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Magnetic properties of postoxidized Pt/Co/Al layers with perpendicular anisotropy

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The magnetic properties of ultrathin Co layers sandwiched between Pt and Al layers are studied as a function of the Al layer oxidation time. The association of three batches of complementary experiments (extraordinary Hall effect, x-ray photoelectron spectroscopy, and tunneling magnetoresistance) allows the authors to finely characterize their samples both magnetically and chemically. The authors show that their oxidation process reduces the coercive field of ultrathin Co layers with perpendicular anisotropy (case of short oxidation time) and can even induce transition from a ferromagnetic to a superparamagnetic state (lengthy oxidation time). © 2007 American Institute of Physics. [DOI: 10.1063/1.2734378]

Magnetic tunnel junctions (MTJs) with perpendicular anisotropy are promising candidates as base element of magnetic random access memory. Indeed, their magnetic properties are less sensitive to border defects than junctions with in-plane magnetization. Moreover, recently Mangin *et al.* have shown that the perpendicular geometry of magnetization is more efficient for current induced magnetic switching.¹ This is a clear advantage in terms of power consumption during the bit writing process. A key aspect of MTJ fabrication is the tunnel barrier growth. Actually, in the case of MTJ with perpendicular anisotropy, this becomes of primary importance because the magnetic properties of the underlying electrode are very sensitive to under- or overoxidation of the tunnel barrier.^{2,3} In this letter, we report on the observation of ferromagnetic to paramagnetic transition due to the barrier overoxidation. We emphasize the differences between our results and conclusions, and the seminal work of Monso and co-workers.^{2,3}

We present an experimental study on the oxidation of a thin aluminum layer covering a cobalt/platinum bilayer. We have focused our attention on the influence of the Al layer oxidation time on the magnetic properties of the Co layer. Three complementary experimental techniques have been used to explore this influence, and three kinds of stacks have been grown depending on the used technique: The magnetic properties investigations were carried out by an extraordinary Hall effect (EHE). The cobalt/aluminum interface was studied using the strong sensitivity to interfacial properties of the two techniques: spin polarized tunneling effect and x-ray photoelectron spectroscopy (XPS). Indeed, spin polarized tunneling effect is known to be very sensitive to the under- or overoxidation of an Al layer forming a tunnel barrier. X-ray photoelectron spectroscopy analysis allows a direct measurement of the chemical composition of the interface. Combining these three techniques, we have been able to link the change in magnetic properties to the chemical composition of the Co/Al system.

The samples presented in this study were sputtered onto float glass substrates in an Alliance Concept UHV sputtering and they all have a Ta/Pt buffer layer. The Pt film has a

strong (111) texture according to x-ray diffraction measurements in $\theta/2\theta$ mode (not shown in this letter). Onto the buffer, a Co layer is deposited. A tunnel barrier was then formed by deposition of a thin Al layer (2 nm) and a postoxidation process in a RF Ar/O₂ plasma similar to the one described in Ref. 4. The oxidation time varies from 0 to 95 s.

Figure 1 presents results of EHE measurements obtained in a standard four-probe Hall geometry as a function of the magnetic field applied perpendicularly to the sample plane. The stacks used for this batch of experiments are Ta 5/Pt 5/Co 0.6/Al oxide (the numbers are thicknesses in nanometer). The transverse resistivity measured in this configuration is proportional to the magnetization component perpendicular to the sample planes.⁵ So, the EHE allows us to investigate the magnetic properties of the 0.6 nm thick Co layer sandwiched between the Pt and Al oxide films. To understand the sample's magnetic behavior, four anisotropy sources have to be considered: (i) the Pt/Co interface, (ii) the

