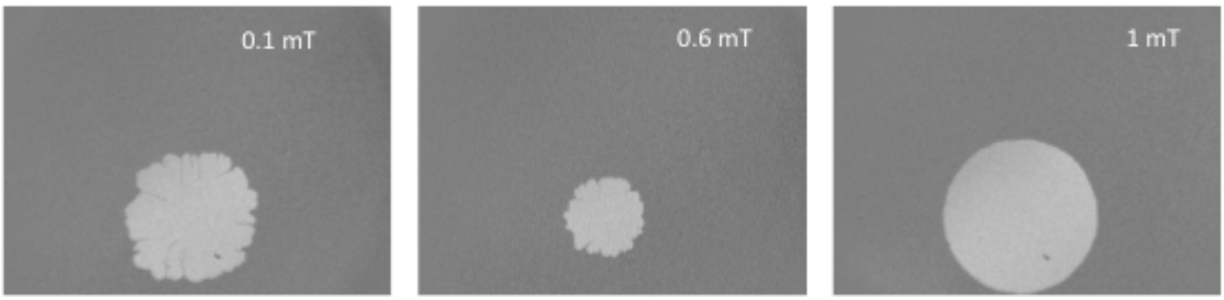

***Figure 8** : Typical domain shape at 0.1, 0.6 and 1 mT. For this latter field, the DW propagates in the flow regime above the depinning regime.*

In addition, **high DW mobility and high DW velocity (up to 25 m/s) have been found under relatively low applied fields up to 25 mT**. **These results are consistent with unprecedented low density of pinning defects in materials with PMA.** Any of these 3 different stoichiometries is susceptible to be integrated in the demonstrator. However so far, the $Co_{20}Fe_{60}B_{20}$ composition gives promising values in terms of TMR (see annex).

As described, the CoFeB films with a perpendicular anisotropy are a promising candidate for the application in a race track memory. For the reading of the information in a nanowire a combination with a perpendicular magnetic tunnel junction (MTJ) is necessary. Depending on the write current we will also use a perpendicular MTJ for the write head.

3. Conclusion

According to the structural and magnetic results reported in the present document, it is confirmed that the best material choice to be integrated in the demonstrator is a **Ta/CoFeB/MgO/CoFeB-F2** structure. Particular crystalline direction relationships and spacings from XRD (superlattices) and TEM (single stack) have been identified in the stacks with Ta buffer layer, most likely correlated with its favourable PMA properties, when compared to stacks with different buffer layers (i.e .Ru).
The decision on the above identified best material for the demonstrator, is mainly based on the very high PMA observed (up to K_u= 2-3 x 10^7 erg/cm^3) together with the favourable DW motion properties obtained following the 300 °C 2 hours thermal annealing. Currently, different stoichiometry of CoFeB material and optimization of the hard layer stack is under development at SINGULUS in order to enhance TMR values for optimized CoFeB-F2 composite hard layer.