Oxidation processes at the metal/oxide interface in CoFe$_2$/CoFe$_2$O$_4$ bilayers deposited by pulsed laser deposition

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Abstract

CoFe$_2$/CoFe$_2$O$_4$ bilayers were made by pulsed laser ablation of a CoFe$_2$ target on Si(100) substrates. The metallic layer was deposited first, in vacuum. The oxide was then deposited in an oxidizing O$_2$/N$_2$ (20:80) atmosphere. Two different procedures were used for the introduction of the oxidizing atmosphere in the deposition chamber: the laser ablation of the target was either stopped (discontinuous deposition process) or maintained (continuous deposition process) during the 20 min necessary for the establishment of the desired O$_2$/N$_2$ pressure. In both cases, the different electronegativities of Fe and Co cause an important modification of the Fe/Co ratio at the metal/oxide interface, with a depletion of Fe in the metal region and of Co in the oxide region. In the continuous procedure, the combination of the kinetic energy given by the ablation process to the Fe and Co adatoms with the one they get from their different affinity towards oxidation allows the formation of a low roughness metal/oxide interface with a high (111) preferred orientation of the CoFe$_2$O$_4$ layer, an induced re-crystallisation of the metal layer underneath and an unusual antiferromagnetic metal/oxide magnetic coupling.

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1. Introduction

Magnetoresistive spin valves devices are currently receiving considerable attention due to their practical applications in magnetic memory cells and sensors. A spin valve consists, in its simplest form, of two ferromagnetic electrodes sandwiching a non-magnetic spacer. The electrical resistance of such a device depends on the relative orientation of the two magnetic layers: low when they are parallel and high otherwise. The control of this relative orientation relies on the possibility of pinning the magnetization of one of the magnetic layers while the other one remains free to rotate under the action of an external field. Two key points for the development of such devices are a high spin polarization of the magnetic layers combined with the use of an efficient and simple pinning layer. In these respects, the CoFe$_2$/CoFe$_2$O$_4$ system is of significant interest. Indeed, the metallic iron cobalt alloy CoFe$_2$ presents an interestingly high spin polarization and is therefore a good choice for the ferromagnetic electrode [1]. CoFe$_2$O$_4$, being a hard ferrimagnet with a high Curie temperature (793 K) [2] is an excellent candidate as a pinning layer and presents many advantages over the materials currently used in magnetoresistive devices. It does not necessitate any in field high temperature annealing, as in the case of an antiferromagnetic pinning layer having a high Néel temperature. Such an annealing is detrimental to the quality of the interfaces of multilayered devices because of diffusion phenomena. The system is also simple and non corroding, in comparison to an artificial antiferromagnetic structure consisting of at least three metallic...
layers sensitive to oxidation. The insulating properties of CoFe₂O₄ are also an advantage since they will allow the pinning layer not to shunt the current away from the active layers in current-in-plane configurations. The actual insertion of the CoFe₂/CoFe₂O₄ system in magnetoresistive devices necessitates the study of the magnetic coupling between the two phases. The great potential offered by the CoFe₂/CoFe₂O₄ system in terms of the variety of magnetic coupling behaviours has been discussed elsewhere [3]. The nature of the coupling is likely to be closely related to the nature of the metal/oxide interface. In a previous work [4], we have performed a structural study of the plasma oxidation of a sputtered body-centred cubic (bcc) CoFe₂ metallic layer that led to the formation of a thin (3 nm max.) CoFe₂O₄ spinel oxide layer. It was shown that the close cubic structures of the two phases allow the following epitaxial relationship oxide (100) [100] metal (100)[110], thus strengthening the interest given to the CoFe₂/CoFe₂O₄ system.