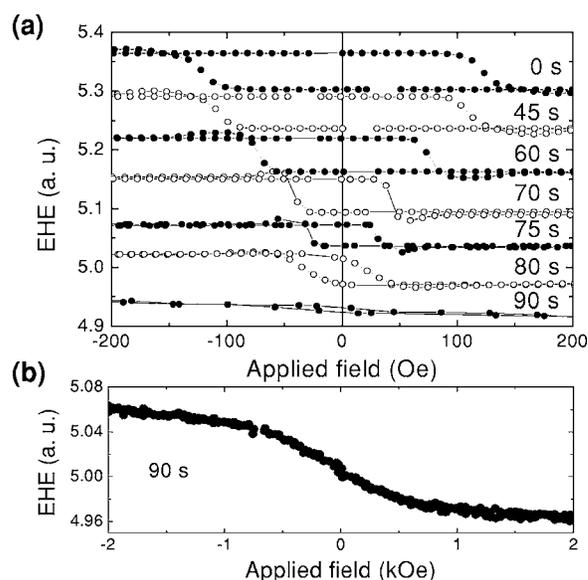


FIG. 1. Extraordinary Hall effect measurements as a function of the applied magnetic field recorded at room temperature for samples with different oxidation times: varying from 0 to 90 s for (a) and 90 s for (b).

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top Co interface (either Co/Al, Co/Al oxide, or Co/Co oxide), (iii) the shape anisotropy, and (iv) the stress induced anisotropy. Concerning the sample without Ar/O₂ plasma exposure (oxidation time equal to 0 s), a hysteretic behavior is recorded. It means that the combination of these four sources results in an anisotropy perpendicular to the plane. This is observed for all oxidation times below 90 s. It should be noted that a remanence of 100% is recorded for oxidation times up to 75 s. Furthermore, increasing progressively the oxidation time leads to a coercive field reduction. For an oxidation time of 90 s, the EHE signal presents drastic differences [see Fig. 1(b)]. The saturation field is about one order of magnitude higher than the previously discussed cases. The EHE signal is nonhysteretic and no remanence is observed. These features could correspond to an in-plane anisotropy, and this change of magnetic properties had been attributed to a modification of the top interface chemical composition.^{2,6} This suggests that the Pt/Co/Al (short oxidation time) system exhibits a perpendicular anisotropy, whereas the Pt/Co/Al oxide and/or Pt/Co/Co oxide (long oxidation time) has an in-plane anisotropy. As far as the decrease in coercive field is concerned, different origins have been invoked to explain such variations as the change of the magnetic dead layer, the mixing at the Co/Al interface⁷ or the change of the stress state inside the Co layers, and the related stress induced anisotropy.^{8,9} The structure and the microstructure have been determined by x-ray diffraction with a combination of classical geometry ($\theta/2\theta$) and grazing incidence scattering (GIS). By combining these two experiments any existing texture can be highlighted. No change in the peak positions ($\theta/2\theta$ and GIS) could be observed when increasing the oxidation time. The full width at half maximum is also constant. So, the Pt is (111) textured and its out-of-plane parameter is not affected by the oxidation process. This suggests that the change of stress is not at the origin of the evolution of the coercive field. However, to rule out this possibility in the Co layer specific experiments are required. The artificial modulated structure was also investigated by small angle x-ray scattering. This experiment allowed us to measure the thickness, the electron density, and the roughness of each layer. The experimental spectra were fitted using the software REFLEX.¹⁰ All the layer thickness and roughness, element densities, and interdiffusion were kept constant except at the Co/Al interface: increasing the oxidation time decreases either the Co roughness and/or the Co/Al interdiffusion. Then, the change of the mixing at the Co/Al interface as shown by Misuzuki *et al.*⁷ could be at the origin of the coercive field decrease. This hypothesis is, however, under investigation and will be discussed in a future report. Nevertheless, those results could explain the difference with the results of Monso and co-workers.^{2,3} They report an in-plane magnetization at zero oxidation time, which is clearly not the case in our study. A higher Co roughness or a decreased texture can induce an in-plane magnetization at zero oxidation time; increasing the oxidation time decreases Co roughness or interdiffusion leading to the appearance of a perpendicular film plane magnetization.

