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Spin reorientation in single-crystal $CoFe_2O_4$ thin films

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Abstract
Reorientation of magnetic anisotropy has been observed in single-crystal $CoFe_2O_4$ thin films deposited on (100) MgO substrate by pulsed laser deposition (PLD). The as-grown film exhibits a perpendicular anisotropy whereas after annealing the magnetization easy axis switches to be parallel to the film plane. The origin of such spin reorientation is explained in terms of competition between stress and magnetocrystalline anisotropies. The as-prepared film is under tensile stress, which induces a huge perpendicular uniaxial anisotropy dominating the in-plane magnetocrystalline component. Annealing releases the stress by relaxing the film lattice. Consequently, the perpendicular stress anisotropy is considerably reduced and magnetocrystalline anisotropy prevails, leading to an in-plane alignment of the easy axis.

(Some figures in this article are in colour only in the electronic version)

Despite the considerable progress achieved in magnetism, anisotropy in magnetic materials remains one of the fascinating research subjects motivated by scientific curiosity as well as by technological demands. In spin-reorientation phenomena several anisotropies are involved and compete with each other for the control of magnetic properties. In contrast to the bulk magnetism mainly dominated by volume effects, other sources of anisotropy are enhanced in low dimension systems and may contribute to their properties. For example, the broken symmetry in ultra-thin films may induce a huge anisotropy, which can easily overcome the shape anisotropy and stabilize the magnetization easy axis out of plane [1, 2]. Such surface anisotropy only prevails if the film thickness does not exceed a few monolayers [3]. In a recent work we have reported the existence of an in-plane reorientation of anisotropy in obliquely sputtered metallic thin films [4]. In such a structure the anisotropy is aligned along the film

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plane, but depending on the film thickness the easy axis can be parallel or perpendicular to the longitudinal direction (projection of the deposition direction in the film plane). The origin of such spin reorientation is mainly the low magnetocrystalline anisotropy, which is dominated by the shape of columns and nuclei at large and low thicknesses respectively.

Hard ferrite materials such as hexagonal ($BaFe_{12}O_{19}$) and cubic ($CoFe_2O_4$) are chemically stable and attractive for microwave and magnetic recording applications. Recently $CoFe_2O_4$ has been successfully integrated as the pinning layer in spin valve structures with large magneto-resistance [5, 6]. Beside the technological importance of cobalt ferrite, rich physics is expected in artificial structures based on this material for several reasons. (1) $CoFe_2O_4$ exhibits a high cubic magnetocrystalline anisotropy and large magnetostriction in the bulk form. (2) 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 properties are expected to manifest themselves and compete with each other in the thin-film form.

In this paper we report on the observation of spin reorientation in epitaxial $CoFe_2O_4$ thin films. The as-deposited layer exhibits a perpendicular anisotropy whereas after being annealed the easy axis switches to become parallel to the film plane. Our layers have been grown by pulsed laser deposition (PLD) on (100) MgO. Such a substrate is expected to be a perfect template to achieve epitaxial films due to its cubic structure with a very low lattice mismatch to the bulk cobalt ferrite (0.47%). More details about the film preparation are reported in [7]. During the growth the substrate was heated at 200 °C and a controlled oxygen pressure of 50 mTorr was supplied to the vacuum chamber. However, the repetition rate and the energy density of the laser were maintained at 3 Hz and 1.5 J cm^{-2} respectively. Thin and thick films (50–350 nm) have been prepared by adjusting the number of laser shots.

Figure 1(a) shows the in-plane and perpendicular magnetic loops of as-deposited 300 nm thick film, grown in the conditions reported before. The measurements have been performed using a vibrating sample magnetometer (VSM) with 3 T as maximum field. Although hysteresis exists in both loops the coercivity and remanence are considerably reduced in the in-plane magnetization. However, despite the shearing induced by the demagnetizing field the perpendicular loop exhibits a large coercivity (0.35 T) and requires a low saturation field. With a simple comparison it is easier to confirm that the anisotropy is oriented perpendicular to the film plane. After being annealed in an oven at 500 °C for 3 h the sample has been measured and the result is presented in figure 1(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 of the film thickness (50–350 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. In such measurements a constant rotating field of 1.7 T was applied to the sample. At 0° and 90° the field lies along the normal and parallel directions to the film plane respectively. Typical torque curves of 300 nm thick film measured before and after annealing are presented in figure 2. In contrast to the cubic anisotropy of the bulk the torque curve of as-deposited film illustrates the existence of two uniaxial anisotropies with two different orientations. The large component of the anisotropy is out of plane whereas the smallest one shows an in-plane alignment. Moreover, the existence of rotational hysteresis at field directions parallel and perpendicular to the film plane reveals

