EXOTIC THIN FILMS MADE FROM COBALT FERRITE

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ABSTRACT

Epitaxial $CoFe_2O_4$ thin films have been grown by PLD on (100) MgO substrate. Two types of spin-reorientation have been observed in such films upon annealing or increasing the film-thickness. In the as-deposited layers and at low thickness the easy axis is confined to the normal to the film plane whereas at large thickness the film plane becomes the preferential direction of the magnetization. On the other hand annealing induces a reorientation of magnetic anisotropy, which switches from the normal to the film plane in the as-deposited film to be in-plane aligned in the annealed state. The origin of both reorientations is explained in term of competition between stress and magnetocrystalline anisotropies. In the as-deposited state the tensile stress induces a huge perpendicular anisotropy, dominating the in-plane magnetocrystalline component. However annealing or increasing the film thickness releases the stress and allows the in-plane magnetocrystalline anisotropy to take the lead.

1. INTRODUCTION

The search for new magnetic materials is driven by technological demands such as increasing the magnetic recording density. One of the big challenges facing such technology consists of beating the superparamagnetic limit since ultra-small nano-sized structures are required for ultra-high recording density. Materials possessing a large magnetic anisotropy are suitable media to meet such requirements since a stable magnetization can be promoted in nano-structures. Hard ferrites such as the hexagonal ($BaFe_{12}O_{19}$) and the cubic ($CoFe_2O_4$) are attractive for such kind of applications due to their large magnetocrystalline anisotropy and high chemical stability. On the other hand recent studies demonstrated that cobalt ferrite can be applied as a pinning layer in spin valve structures with large magnetoresistance [1-2]. In low dimension systems such as thin films the magnetic properties can be very sensitive to various effects such as the grain size, the chemical composition, the ion occupation site, the substrate matching and the film thickness. In epitaxial hexaferrite thin films the uniaxial magnetocrystalline anisotropy dominates all the other sources of anisotropy and keeps the orientation of the easy axis constant regardless the film thickness or the thermal treatment [3-4]. However for cobalt ferrite the situation is different due to the cubic magnetocrystalline anisotropy of the bulk and the very large magnetostriction that can promote stress anisotropy which can be an important competitor in thin films. Additionally the large number of empty sites in the $CoFe_2O_4$ lattice offers an open structure where it is easy to manipulate the ratio between both occupied sites (tetrahedral and octahedral). All these phenomena are expected to manifest themselves and compete between each other to offer unique properties in $CoFe_2O_4$ thin films. In this paper we report on magnetic properties of thin single crystalline $CoFe_2O_4$ films epitaxially grown on (100) MgO substrate. Despite the complex stoichiometry of cobalt ferrite the introduction of PLD technique has allowed to prepare films with the right composition and exotic properties, different from those typically known in the bulk phase. The reasons for such performance are multiple but mainly due to the following aspects: (a) the growth can be easily achieved in high oxygen pressure to overcome the problem of oxygen deficiency in the films; and (b) the high energy of atoms in the PLD plume can promote the growth process in non-equilibrium materials to some extent.

2. EXPERIMENTAL PROCEDURE

The films have been grown with PLD from polycrystalline $CoFe_2O_4$ target (1 inch of diameter and 5 mm thick). Our PLD setup consists of a vacuum chamber together with a KrF excimer laser (248 nm wavelength). The laser beam is focused with a lens on rotated $CoFe_2O_4$ target positioned at 60 mm from the substrate in order to ablate with an energy density of 1.5 $J.cm^{-2}$. Prior to each growth the vacuum system was evacuated down to base pressure (10^{-6} Torr) with a turbomolecular pump. However during deposition the substrate was heated at a certain temperature (200-800 °C) and a controlled oxygen pressure was supplied to the chamber in order to achieve stoichiometric films. The repetition rate of the laser was maintained at 3 Hz whereas the number of laser shots was adjusted for each experimental run to grow the desirable film thickness in the range 50-500 nm. One polished side (100) MgO substrate has been used for the growth. The choice of MgO is motivated by its very small lattice mismatch to $CoFe_2O_4$ (0.48%), which can promote an epitaxial growth. The deposited films have been investigated using different techniques including structural analyses such as XRD and AFM as well as magnetic measurements performed with torque, VSM and MFM.

