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X-ray reflectivity (XRR) is used to determine the oxidation front at the nanometer scale in sputtered perpendicular semi tunnel junctions, as the form Pt/Co/AlO_x, by varying the oxidation time t_{Ox} of the capping layer. From XRR simulations, we show that the nature of the stack is gradually defined according to the value of t_{Ox}. For low t_{Ox} values (<40 s), a simple Pt/Co/Al/AlO_x multilayer is appearing whereas a Pt/Co/CoO/AlO_x architecture takes place for higher t_{Ox}. The oxygen-induced magnetic properties obtained by extraordinary Hall effects measurements are explained by the structural results. The increase of Co-O bondings with t_{Ox} is at the origin of the appearing of the perpendicular magnetic anisotropy (PMA).

***Index Terms*— X-ray measurements, X-ray chemical analysis, Perpendicular magnetic anisotropy, Metal-insulator structures, Magnetic layered films, Oxidation, Reflectometry, Simulation, X-ray chemical analysis**

I. Introduction

Multilayered magnetic systems containing magnetic (MM) and nonmagnetic materials (NM) constitute a wonderful challenge from a fundamental and industrial point of view, since these artificial media exhibit fascinating properties. For example, magnetic tunnel junctions, consisting of thin insulating barriers layers (~ 1-2 nm) sandwiched between ferromagnetic layers, have been intensively studied over the last 14 years [1]. In measured Tunnel MagnetoResistance (TMR) effects, the exact chemical composition along the different interfaces (between MM and NM layers) plays a very significant role since it determines the degree of polarizations (related to TMR) of the tunnelling electrons. Furthermore, the presence of selected layers for magnetic electrodes could induce a perpendicular magnetic anisotropy which is more interesting than in-plane magnetic anisotropy (high density hard disk media and magneto-optical recording). In this field, Pt/Co seems to be a model system due to the good control of the form of the magnetic loop from deposition parameters (different thicknesses, natures of buffer and protective layers), as published in the literature. As a consequence, the Pt/Co/AlO_x system with a perpendicular magnetic anisotropy [2], which is the studied structure in the present paper, has specific interests (MRAM, less sensitivity to border defects).

In order to investigate the oxidation dynamic of subnanometer Al and underlayed layers, the oxidation time of Al, namely $\boldsymbol{t_{Ox}}$, is an interesting deposition parameter to explore. Because by modifying it, different oxidation regimes appear: The [*under - optimized - over*] state is obtained when $\boldsymbol{t_{Ox}}$ is progressively increased. Thus, the physical characteristics, such as TMR or the magnetic anisotropy (in plane vs. out of plane) are strongly dependent on the quantity of O_2 in different layers. For instance, in the reference [2], the oxygen-induced perpendicular magnetic anisotropy induced by varying the plasma oxidation time ($\boldsymbol{t_{Ox}}$) was studied in Pt/Co/AlO_x. A set of characterizations (x-ray photoelectron spectroscopy, x-ray absorption spectroscopy, and Extraordinary Hall Effect) showed that the maximum of out-of-plane magnetic anisotropy seems to be related to the appearance of a significant density of Co-O bonds at the Co-interface. The aim of the present study is to confirm this hypothesis, by using hard x-ray reflectivity technique.

These physical properties (TMR and/or anisotropy) of such magnetic compounds have been clearly related to structural characteristics (the presence of O_2 in different metallic layers), as in [3]-[6]. But, the studied systems in these precedent references are complex, with a lot of elements (Mn, Ni, Fe, Co, Al, O, Ta). In addition, several oxidized metals (FeO_x, CoO_x, AlO_x) are appearing and insufficient structural techniques are devoted to the series with different $\boldsymbol{t_{Ox}}$. Consequently, it leads to a difficult understanding of experimental results in these references [3]-[6].