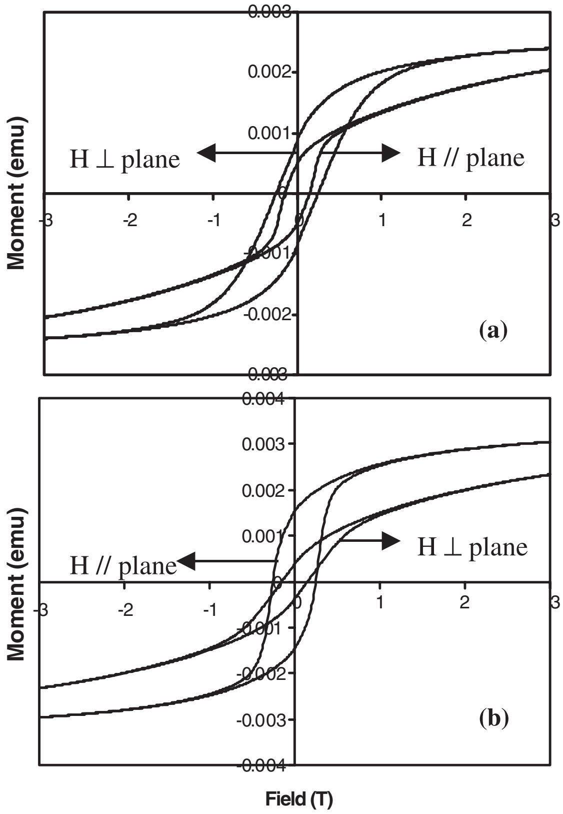

Figure 1. In-plane and perpendicular hysteresis loops of 300 nm thick $CoFe_2O_4$ film in (a) as-deposited and (b) annealed states.

an irreversible mechanism related to the magnetization switching due to the high anisotropy field of each component in comparison to the measurement field (1.7 T). On the other hand, the angular separation between the two components of rotational hysteresis suggests that both anisotropies are acting in two different regions of the film. Annealing produces a drastic change in the torque curve as illustrated by figure 2(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. Figure 2(b) shows clear evidence that the in-plane anisotropy takes the lead in annealed film, which is in complete agreement with the hysteresis loop measurements reported before. 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. The analyses of structure and composition are necessary to clarify the observed effects and to support the magnetic measurements. X-ray photoelectron spectroscopy (XPS) measurement (depth profile) has been performed to establish the film composition before and after annealing. The result illustrates a constant chemical composition in the film and denies any contamination during the annealing process. Figure 3 shows the microstructure and magnetic domains of as-deposited 300 nm thick film measured by magnetic force microscopy (MFM). The topography of the film consists of single-crystal structure with extremely smooth surface. The surface roughness was estimated at 0.24 nm. The magnetic image (figure 3(b)) shows a cluster-like structure where the magnetization is confined up and down due to the domination of the out-of-plane component of anisotropy. However, annealing induces an increase of the roughness (0.6 nm) and a significant reduction of the contrast in