Spin polarized tunneling effect has been used to shed light on the transition origin. Indeed, the TMR amplitude is known to be very sensitive to over- or underoxidation of the Al layer¹¹ and, more precisely, to the chemical nature of the electrode/tunnel barrier interface.¹² So, we have deposited and prepared MTJs to study the variation of TMR amplitude

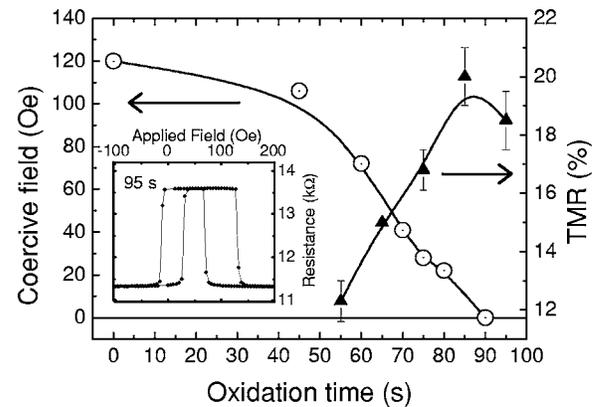


FIG. 2. (—○—) Coercive field (left axis) and (—▲—) tunnel magnetoresistance (right axis) as a function of the oxidation time both recorded at room temperature. Inset: Resistance vs applied magnetic field of a MTJ with an Al layer oxidized for 95 s.

versus the oxidation time. The stacks used for this batch of experiments are Ta 5/Pt 10/Co 5/Al oxide/Co 2/Ta 0.5/Co 3/Ir20Mn80 5/Pt3. These MTJs were annealed with an in-plane applied field of 300 Oe at 200 °C for 30 min to activate the top electrode pinning. Under these conditions thermal annealing does not affect the oxygen distribution in the tunnel barrier.¹³ Both ferromagnetic electrodes have an in-plane anisotropy and the oxidation time has been varied from 55 to 95 s. The inset in Fig. 2 presents a typical TMR curve as a function of the applied field. The field is applied in the sample plane along the easy axis of magnetization of both electrodes. An exchange biased top electrode allows us to reach a well defined antiparallel state of magnetizations for a large range of magnetic field as well as to determine without ambiguities the TMR values. As expected, the TMR (“▲” symbols in Fig. 2) reveals an initial increase for moderate oxidation time followed by a decrease for lengthy oxidation time. According to Telling *et al.*,¹² the TMR variation allows one to distinguish three different electrode/tunnel barrier interfaces: Al/Al oxide, Co/Al oxide, or Co/Co oxide, corresponding, respectively, to the increase, the maximum, and the decrease of the TMR amplitude. In our case, the maximum of TMR amplitude is obtained for an oxidation time of 85 s. At this point, it is quite interesting to compare the TMR variation to the coercive field variation extracted from the EHE experiments presented earlier in this letter. These measurements are represented by the “○” symbols in Fig. 2. For oxidation time below 85 s, the TMR increase is accompanied by a coercive field decrease. Above 90 s, the coercive field value is reduced to zero and this corresponds to a TMR decrease. The TMR value is maximum for an oxidation time corresponding to the magnetic transition observed by EHE measurements. This suggests that the transition occurs when the top Co interface changes from Co/Al to Co/Al oxide. For oxidation time beyond 90 s, an overoxidation of the aluminum layer takes place.

XPS measurements have been carried out to confirm this last hypothesis. Indeed, we have to be able to characterize directly the chemical composition of the Co/Al interface corresponding to an oxidation time of 90 s. The Al 2s and Co 2p levels were recorded with the Mg K α radiation ($h\nu = 1253.6$ eV). A reference sample has been grown to obtain the spectra of oxidized and unoxidized Co on our XPS setup. Both spectra are presented in gray in Fig. 3(a) (denoted

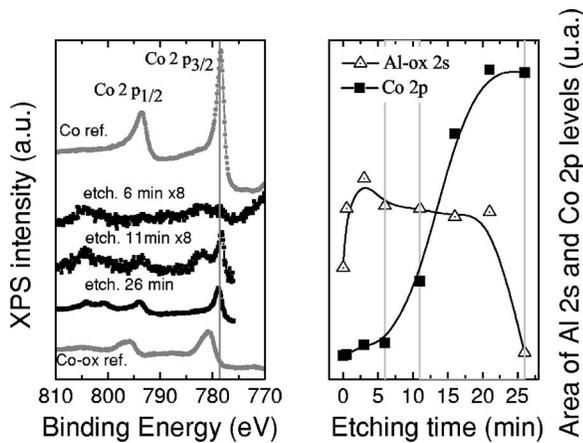


FIG. 3. (a) Co 2*p* XPS spectra corresponding to an oxidation of 90 s recorded after different etching times. The gray plots are Co and Co oxide reference spectra. (b) Area of Al oxide 2*s* and Co 2*p* levels vs etching time. Each vertical gray line corresponds to an etching time after which XPS spectra presented in (a) are recorded.