X-ray reflectivity is a relevant, non destructive and large area sensitive technique for detailing with a high precision the architecture of magnetic nanostructures [7]. It leads to a better understanding of physical properties. However, systematic XRR studies on magnetic nanostructures when the deposition time is varied in a series of samples are surprisingly scarce in the literature [9]. In this work, we intensively have used hard X-Ray Reflectivity (XRR) in the aim to explore the thickness, the roughness and the density of different layers by supposing a change of the stack architecture related to $\boldsymbol{t_{Ox}}$. Magnetic properties, as found in [2] and in this present paper, are clearly explained with respect to their chemical composition thanks to XRR results. In particular, the role of oxygen for sufficient dose is to increase the magnetic coupling between the ferromagnetic Co layer and the antiferromagnetic CoO entities.

II. EXPERIMENTS

In a first step, Pt/Co/Al trilayers were successively deposited onto thermally oxidized Si by conventional dc-magnetron sputtering. The nominal thicknesses were 3, 0.6 and 1.6 nm for Pt, Co and Al respectively. Secondly, samples were then transferred under vacuum in a separate treatment chamber and oxidized using an oxygen rf plasma during an oxidation time t_{Ox} in the range [15-60] seconds. More information on the samples is detailed in reference [2]. The reflectometry was carried out with a Bruker D8 Discover diffractometer using a line focus from a Cu target x-ray tube. Göbel multilayer optics was used to select Cu K<α> wavelength (λ=1.5418 Å) and to make the beam quasi-parallel (divergence ≤ 0.028°). The beam size at sample position was 50 µm in the incidence plane. The sample size was 3 mm wide by 12 mm long and the same pieces were used for magnetic measurements. Data were collected using a scintillation detector in the [0-16°] 2Θ angular range, with an increment of 0.04° and an acquisition time of 40 sec/step. The interpretation of XRR measurements is carried out by fitting the experimental scans with theoretical curves using Bruker LEPTOS® software [8]. The magnetic properties were carried out by extraordinary Hall Effect (EHE) measurements for different temperatures T (4-293K) and magnetic fields H (0-5 Teslas) perpendicular or parallel to the sample plane.

III. RESULTS

A. Magnetic characterization

Perpendicular magnetic normalized measurements, performed by EHE at different temperatures T (4.2-293K) for t_{Ox}=40 s, are shown in Fig. 1. Only the half part of the hysteresis is represented for H comprised between 0 and 1.5 T, and the return to 0 T (see the arrows in Fig. 1 indicating the magnetization reversal at 4.2K).

FIG. 1 HERE

This sample exhibits a square jump. Magnetic measurements with in-plane applied field indicate that the saturation magnetization is difficult to obtain, with a saturation field comprising between 1.2 and 2 teslas from RT to LT respectively (curves not shown). These results indicate that the out-of-plane direction is an easy magnetic axis for t_{Ox}=40 s. For the oxidation time ranging from 15 to 60 s, a crossover for the anisotropy from in-plane to out-of-plane appears around t_{Ox}=25 s. In the next part, we will research the possible reasons of this crossover, and the maximized out-of-plane anisotropy close to t_{Ox}~40 sec as previously found in [2].

B. Structural characterizations by reflectivity

Fig. 2 displays a series of X-ray reflectivity curves for different oxidation times t_{Ox} ranging from 15 to 60 s.

FIG. 2 HERE

XRR curves indicate that, for increasing t_{Ox}, it appears clear Kiessig's fringes more and more pronounced and differently positioned. We note a progressive change of these curves with t_{Ox}, indicating that a weak variation of the oxygen treatment remarkably changes the structure of semi tunnel junctions. XRR data are simulated using different appropriate stacking models. The main difficulty of the study resides on the fact that the layers thicknesses are very low. In order to evaluate the sensitivity of the XRR for sub-nanometer layers, we have simulated the reflectivity for different architectures (see Fig. 3): Pt/Al/AlO_x without Co, Pt/$Co_{0.3nm}$/Al/AlO_x and Pt/$Co_{0.6nm}$/Al/AlO_x with a Co thin layer.