In this paper, we present a structural and analytical study of the interface between metal and oxide in CoFe₂/CoFe₂O₄ bilayers deposited by pulsed laser ablation. We show that the nature of the magnetic coupling exchange depends on the crystallographic orientation of the oxide layer at the interface, which can be tuned by the deposition parameters. A complete description of the raw structural (X-ray diffraction patterns and transmission electron microscopy images) and magnetic (superconducting quantum interference device magnetometer (SQUID) measurements) of the samples concerned by the present study may be found in [3]. The main results will be briefly recalled. Their working out has only been possible thanks to supplementary results obtained by electron energy loss spectroscopy (EELS). It has led to the formulation of an explanation about the origin of the different magnetic behaviours of the samples.

2. Experimental

2.1. Samples preparation

CoFe₂/CoFe₂O₄ bilayers were deposited onto (100) Si substrates heated to 200 °C by pulsed laser deposition. Prior to deposition the substrates were cleaned with a 15% water diluted HF (40%) – HNO₃ (60%) solution. An excimer laser XeCl (λ = 308 nm) was used to ablate a rotating metallic CoFe₂ target. The pulse length of the laser was 20 ns at a repetition rate of 10 Hz and a maximum energy of 23 mJ/pulse. The laser fluence was 2 J/cm². A 17 nm thick metallic CoFe₂ layer was deposited first onto the substrate, in vacuum (1.3 × 10⁻³ Pa). Two different procedures (a) and (b) were then used for the deposition of a ca. 300 nm thick oxide layer: (a) the ablation was stopped during the introduction of the oxidizing atmosphere and only turned back on again after 20 min, when a stable 6.7 Pa O₂:N₂ (20:80) pressure was reached; (b) the ablation was maintained during the establishment of the 6.7 Pa O₂:N₂ (20:80) pressure.

2.2. Characterization

X-ray diffraction (XRD) data were collected at room temperature by a D500 Siemens diffractometer equipped with a quartz monochromator and cobalt radiation (Kα = 0.178901 nm). The overall Fe/Co = 2 ratio of the bilayers was checked at large scales (1 μm) by means of energy dispersive X-ray spectroscopy (EDX) coupled to a JEOL 6700 F scanning electron microscope, with observations made perpendicular to the surface. High resolution images of the bilayer cross sections were observed with a TOPCON 002B high resolution transmission microscope (HR-TEM) operating at 200 kV (point to point resolution of 0.18 nm). Quantitative analysis of these cross sections was performed by EELS using a JEOL 3000F with a GIF2000 spectrometer. The collection angle was approximately 1.4 mrad and the extraction voltage of the FEG set to 1.7 kV. Spectra were quantified making use of EEL- MODEL [5]. A model was constructed from a log polynomial background and Hartree Slater cross sections for the Co L₂,₃, Fe L₂,₃ and O K-edges. Multiple scattering was included by convolution with the low loss spectrum. Expected accuracy was estimated to be better than 20%. The magnetic behaviour of the samples was studied with a SQUID (Quantum Design MPMS-XL model) at room temperature.

3. Results and discussion

3.1. Structure

The X-ray diffractograms of the CoFe₂/CoFe₂O₄ bilayers only present peaks corresponding to bcc CoFe₂ and spinel CoFe₂O₄ phases (Fig. 1). When the bilayer was fabricated with an interruption of the ablation between the metal and oxide layers (case (a)), both phases are polycrystalline and show no preferential orientation. When there was no interruption of the ablation during the establishment of the oxidizing atmosphere (case (b)), the oxide spinel phase presents a strong (111) orientation. The

![Fig. 1. X-ray diffraction patterns for samples (a) and (b).](image-url)
metallic phase is still polycrystalline, but shows a higher degree of crystallisation (more intense (110) and (200) diffraction peaks) than for sample (a), and higher even than for a metal layer only sample deposited in the same conditions.

The HR-TEM cross section views of both samples (Fig. 2) show a 5 nm thick silicide layer at the interface between the Si substrate and the metal. The strong (111) orientation observed by X-ray diffraction for sample (b) is also clearly visible on the cross section micrograph.