3. MAGNETIC ANISOTROPY AND SPIN-REORIENTATION

In the bulk phase $CoFe_2O_4$ exhibits a fully inverted structure where Co ions occupy the octahedral sites whereas Fe ions are equally distributed in both sites (tetrahedral and octahedral). On the other hand the crystallographic structure confers to such material a cubic anisotropy with easy axis parallel to [100]. Now the crucial question arises if it is possible to preserve the bulk properties in our layers. If not what are the sources of anisotropy involved in controlling the magnetic properties. To answer these questions we have performed two different kinds of experiments. In the first set we studied the evolution of magnetic properties versus the film thickness whereas in the second experiment the annealing effect has been investigated. For both cases the films have been prepared at relatively low substrate temperature (200 and 300 °C respectively).

3.1. THICKNESS EFFECT

Fig. 1 shows the in-plane and perpendicular magnetic loops of 60 and 400 nm thick films. In the thinner layer (Fig. 1(a)) the perpendicular loop exhibits a high coercivity (0.6 T) and a large hysteresis despite the significant shearing induced by the demagnetizing field. However the behavior of the in-plane magnetization consists of two regimes. A fast jump with a very small hysteresis appears at low fields whereas a linear increase is noticed at large fields without saturation even at 3 T. The huge difference between the in-plane and out-of-plane loops suggests that the magnetization easy axis is oriented perpendicular to the film plane. However the vertical switching with hysteresis in the in-plane magnetization (Fig. 1(a)) reveals the existence of an additional component of anisotropy oriented parallel to the film plane. Upon increasing the film thickness a drastic change affects the magnetic properties as illustrated by Fig. 1(b).

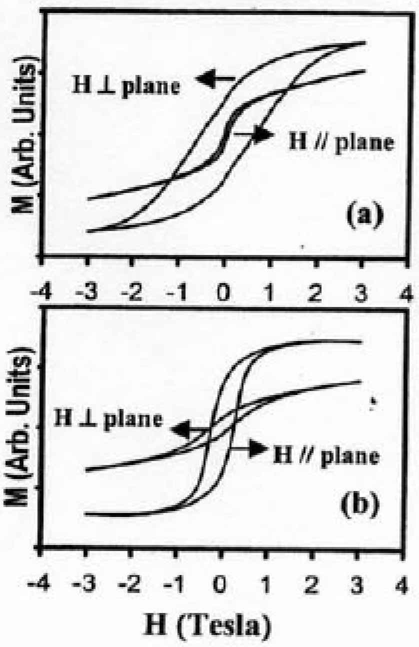

Fig. 1 In-plane and perpendicular hysteresis loops of (a) 60 and (b) 400 nm $CoFe_2O_4$ thick films

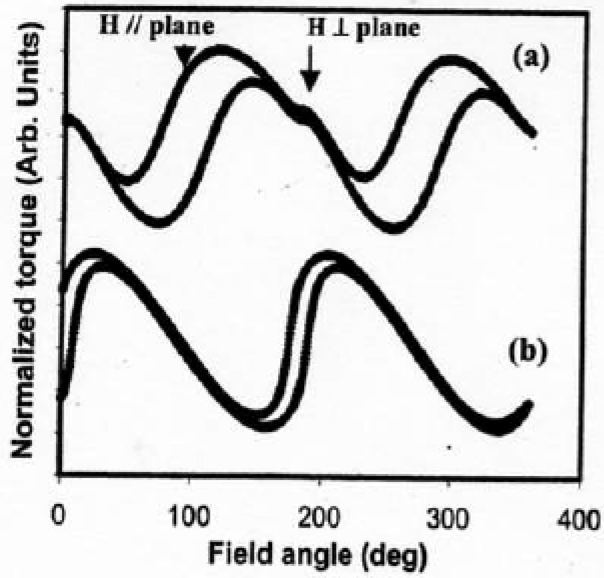

Fig. 2 Out-of-plane torque curves measured at 1.7 T for (a) 60 and (b) 400 nm $CoFe_2O_4$ thick films