FIG. 3 HERE

Here, the fixed thicknesses Th were Th_{Pt}=3 nm, Th_{Al}=1.2 nm and Th_{AlO_x}=0.8 nm. The densities values were the bulk ones and the roughness was 0.2 nm at each interface. This architecture is corresponding to the low t_{Ox} regime (non oxidized Co and partially oxidized Al). We note that a low Co thickness value significantly affects the curves. In the same way, we adopt the following architecture: Pt/Co/CoO/AlO_x corresponding to the high t_{Ox} regime (partially oxidized Co and fully oxidized Al). Table 1 lists the nominal values of density taken in the reflectivity models.

Table. 1 HERE

Firstly, we start the adjustment for the least oxidized sample (15 s). The reason lies on the architecture of the trilayer including only AlO_x slab on the top with no *a priori* known thickness value. Taking into account the best set of parameters for t_{Ox}=15 s as starting values, we were able to adjust subsequent oxidized sample data with the stack: Pt/Co/Al/AlO_x. The procedure is iteratively repeated for the sample's series. Due to the large number of parameters in the model, density and thickness of Co and Pt layers were fixed to nominal values at the beginning of the simulation and released only for the final fit. The last point to consider in the fit analysis is the appearing of a CoO layer for higher t_{Ox} values as mentioned above, inducing the stack Pt/Co/CoO/AlO_x. It occurs with the full oxidation of the Al layer at a certain t_{Ox} value noted t^*_{Ox}. The crossover oxidation time t^*_{Ox} is obtained at 40 s, this value being the best compromise between both architectures from the obtained fits.

We individually extract for each fitted curve, three fit parameters as mentioned above: thickness (Th), roughness (σ) and density (ρ) for each layer of the architecture. For improving the understanding of these results, we combine both ρ and Th for a considered layer, and we then define the following ratios R for Al [(1)] and AlO_x [(2)]:

$$R_{Al} = \rho_{Al} \cdot Th_{Al} / (\rho_{Al} \cdot Th_{Al} + \rho_{AlOx} \cdot Th_{AlOx}) \quad (1)$$

and

$$R_{AlO_x} = 1 - R_{Al}. \quad (2)$$

The reason is to take into account into the density in the extracted quantity of atoms. The ratios of Co and CoO are defined in the same way. The evolutions of R_{Al} and R_{AlOx} are

shown in top-left panel in Fig. 4(a).

FIG.4 HERE

The oxidation time dependences of ratios for the (Al, AlO_x) couple clearly indicate that oxygen penetrates progressively inside the Al layer when t_{Ox} increases. The behaviors of Co and CoO ratios [bottom-left panel in Fig. 4(b)] follow the same tendency. These results show a change from a mixed phase of Al and AlO_x to a pure AlO_x, followed at $t_{Ox}=t^*_{Ox}$~40 s by a change from a quasi pure Co to mixed Co, CoO phase for longer oxidation times. Concerning the roughness, it follows the same tendency as the thickness of the corresponding element [top-right (c), bottom-right (d) panels of Fig. 4 for {Al,AlO_x} and {Co,CoO} couples respectively].

The oxidation process is usually considered as homogeneous in the surface plane of the layers with a diffuse interface which is quantified by the σ roughness parameter. Here, the σ values are high (see right panel in Fig. 4) comparatively to thicknesses in these slabs. The oxidation process could induce a degradation of the interfaces. Due to these high *rms* roughness and the low thickness, the density or composition profile is non abrupt. Consequently Co and O atoms can he bonded before a complete disappearance of the Al layer. This result is important for understanding magnetic results as detailed in the next part.