“Co-ox ref.” and “Co ref.”). The presence of oxidized Co induced a shift of 2.3 eV of 2*p*_{3/2} levels as already reported in the literature.¹⁴ On these bases, we have been able to investigate the chemical composition of the Co/Al interface corresponding to an oxidation time of 90 s. The multilayer composition is Ta 5/Pt 5/Co 0.6/Al oxide/Cu 3.5/Ta 5. Eight XPS spectra have been recorded increasing progressively the etching time. Figure 3(b) presents the area of Al oxide 2*s* and Co 2*p* levels versus the etching time. The variation of the areas indicates the probed part of the sample. For an etching time of 11 min, both Al oxide 2*s* and Co 2*p* levels are detected. The measured signal contains information about the chemical composition of the Co/Al interface. The three XPS spectra recorded for etching time of 6, 11, and 26 min are reported in Fig. 3(a). Note that the Co 2*p*_{3/2} peak amplitude is about eight times smaller after 11 min of etching than that after 26 min. Moreover, the energy at which this Co 2*p*_{3/2} emission line appears corresponds to the energy of an unoxidized Co (see Co ref. spectrum). This indicates that the probed surface is mainly composed of unoxidized Co. Simulations of XPS spectra for different proportions of oxidized and unoxidized Co support that less than 5% of the probed Co is oxidized.

To shed light on the magnetic state of the overoxidized Ta/Pt/Co/Al system, we have grown a specific MTJ. It is quite identical to the one presented earlier, except for the Co bottom electrode thickness which is now 0.6 nm thick. The Al layer sandwiched between the two Co electrodes has been exposed to the Ar/O₂ for 110 s, leading to an overoxidized tunnel barrier. The magnetoresistive response obtained is shown in Fig. 4. In this case, the magnetic field is applied in the substrate plane. The pinned counterelectrode reversal is observed for relatively low magnetic fields as expected (see inset in Fig. 4 and inset in Fig. 2). The progressive increase and decrease of resistance are attributed to the magnetization reversal of the Co bottom layer. Note that the same behavior was observed by EHE with a magnetic field applied perpendicularly to the plane. This rules out the hypothesis of an in-plane magnetization. So, we conclude that the overoxi-

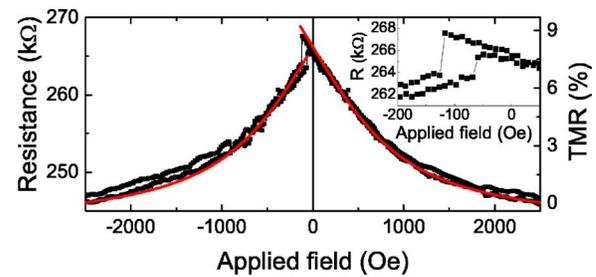


FIG. 4. (Color online) Resistance vs applied field recorded at room temperature. Inset: zoom in on the low field region.

dized Ta/Pt/Co/Al system is superparamagnetic. Furthermore, the TMR amplitude at zero magnetic field is equal to 7.7%; it is about half the TMR expected for this oxidation time (see Fig. 2). This is consistent with a superparamagnetic state. Finally, we have been able to fit the magnetoresistive response of the bottom Co layer magnetization using the Langevin equation for paramagnetism, and a grain diameter of 12 nm could be extracted on the hypothesis of noninteracting clusters (red line in Fig. 4).

In summary, concerning overoxidized samples, XPS measurements show that the ultrathin Co layer oxidation is not uniform. This suggests the existence of preferential sites where the Co oxidation takes place. These preferential sites could be crystalline defaults or grain boundaries as already suspected in the case of thin Al layers.¹⁴ We believe that this oxidation mechanism leads to weakly coupled Co clusters separated by vertical walls of Co oxide. This is consistent with the superparamagnetic behavior observed at room temperature. This result highlights how critical is the control of the oxidation process to realize MTJs with perpendicular anisotropy. Furthermore, we show a way to control the coercive field value of thin films with perpendicular anisotropy.

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