The vertical switching of the magnetization and the large hysteresis of the in-plane loop confirm that the film plane becomes the preferential direction of the magnetization. Fig. 1 shows that the orientation of the easy axis is controlled by the film thickness and illustrates the spin-reorientation transition in the layers. Several effects may be responsible for the hysteretic behavior of both the in-plane and perpendicular loops and can be listed as follow. (a) Possible involvement of a cubic anisotropy, which can induce a hysteresis in both directions (in-plane and out-of-plane). This might be related to the influence of the bulk properties (cubic anisotropy). However such possibility is hardly conceivable in our films since the out-of-plane and certain in-plane directions are expected to be equivalent for cubic anisotropy. Consequently no spin-reorientation could result from a cubic anisotropy, which is in complete contradiction to the Fig. 1 revelation. (b) In the case of uniaxial anisotropy the hysteretic behavior of the magnetic loops suggests two eventual options about the film structure. (i) The layers could be not oriented and could consist of crystals with random easy axes. (ii) The films could be grown epitaxial but for that particular case the in-plane and perpendicular anisotropies must have different sources and be acting or prevailing in two different regions of the layers. If this is not the case their superposition will lead to one effective anisotropy oriented parallel or perpendicular to the film plane without any hysteresis in the hard direction. In Fig. 2 the torque curves of 60 and 400 nm thick films are presented. During such measurement a constant rotating field of 1.7 T was applied to the sample and the magnetic torque was recorded for each rotation step of the magnet (1°). At 0 and 90° the field orientation lies along the normal and parallel directions to the film plane respectively. In contrast to the cubic anisotropy of the bulk the torque curve periodicity (180°) of the thinner layer (Fig. 2(a)) is a clear indication of the domination of oriented uniaxial anisotropy. Moreover the existence of a large rotational hysteresis around 90° reveals two important points. (a) The anisotropy field H_k in such film is much higher than the measurement field (1.7 T). (b) The easy axis is oriented perpendicular to the film plane due to the reversible and irreversible (hysteresis) behaviors of the magnetization when the field direction approaches the easy and hard axes respectively. It is important to point out the existence of an anomalous effect, which consists of a small kink in the torque curve. This kink exhibits a periodic behavior (180°) and is localized at field angles close to the normal to the film plane (0 and 180°). The origin of the kink could be a small uniaxial in-plane anisotropy responsible of the hysteretic vertical switching in the in-plane magnetization of Fig. 1(a). Further increase of the film thickness leads to a surprising result as illustrated by Fig. 2(b). Despite a persistence of rotational hysteresis around 90° the out-of-plane anisotropy vanishes whereas the in-plane component arises and takes the lead. The torque measurement confirms the existence of two uniaxial anisotropies competing each other. Moreover the existence of two separated components of rotational hysteresis indicates a double switching of the magnetization, which can be realized only if both anisotropies (in-plane and perpendicular) are prevailing in two different regions of the film. Additional analyses including in-plane torque and magnetic hysteresis loops measured at different directions in the film plane reveal an isotropic behavior of the in-plane magnetization. It is clear that the magnetic properties of our films are controlled by two uniaxial anisotropies (oriented perpendicular and in-plane randomly), which prevail in two different regions of the layers. The crucial questions are what are the sources of both anisotropies and in which film region is each component dominant. From the thickness dependence of the torque and magnetic loop the two following points have been established. (a) The critical thickness t_c for the spin-reorientation transition was estimated to be 300 nm. (b) The out-of-plane anisotropy seems to prevail in the bottom of the film (region close to the film-substrate interface) whereas the in-plane component is leading at the top of the film.

3.2. ANNEALING EFFECT

Fig. 3(a) shows the in-plane and perpendicular magnetic loops of as-deposited 300 nm thick film grown at 200 °C. Although hysteresis exists in both loops the coercivity and remanence are considerably reduced in the in-plane magnetization. However the perpendicular loop exhibits a large coercivity (0.35 T) and requires a low saturation field. By a simple comparison it is easy to confirm that the anisotropy is oriented perpendicular to the film plane. After being annealed in an oven at 500 °C for 3 hours the sample has been measured and the result is presented in Fig.

3(b). It is surprising to see a drastic change in the orientation of the anisotropy. The large hysteresis and the vertical switching in the in-plane loop suggest that the easy axis becomes aligned parallel to the film plane. It is important to point out the following effects in our layers. (a) In the as-deposited films the anisotropy is always perpendicular regardless the film thickness (50-300 nm) but shows a considerable reduction for thicker films. (b) No spin-reorientation has been observed in annealed thinner films (below 150 nm) despite a substantial reduction of the perpendicular loop hysteresis. (c) Annealing at higher temperatures (above 700 °C) creates a large interdiffusion and destroys the magnetic properties of the film. In order to establish the acting anisotropies we performed torque measurements before and after annealing.