C. Discussion

In the present study, we have studied the oxidation time dependence in XRR data in semi tunnel junctions. This method of XRR analysis permits to obtain the structural evolutions provoked by the oxidation front of the oxygen plasma. In our Pt/Co/AlO_x trilayers, the oxygen atoms progressively penetrate in the material in a non uniform way, as indicated by the values of thickness and roughness. The effect of the oxidation process on fitted XRR data has been seen in [7] where the authors have shown the change of the electron density profile for CoFe/Ru/CoFe and CoFe/RuO_x/CoFe thin layers.

In our trilayers, the extracted quantities from fitted XRR data corroborate the magnetic measurements at fixed temperature in the range (4.2-293K). From our magnetic measurements, an out-of-plane easy axis is seen for t_{Ox}>25 s whereas the in-plane easy axis is obtained for lower t_{Ox}. This crossover at t_{Ox}~25 s has previously been seen in [2] at room temperature. The authors have interpreted these results by the substantial amount of oxygen atoms at this interface which induces a strong perpendicular magnetic anisotropy PMA, overcoming the in-plane anisotropy of the Co layer. The present results confirm this hypothesis. Due to the roughness of layers, the Co layer is very close to the AlO_x one for t_{Ox}~25-30 s. This is why we observe that this value is lower than t^* (40 s, see Fig. 4) where a CoO layer appears in the structure. The thermal evolution of magnetic properties for out-of-plane measurements will be discussed now in the light of our structural characterizations.

For t_{Ox}<25 s the easy magnetic axis is in the plane of the Co layer and a weak thermal dependence appears in the magnetic data. In addition, there are no oxygen atoms at interfaces of the Co layer as deduced from XRR data. Hence, only the interfacial anisotropy coming from Pt/Co and Co/Al, which favour an in-plane anisotropy, contributes to the total interfacial anisotropy. Perpendicular magnetic anisotropy of the Co layer for low oxidation times is only observed for higher Pt thickness (~ 5 nm) and a Ta buffer layer [10].

For t_{Ox} above 25 s, it appears a noticeable variation of EHE with T. This crossover coincides with the emergence of the perpendicular easy axis at RT as observed in reference [2]. In this t_{Ox} regime, XRR data clearly show the presence of oxygen atoms at the top of the Co layer. As a result, we have to consider an additional interfacial anisotropy, K(Co/Oxygen). This might be at the origin of the PMA.

For t_{Ox}>40 s, XRR analysis reveals a CoO layer, and the persisting out-of-plane anisotropy as observed in [2] at RT. Indeed, the additional magnetic coupling between Co and CoO becomes non-negligible in the high t_{Ox} regime. Consequently, the strong increase of H_c when decreasing T could be explained by the thermally induced increase of the antiferromagnetic pinning strength, as in [11] for Co/CoO nanostructures. A forthcoming work will focus on the T dependence of the magnetic properties on Pt/Co/AlO_x trilayers for different t_{Ox} [12]. Our results indicate that the magnetic interaction is proportional to t_{Ox} in the 25-60 sec range. CoO favouring in-plane anisotropy, the optimization of PMA (40 sec), see in [2], is explained by the compromise between both precedent regimes.

To our knowledge, it does not exist a systematic study combining structural analysis and temperature dependent magnetic properties for a series of oxidized multilayers. Only, fixed temperatures (LT and/or RT) have been used in the literature ([3], [6] and [13]). In these papers, no systematic structural studies with t_{Ox}, explaining the magnetic results, have been reported contrary to the present study.

IV. CONCLUSION

We have shown that the oxidation time t_{Ox} remarkably changes the structure of Pt/Co/AlO_x. For t_{Ox}<25 seconds, the Co layer contains a weak quantity of oxygen atoms at least localized on the top Al protective layer. It becomes a mixture of "Co-CoO layer" with a fully oxidized Al at higher t_{Ox} ($\approx$ 40 s). Consequently, the perpendicular anisotropy found in [2] at RT is explained by the presence of oxygen at the interface between Co and AlO_x. It will be interesting to study the coordinance of Co atoms as a function of both t_{Ox} (as well as the annealing temperature) using x-ray absorption methods.