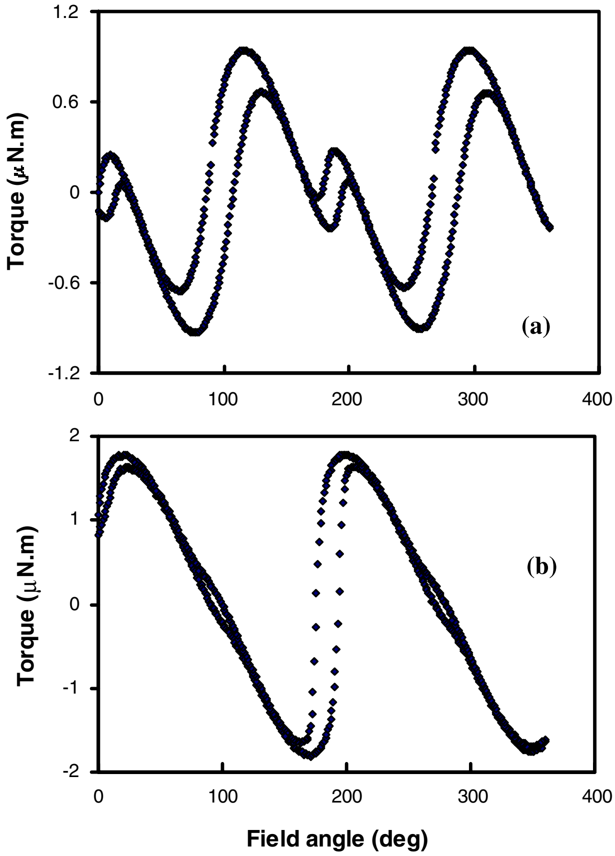

Figure 2. Torque curves measured at 1.7 T for 300 nm thick $CoFe_2O_4$ film in (a) as-deposited and (b) annealed states.

the magnetic domain structure. The latter effect can be understood from the weakness of the out-of-plane anisotropy in annealed film. The single-crystal structure of the films suggests the absence of any anisotropy related to the shape of grains or columns. Consequently, only magnetocrystalline and stress anisotropies could be involved in the control of the film properties. Figure 4 shows the x-ray diffraction (XRD) measurement ($\theta/2\theta$ scan) of $CoFe_2O_4$ film before and after annealing. Both spectra reveal a single $CoFe_2O_4$ phase in the film with reflections parallel to the (100) texture. Moreover, the sharpness of the rocking curve (0.12° full width at half maximum) confirms highly oriented films. However, the major difference between both spectra of figure 4 consists of the (400) $CoFe_2O_4$ peak position. 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. From figure 4 annealing induces a significant increase of the lattice parameter normal to the film plane ($a_\perp$) from 8.287 to 8.375 Å. In order to determine the stress nature (tension or compression) we performed an asymmetric scan of the (511) $CoFe_2O_4$. Figure 5 also reveals a shift of the (511) peak position after annealing, which is indicative of a stress relaxation in the film. The interplanar spacing (d) of the (511) plane is related to both lattice parameters (normal ($a_\perp$) and parallel ($a_\parallel$) to the film plane). By determining $a_\perp$ and d from symmetric and asymmetric scans respectively, $a_\parallel$ was estimated to be 8.522 Å. Such a value is larger than that typically known for the bulk (8.38 Å) [8], indicating that the film is under tension in the as-deposited state. It is important to point out

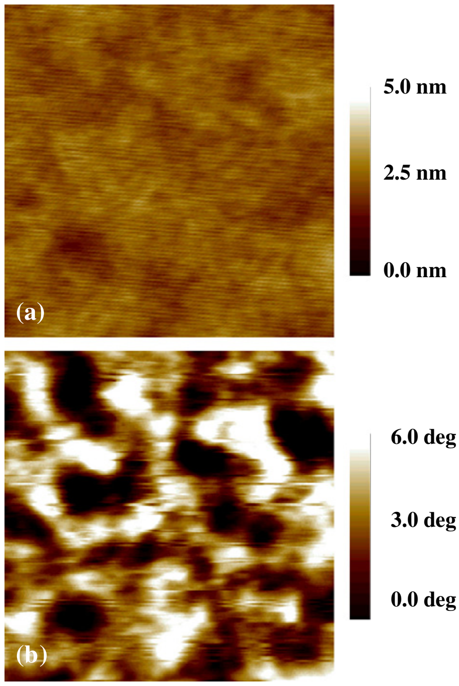

Figure 3. (2 μm × 2 μm) (a) AFM and (b) MFM images of as-grown $CoFe_2O_4$ film.