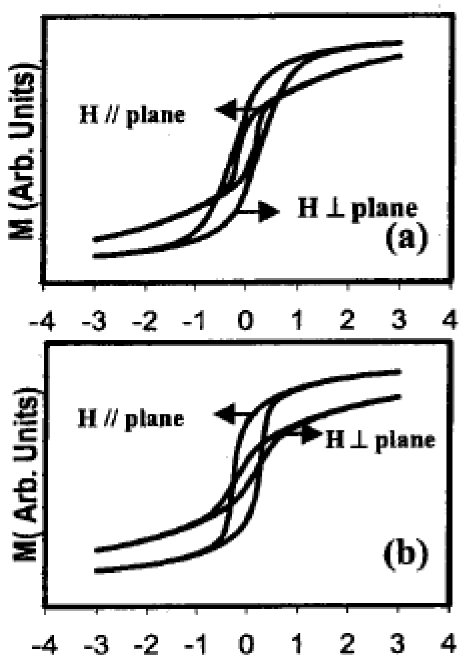

Fig. 3 In-plane and perpendicular hysteresis loops of 300 nm thick $CoFe_2O_4$ film in (a) as-deposited and (b) annealed states

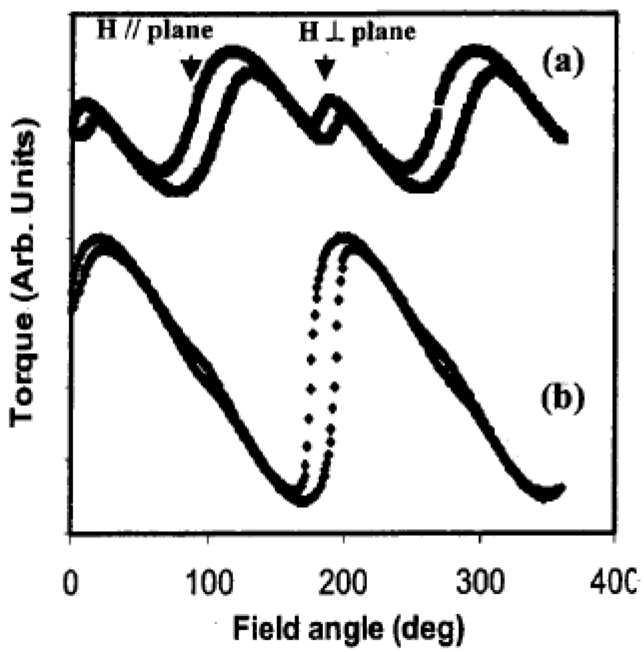

Fig. 4 Torque curves measured at 1.7 T for 300 nm thick $CoFe_2O_4$ film in (a) as-deposited and (b) annealed states

Typical torque curves of 300 nm thick film measured before and after annealing are presented in Fig. 4. The torque curve of as-deposited film illustrates the existence of two uniaxial anisotropies with two different orientations. The large component of anisotropy is out-of plane whereas the smallest one shows an in-plane alignment. Annealing produces a drastic change in the torque curve as illustrated by Fig. 4(b). The large perpendicular anisotropy vanishes and only a small hysteresis is left around 90° whereas the in-plane component shows a substantial increase after annealing. Fig. 4(b) shows a clear evidence that the in-plane anisotropy takes the lead in annealed film, which is in complete agreement with the hysteresis loop measurements (see Fig 3). In order to understand the origin of such spin-reorientation it is important to establish the sources of anisotropy contributing to the magnetic properties of the films. Structural analyses are necessary to clarify the observed effects and to support the magnetic measurements.

4. STRUCTURAL ANALYSES

Fig. 5 shows the typical topography and magnetic domain structure of our films imaged by AFM/MFM using the tapping-lift mode. The measurement tip consists of Si coated with CoCr thin film (30 nm). The imaging was performed in the demagnetized (as-prepared) state of the sample whereas the tip was vertically magnetized. The morphology of the film exhibits a single crystal structure with an extremely smooth surface (see Fig. 5(a)). The surface roughness was estimated to be as low as 0.23 nm. On the other hand the magnetic image (Fig. 5(b)) reveals magnetic domains with a cluster-like structure. For thinner films the magnetization orientation in each cluster is confined up or down due to the strong perpendicular anisotropy. However in thicker films the situation is more complicated due to the contribution of both anisotropies (in-plane and out-of-plane) to the stray field imaged by MFM.