REFERENCES

[1] J. S. Moodera, L. R. Kinder, T. M. Wong and R. Meservey, "Large Magnetoresistance at Room Temperature in Ferromagnetic Thin Film Tunnel Junctions", Phys. Rev. Lett vol. 74, pp. 3273-3276, 1995.

[2] B. Rodmacq, A. Manchon, C. Ducruet, S. Auffret, B. Dieny, "Influence of thermal annealing on the perpendicular magnetic anisotropy of Pt/Co/AlOx trilayers ", Phys. Rev. B vol. 79, pp. 024423-1/-024423-8, 2009.

[3] D. Lacour, M. Hehn, M. Alnot, F. Montaigne, F. Greullet, G. Lengaigne, O. Lenoble, S. Robert, and A. Schuhl, "Magnetic properties of postoxidized Pt/Co/Al layers with perpendicular anisotropy", Appl. Phys. Lett. vol. 90, pp. 192506-1/192506-3, 2007.

[4] N. D. Telling, G. van der Laan, S. Ladak and R. J. Hicken, and E. Arenholz, "Evidence of a barrier oxidation dependence on the interfacial magnetism in Co/alumina based magnetic tunnel junctions", J. Appl. Phys. vol. 99, pp. 08E505-1/08E505-3, 2006.

[5] J. J. Sun, V. Soares, and P. P. Freitas, "Low resistance spin-dependent tunnel junctions deposited with a vacuum break and radio frequency plasma oxidized", Appl. Phys. Lett. vol. 74, pp. 448-450, 1999.

[6] K. S. Yoon, J. Y. Yang, W. J. Choi, C. O. Kim, J. P. Hong, and H. Jung Kim, "Effect of localized antiferromagnetic phases at interfaces between AlOx insulating barriers and Co50Fe50 electrodes in magnetic tunnel junctions", Phys. Rev. B vol. 69, pp. 012407-1/012407-3, 2004.

[7] S. Asgharizadeh, M. Sutton, Z. Altounian, M. Mao, and C. L. Lee, "Ruthenium nano-oxide layer in CoFe-Ru-CoFe trilayer system: An x-ray reflectivity study". J. Appl. Phys. vol. 103, 094904-1/094904-5, 2008.

[8] A. Quade and H. Wulff, "Investigation of oxidation process on plasma treated thin Al-films by GIXR and GIXRD", Thin Solid Films vol. 355-356, pp. 494-499, 1999.

[9] Leptos version 3.03, available from Bruker AXS, Karlsruhe, Germany.

[10] B. Carvello, C. Ducruet, B. Rodmacq, S. Auffret, E. Gautier, G. Gaudin, and Bernard Dieny, "Sizable room-temperature magnetoresistance in cobalt based magnetic tunnel junctions with out-of-plane anisotropy", Appl. Phys. Lett. vol. 92, pp. 102508-1/102508-3, 2007.

[11] D. Tripathy and A. O. Adeyeye, "Probing the exchange bias in Co/CoO nanoscale antidot arrays using anisotropic magnetoresistance", Phys. Rev. B vol. 79, pp. 064413-1/-064413-10, 2009.

[12] H. Garad, F. Fettar, L. Ortega, A. Ramos, B. Zawilski, P. Plaindoux, J. Marcus, B. Rodmacq, S. Auffret, B. Dieny, A. Barla, P. Gambardella, and J. Nogues (unpublished).

[13] Y. Lu, C. Deranlot, A. Vaurès, F. Petroff, and J-M. George, "A magnetometry study of Co oxidation in Co/MgO bilayers grown by sputtering", J. Appl. Phys. vol. 104, pp. 073907-1/043914-5, 2008.