3.2. Electron energy-loss spectroscopy

EELS analysis results concerning the Fe/Co and O/(Fe + Co) ratios of the (a) and (b) samples cross sections are presented in Fig. 2. Both samples present an important modification of the Fe/Co ratio at the metal/oxide interface, with a depletion of Fe in the metal region and of Co in the oxide region. The interfacial value of the Fe/Co ratio reaches 0.5 and 2.5 on the metal and oxide sides, respectively, while it is of ca. 2.0, as expected, away from the interface. Platt et al. [6] and Gillies and Kuiper [7], when studying the native oxide layer formed on top of a CoFe alloy layer, also qualitatively observed a preferential oxidation of Fe versus Co using X-ray photoelectron spectroscopy. This can be explained by the difference in electronegativity of the two metals. The Fe atoms are more readily oxidized than the Co ones, and tend to migrate towards oxygen rich regions, while the cobalt atoms act the opposite way. For sample (a), the Fe/Co ratio modification affects the entire metallic layer, while for sample (b), only about 5 nm of the metallic phase is altered. The O/(Fe + Co) ratio increases abruptly at the interface when moving from the metallic to the oxide phase for both samples. For sample (a), one also observes a slight increase in the oxygen concentration in the metal region close to the interface, over a 3 nm thickness. In that part, the O/(Co + Fe) ratio reaches 0.4. This is too low for a stoichiometric iron or cobalt oxide. Indeed, the less oxidized iron or cobalt containing compounds are FeO or CoO, in which the oxygen over cation ratio is 1. One can assume an inhomogeneity in the repartition of the oxygen in that region, with fully oxidized grains neighbouring metallic ones. The O/(Fe + Co) ratio in the substrate is unreliable because of the vanishing Co and Fe signal.

The differences in the Fe/Co and O/(Fe + Co) ratios observed between the two samples may be explained by the different oxidation procedures used. Sample (a) was maintained, after the deposition of the metallic layer, in an oxidizing atmosphere for ca. 20 min before the laser deposition was started again. This results in a slight oxidation of the three superficial nm of the metal and in a deep and progressive reorganisation of the Fe and Co atoms concentration over the entire metallic layer: the Fe atoms moving towards the slightly oxidized layer, the Co atoms in the opposite manner (Fig. 3(i)). When the laser deposition is

Fig. 2. Cross section HR-TEM observations of samples (a) and (b), together with the Fe/Co and O/(Fe+Co) ratios determined by EELS.
started again, the fact that the oxygen atoms are inserted in the deposited layer is important, and this leads to the abrupt increase in the O/(Fe + Co) ratio. The newly formed oxygen rich layer again results in the mobility of the Co and Fe atoms. This leads to the displacement of the Fe/Co ratio inversion towards the metal/oxide interface (Fig. 3(iii)). The oxygen anions present in the slightly oxidized zone of the metal, which are far less mobile than the metallic atoms, remain in their location. For sample (b), the deposition is maintained during the establishment of the 6.7 Pa oxidizing atmosphere. This allows an important integration of oxygen anions in the deposited layer. The Fe/Co ratio inversion takes place in the thickness of what is being deposited, and not in the thickness of what has already been deposited, as in case (a). The modification covers 5 nm on each side of the metallic and oxide layer. This abrupt inversion is favoured by the mobility of the just-deposited species and rapidly leads to the desired equilibrium of the chemical potentials and prevents any propagation of composition modifications across the entire metallic phase. The roughness at the metal/oxide interface is extremely low, of the order of an atomic plane (Fig. 2(b)), thanks to the absence of any pre-formed slightly oxidized layer, as observed for (a). This low roughness, as well as the high mobility of the deposited atoms which is increased by the composition inversion process (chemical energy), allows the deposition of the spinel CoFe$_2$O$_4$ oxide with a strong (111) orientation. The (111) orientation is indeed the one for which the surface energy is minimized in spinels [8].