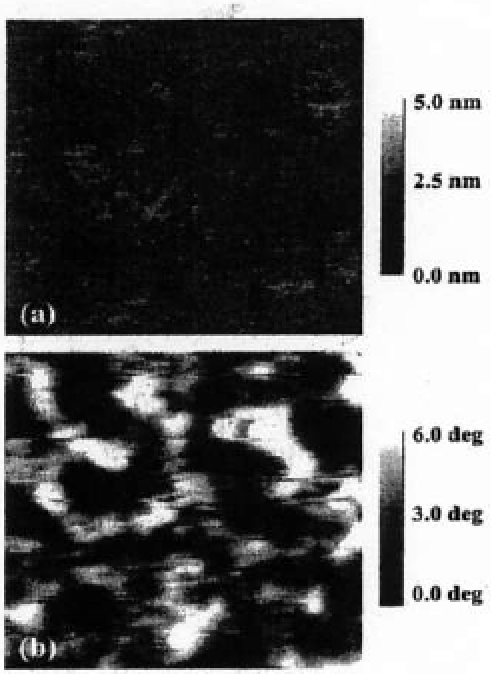

Fig. 5 (2μm×2μm) (a) AFM and (b) MFM images of as-grown $CoFe_2O_4$ film

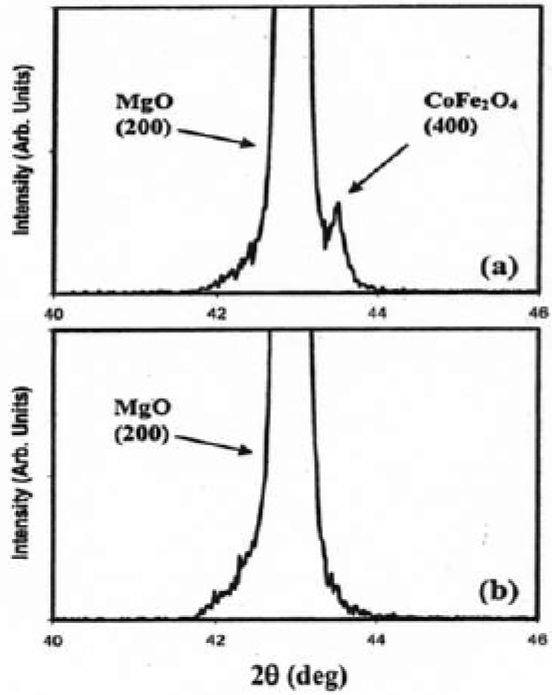

Fig. 6 $\theta/2\theta$ scan of (a) 60 and (b) 400 nm $CoFe_2O_4$ thick films

No stripe structure has been observed in our films even in those with a strong perpendicular anisotropy. It is important to point out that stripe structure exists in films with a low coercivity and a pronounced shoulder at the nucleation field [4-7], which is unlikely to be the case in our samples. Fig. 6 shows the XRD spectra ($\theta/2\theta$ scan) of 60 and 400 nm thick films. It is important to notice the following effects in all spectra regardless the film thickness. (a) $CoFe_2O_4$ is the unique phase composing our layers. (b) All the reflections are parallel to the (100) texture.

Moreover the very narrow rocking curve (0.16° as FWHM) is a clear confirmation of highly oriented films. However Fig. 6 shows a significant dependence of the peak position of $CoFe_2O_4$ on the film thickness. For thinner film (60 nm) the (400) peak of cobalt ferrite appears to be well separated from the substrate peak whereas upon increasing the film thickness it is considerably shifted to overlap with the (200) MgO reflection. The shift of the (400) peak in Fig. 6 illustrates an important lattice relaxation in the film. For example changing the film thickness from 60 to 240 nm induces an increase in the lattice parameter normal to the film plane ($a_\perp$) from 8.31 to 8.35 Å. The annealing effect may also induce an important lattice relaxation as illustrated by Fig. 7. In the as-deposited film both reflections relative to the film and substrate are well separated whereas in the annealed state the (400) $CoFe_2O_4$ peak is significantly shifted to become a shoulder of the (200) substrate reflection. Since the only planes reflecting in the θ/2θ scan configuration are those parallel to the film plane additional measurements are necessary in order to estimate the lattice parameter parallel to the film plane ($a_{//}$) and to establish whether the stress is tension or compression in our films. Fig. 8 shows the annealing effect on the (511) $CoFe_2O_4$ peak in the asymmetric scan configuration. The shift of the (511) peak is a good illustration of the lattice relaxation upon increasing the film thickness or annealing the layer.

