Thermodynamic conditions during growth determine the magnetic anisotropy in epitaxial thin-films of La$_{0.7}$Sr$_{0.3}$MnO$_3$

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Received 3 March 2016, revised 9 June 2016
Accepted for publication 20 June 2016
Published 14 July 2016

Abstract

The suitability of a particular material for use in magnetic devices is determined by the process of magnetization reversal/relaxation, which in turn depends on the magnetic anisotropy. Therefore, designing new ways to control magnetic anisotropy in technologically important materials is highly desirable. Here we show that magnetic anisotropy of epitaxial thin-films of half-metallic ferromagnet La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) is determined by the proximity to thermodynamic equilibrium conditions during growth. We performed a series of x-ray diffraction and ferromagnetic resonance (FMR) experiments in two different sets of samples: the first corresponds to LSMO thin-films deposited under tensile strain on (0 0 1) SrTiO$_3$ by pulsed laser deposition (PLD; far from thermodynamic equilibrium); the second were deposited by a slow chemical solution deposition (CSD) method, under quasi-equilibrium conditions. Thin films prepared by PLD show fourfold in-plane magnetic anisotropy, with an overimposed uniaxial term. However, the uniaxial anisotropy is completely suppressed in the CSD films. This change is due to a different rotation pattern of MnO$_6$ octahedra to accommodate epitaxial strain, which depends not only on the amplitude of tensile stress imposed by the STO substrate, but also on the growth conditions. Our results demonstrate that the nature and magnitude of the magnetic anisotropy in LSMO can be tuned by the thermodynamic parameters during thin-film deposition.

Keywords: magnetic anisotropy, thin-film deposition, ferromagnetic resonance

(Some figures may appear in colour only in the online journal)
(α = b > c) imposed by the cubic substrate to the incommensurate rhombohedral lattice of bulk LSMO induces an equal in-(out-) phase rotation of the MnO$_6$ octahedra along the a-(b-) axis, and no rotation along the c-axis (a’ a c’$^0$ in the Glazer notation [14]). Sandiumenge et al [3] proposed a complex relaxation pattern in which several phases with different symmetry can be distinguished in epitaxial LSMO below 25 nm. These authors identified a critical thickness of ≈2 nm for the build up of a shear strain field, which induces a rhombohedral twinned structure and a progressive compression of the c-axis up to ≈10 nm. Beyond this thickness, an elastic deformation of the lattice without any perturbation of the octahedral tilting sets up to ≈25 nm. Vailionis et al [15] confirmed that the mechanism of strain relaxation changes along the film thickness, due to a combined effect of symmetry mismatch close to the interface, and lattice mismatch in the ‘bulk’ of the film. They showed that in the first ≈two unit cells, stress suppresses octahedral rotations and expands the c-axis parameter; farther away from the interface, tilting of MnO$_6$ octahedra reduce the c-axis parameter consistent with in-plane tensile strain.

An important question is whether this complex relaxation pattern is intrinsic to the accommodation of biaxial tensile stress in LSMO, or if it can be modified by growing the films under very different conditions, thus allowing the system to explore different relaxation paths. After all, previous studies were performed on samples synthesized by PLD and sputtering, far from thermodynamic equilibrium. Here we describe a comparative x-ray diffraction (XRD) and ferromagnetic resonance (FMR) study of LSMO thin films deposited on STO by pulsed laser deposition (PLD; far from thermodynamic equilibrium), and by a slow chemical deposition method (CSD; close to thermodynamic equilibrium). Our results demonstrate that magnetic anisotropy in LSMO depends on the conditions during film growth. As a result, a different pattern of rotation of MnO$_6$ octahedra is accommodated in epitaxial films synthesized by CSD.

2. Experimental details

Thin films of LSMO of different thicknesses were grown on (0 0 1) TiO$_2$-terminated SrTiO$_3$ (STO) substrates. For the PLD films we used an excimer laser (F-Kr, 248 nm) operating at 5 Hz and a fluence of 0.8 J cm$^{-2}$. The films were deposited at 800 °C and 200 mTorr of O$_2$. For chemically grown films (CSD), a precursor solution was spun-coated on similar substrates, and annealed at high temperature, as described in [16]. The growth conditions in both methods were carefully optimized in order to obtain the highest crystalline quality and to minimize the cation interdiffusion at the interface, as observed in [17, 18]. The thickness of both types of films was determined by x-ray reflectivity and TEM analysis of cross-section lamellae. X-band ($\omega$/2$\pi$ ≈ 9.4 GHz) FMR experiments were performed in a Bruker-X spectrometer at different temperatures, with the magnetic field applied rotating parallel to the film-plane.