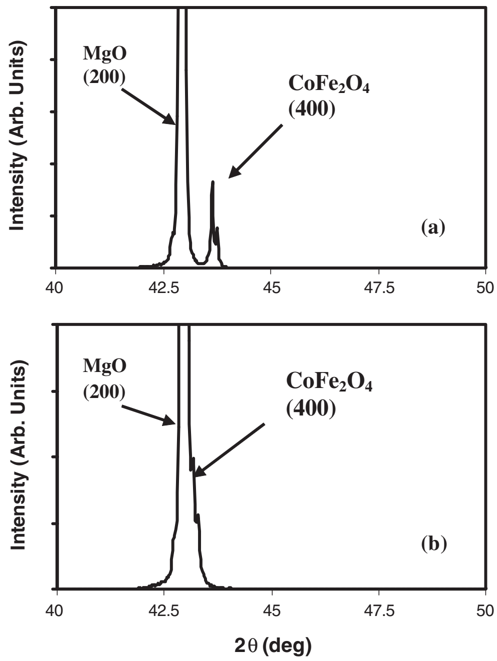

Figure 4. $\theta/2\theta$ scan of $CoFe_2O_4$ film in (a) as-grown and (b) annealed states.

that in magnetostrictive materials the magneto-elastic energy (anisotropy) associated with the strain is given by $K_s = -3\sigma\lambda/2$. λ is the magnetostriction constant and σ is the stress, which is proportional to the strain ε via the Young modulus Y. Since λ is negative for cobalt ferrite [9], two different situations are possible in our (100) $CoFe_2O_4$ films. (1) If the stress parallel to the

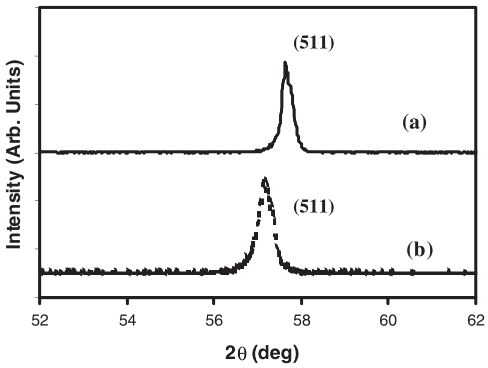

Figure 5. Asymmetric scan for (511) $CoFe_2O_4$ film in (a) as-grown and (b) annealed states.

film plane (in the directions [010] and [001]) is a tension, the strain ε will be positive, leading to positive K_s, which implies a uniaxial anisotropy of stress perpendicular to the film plane. (2) If the stress is a compression, ε will be negative ($K_s < 0$), generating a biaxial in-plane anisotropy. In the as-deposited film the tensile stress illustrated by XRD induces a considerable strain, estimated at 1.6%. In the cubic bulk phase of cobalt ferrite the magnetostriction constant and the Young modulus in the [100] direction are estimated to be $\lambda_{[100]} = -5.9 \times 10^{-4}$ and $Y_{[100]} = 1.5 \times 10^{12}$ dynes cm^{-2} [10]. Based on such values the stress anisotropy in our as-deposited film is estimated at $K_s = 2 \times 10^6$ J m^{-3}. Our results can be explained as follows. The existence of large hysteresis in the in-plane loops suggests that magnetocrystalline anisotropy is in-plane aligned but randomly oriented as confirmed by the in-plane torque curves. In the as-deposited state the estimated perpendicular stress anisotropy is very strong and can easily overcome the in-plane magnetocrystalline component ($K_1 = 3 \times 10^5$ J m^{-3}), leading to an out-of-plane easy axis of the magnetization. The lattice strain is non-uniform in the film and is expected to be strong in the region close to the interface whereas the top of the film is supposed to be more relaxed. Based on this image, the film can consist of two regions with two different orientations of anisotropy: the bottom region, where the perpendicular stress anisotropy dominates the in-plane magnetocrystalline anisotropy, and the top region of the film, where the stress is weak and the in-plane magnetocrystalline anisotropy takes the lead. In the as-deposited film the proportion of the film volume dominated by stress is large, resulting in perpendicular effective anisotropy as shown by magnetic measurements. However, after annealing, the film volume free of stress becomes larger and the in-plane effective anisotropy increases, leading to a spin reorientation. Based on such study, $CoFe_2O_4$/MgO films seem to be a model system for competing stress and magnetocrystalline anisotropies.

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