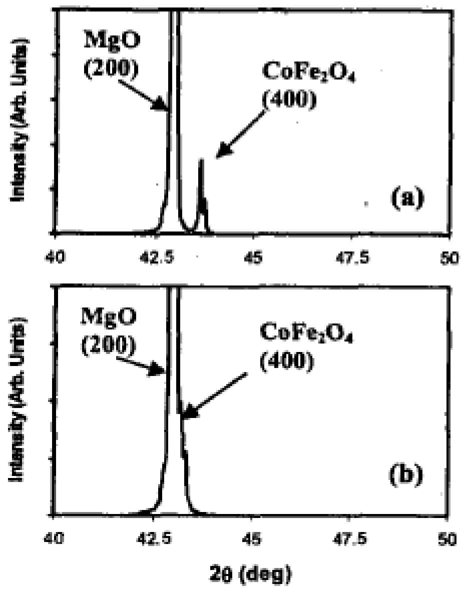

Fig. 7 θ/2θ scan of $CoFe_2O_4$ film in (a) as-grown and (b) annealed states

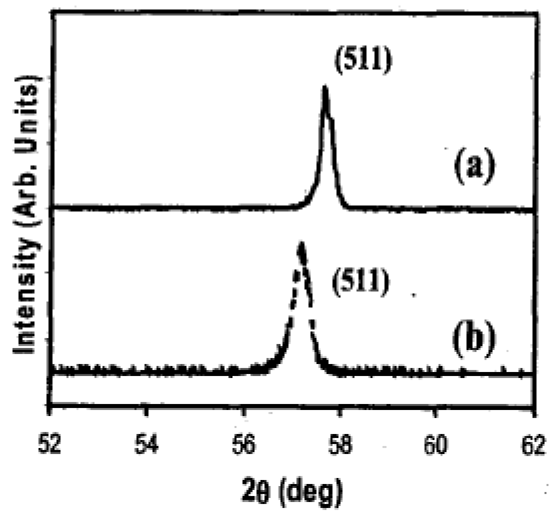

Fig. 8 Asymmetric scan for (511) $CoFe_2O_4$ film in (a) as-grown and (b) annealed states

By combining both scans (symmetric and asymmetric) $a_{//}$ was determined for each film thickness as well as for annealed sample and the following effects have been established. (a) The large value of $a_{//}$ in the thinner film (8.45 Å) in comparison to the bulk value (8.38 Å) [8] is a clear confirmation that the stress is tension rather then compression. (b) Upon annealing or increasing the film thickness the change in $a_{//}$ reveals an important relaxation of the lattice towards the bulk. Such result suggests that the stress is considerably diminished in annealed and thicker films.

5. DISCUSSION

The single crystal structure of our films denies the involvement of any anisotropy related to the microstructure such as the shape of columns or grains. Consequently magnetocrystalline and stress could be the unique sources of anisotropy. The importance of stress anisotropy is related to the lattice state in the film and has been investigated using XRD. Because of the large negative magnetostriction of $CoFe_2O_4$ the tensile stress may induce a huge anisotropy aligned perpendicular to the film plane [9]. The experimentally obtained magnetic behavior can be explained as follows: Because of the perpendicular orientation of stress anisotropy the uniaxial in-plane component is certainly magnetocrystalline related. The in-plane magnetocrystalline anisotropy exhibits a constant magnitude with a random distribution of the easy axis as confirmed by magnetic measurements in very thick films with no stress. At small thickness the stress induces a huge perpendicular anisotropy, which dominates the in-plane magnetocrystalline and stabilizes the magnetization out-of-plane. However upon annealing or increasing the film thickness the stress is progressively released as illustrated by XRD analyses and the in-plane magnetocrystalline anisotropy becomes more competitive. For large thickness the film consists of two regions with two different orientations of anisotropy. The bottom region close to the film-substrate interface is dominated by the perpendicular stress anisotropy whereas at the top of the film the in-plane magnetocrystalline takes the lead. Such image seems to predict our magnetic results and may well explain the spin-reorientation phenomenon reported earlier. The orientation of the easy axis is governed by the magnitude of both anisotropies as well as by the proportion of the film volume controlled by each component. By annealing or increasing the film thickness the proportion of the film volume free of stress and dominated by magnetocrystalline anisotropy grows and leads to a change in the orientation of the easy axis from the normal to the parallel direction to the film plane.

In conclusions, the spin-reorientation illustrated in epitaxial $CoFe_2O_4$/MgO layers upon annealing or increasing the film thickness is the result of competition between stress and magnetocrystalline anisotropies.

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