This highly ordered (111) crystallisation of the oxide seems to induce a re-crystallisation in the underlying 10 nm of the metal layer which would account for the observed higher degree of crystallisation of the metal layer for the (110) and (200) planes. Such a re-crystallisation induced by a post deposited layer has been observed by Magann et al. [9] in epitaxial Fe films deposited on Cu (100) and covered by Cu. As already shown in one of our previous papers [4], the metallic CoFe$_2$ bcc and oxide CoFe$_2$O$_4$ spinel structures are closely related. The (004) planes of the oxide have an interplanar distance of 0.210 nm, very close to the (011) 0.202 nm interplanar distance of the metal phase. A continuation of these planes throughout the metal/oxide interface is very likely. Fig. 4 shows an HR-TEM observation of the metal/oxide interface in sample (b). The (111) planes of the CoFe$_2$O$_4$ phase at 0.48 nm are clearly visible in the oxide part. In the two thirds of the metal that are close to the metal/oxide interface, the (110) planes of the CoFe$_3$ phase are also clearly visible, and present an angle with the interface (and hence with the (111) oxide planes) of ca. 56°. When the CoFe$_2$O$_4$ (111) planes are parallel to the surface, the (004) planes form a 54.7° angle with the interface. The continuation of the oxide (004) planes into the (111) metallic planes through the interface is compatible with the presence of both (110) and (200) planes of the metal parallel to the interface. Indeed, in the bcc CoFe$_2$ alloy, the angles between the (110) and (011) planes on the one hand, and the (200) and (110) planes on the other hand, are 60° and 45°, respectively (Fig. 5). This could explain why the intensity of the (011) and (002) planes is enhanced in the X-ray diffraction 0/2θ scan.

Fig. 4. HR-TEM close-up of the metal/oxide interface in sample (b) showing the relationship between the metal and oxide atomic planes.
3.3. SQUID magnetometry

The room temperature magnetization loops of both samples (not shown here, see [3]) present two magnetic contributions of different hardness: a soft layer (metal) with reversal fields of a few tens of kA/m (a few hundreds Oe) and a hard layer (oxide) with reversal fields of ca. 200 kA/m (ca. 3 kOe). Samples similar to samples (a) and (b) but having different metal layer thicknesses have also been prepared. When the magnetization due to the metallic part (in A m² per surface unit) is plotted against the observed metallic layer thickness including the silicide part (plot not shown here), it presents a 5 nm x-offset. This indicates that the 5 nm silicide layer is non-magnetic. The saturation magnetization of both the metal and oxide parts evaluated from the M-H loops are in perfect agreement with those observed for previously studied bilayers in which the metal was deposited on top of the oxide [10]: about 1600 kA/m (1600 emu/cm³) for the metal (close to the 1800 kA/m usually observed for the bulk CoFe₂ alloy) and 290 kA/m (290 emu/cm³) for the oxide (as already observed in CoFe₂O₄ single layers prepared in the same conditions [11] and close to, but slightly lower than the CoFe₂O₄ bulk magnetisation of 425 kA/m). Minor loops, for which, ideally, only the magnetisation of the magnetically soft metal layer is reversed, were measured from +80 to -80 kA/m and back to +80 kA/m after the polarisation of the sample to +1000 kA/m. For sample (a), the minor loop is centred about $H = 0$ kA/m and shows no offset (Fig. 6(a)). The coercive field of about 20 kA/m (250 Oe) is however much more important than that usually observed for CoFe₂ metal (ca. 2.5 kA/m). Such a behaviour can be either due to the existence of a biquadratic magnetic coupling or to a surface anisotropy of the metal. In the light of the EELS analysis, it appears very likely that the increase in the coercive field is due to the existence of the slightly oxidized top 3 nm layer of the metal. The O/(Fe + Co) ratio in this region is ca. 0.4, less than half that necessary for the formation of a full layer of FeO or CoO type antiferromagnetic oxides. The insertion of oxygen in the metallic network at such a low concentration seems to increase the coercive field of the metal without strongly diminishing its magnetization. This could be explained by the presence of CoO or FeO type oxides at the metal grain boundaries. For sample (b), the coercive field is of the order of that expected for CoFe₂ but the minor loop is shifted towards the positive fields (Fig. 6(b)).