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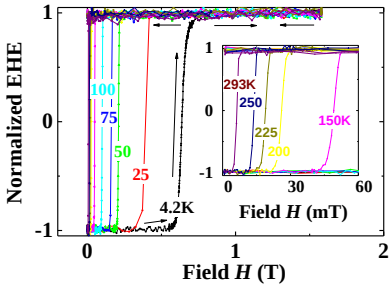

FIG. 1: EHE normalized data as a function of out-of-plane applied magnetic field *H* at different temperatures for $Pt_{3\ nm}/Co_{0.6\ nm}/AlO_x$ oxidized during t_{Ox}=40 s. The arrows show the magnetization reversal at 4.2K.

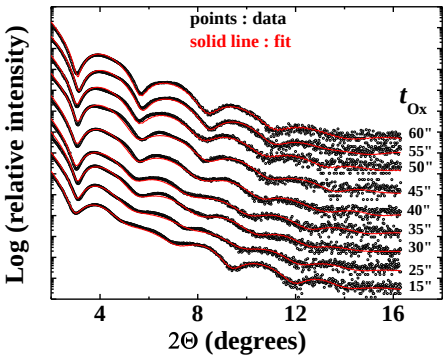

FIG. 2: X-ray reflectivity data (circles) with fits (solid lines) for $Pt/Co/AlO_x$ oxidized during t_{Ox} in the range 15-60 seconds. (Curves are shifted vertically for the sake of clarity).

Table1: Nominal values of density taken in the reflectivity models

compounds	AlO_x	Al	CoO	Co	Pt	SiO_2	Si
density (g/cm^3)	3.98	2.7	6.43	8.9	21.44	2.2	2.33

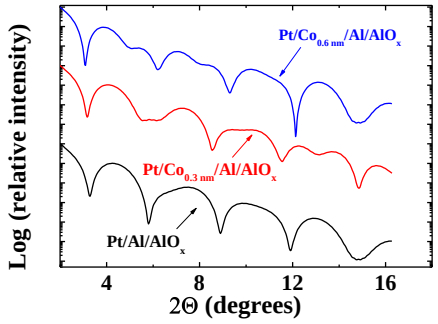

FIG. 3: Simulations of the reflectivity for different architectures: $Pt/Al/AlO_x$, $Pt/Co_{0.3\ nm}/Al/AlO_x$ and $Pt/Co_{0.6\ nm}/Al/AlO_x$ where the thicknesses *Th* are: Th_{Pt}=3 nm, Th_{Al}=1.2 nm and Th_{AlO_x}=0.8 nm. The densities are the bulk values and the roughness is 0.2 nm for each interface. (Curves are shifted vertically).

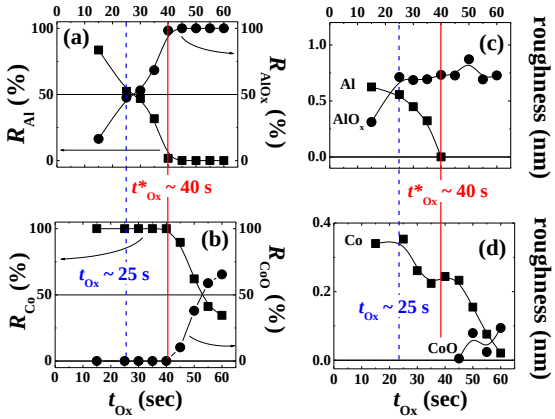

FIG. 4: Ratios [see the text, (1) and (2)] from fits in Fig.

1, R_{Al} and R_{AlOx} vs t_{ox} [top-left panel, (a)]; R_{Co} and R_{CoO} [bottom-left panel, (b)] vs t_{ox}. Roughness σ of layers deduced from fits in Fig. 1 vs t_{ox}: for Al and AlO_x, [top-right panel, (c)]; for Co and CoO [bottom-right panel, (d)]. The dashed lines (25 s) show the anisotropy crossover from in plane to perpendicular by increasing t_{ox}, whereas the straight lines (40 s) indicate the appearance of CoO.