3. Results and discussion

In figure 1 we show a summary of structural results representative of the quality of the samples studied in this work. X-ray reciprocal space maps (RSM) around the (1 0 3) reflection of the perovskite for ≈20 nm thick films show that they grow with in-plane lattice parameters well matched to the STO substrate, and without evidence of lattice relaxation (figures 1(a) and (c)). This is true for every film studied in this work, irrespective of the thickness or the deposition method (CSD or PLD). A high-resolution cross-section TEM image of a thin film of LSMO synthesized by CSD is shown in figure 1(b). The image is representative of the good crystalline quality and abrupt interfaces of all the CSD films reported in this work.

The dependence of the lattice parameters on the thickness is shown in figure 1(d). The c-axis length shows a non-monotonic dependence with the film thickness, passing through a minimum between 10 and 15 nm. Similar behavior was previously reported by Sandiumenge et al [3] for LSMO films synthesized by rf-sputtering. These authors suggested that $t_{\text{cr}}$ marks a crossover from a monoclinic to a homogeneously strained rhombohedral phase. Our results show that the existence of this minimum occurs for PLD and CSD samples, therefore suggesting a universal relaxation mechanism depending only on the total strain imposed by the substrate. However, the incommensurability of rhombohedral LSMO to the cubic (0 0 1) surface of STO has been suggested to result in an orthorhombic symmetry with a monoclinic distortion (P$2_1$/m) [13]. In order to identify the crystal structure in our films, we have performed a careful XRD analysis around different half order reflections. (H2/ I2, K2/ L2) reflections are characteristic of a monoclinic or triclinic symmetry, with $H = K = L$ being an extinction for the rhombohedral R-3c group. For the 20 nm thick sample prepared by PLD, we observed a clear signal around the (1/2, 1/2, 1/2) and (1/2, 1/2, 3/2) reflections, as shown in figure 2. These are consistent with a rhombohedral...
(R-3c) phase, with a monoclinic distortion. Although the (1/2, 0, 1) and (1, 0, 1/2) reflections have not been observed in our films, an orthorhombic phase cannot be completely discarded due to the small intensity characteristic of these reflections, particularly in thin films. On the other hand, half order reflections at $L = 3/2$ and absence at $L = 1/2$ in films prepared by CSD are consistent with a dominant rhombohedral (R-3c) phase. Also, from the analysis of in-plane (2 0 0) and (1 1 0) peaks, a fully structural coherence with the substrate is observed along the whole thickness of the films prepared by CSD (see figure 3). No satellite peaks or diffuse scattering associated to twinnings or strong mosaicity are observed in these samples.

Given the equal in-plane tensile stress imposed by the substrate along the $a/b$ directions, these structural results therefore suggest a different rotation pattern of the MnO$_6$ octahedra to accommodate the tensile stress in samples synthesized by CSD with respect to PLD. We want to remark that this result is reproducible in different samples prepared from CSD under similar conditions.

The structural difference reported in figure 2 is also manifested in the magnetic properties of the CSD and PLD films (see figure 4). The magnetic moment at saturation and the Curie temperature ($T_C$) of $\approx$20 nm thick films are close to the bulk values (590 emu cm$^{-3}$ and 350 K) and are very similar in both sets of samples, discarding any significant variation in their stoichiometry. However, the coercive field ($H_C$) shows a completely different behavior: while the samples synthesized by PLD show a very small, bulk-like, $H_C \approx 50–100$ Oe, it increases by an order of magnitude in the films synthesized by CSD. Therefore, the change in $H_C$ probably implies different magnetocrystalline anisotropy between the CSD and PLD films. This could be due to differences in the strength of Mn-O-Mn exchange interactions along different directions of the crystal, as a result of the structural differences identified before. However, to give a definitive proof of this subtle structural distortion in thin-films prepared by different methods is very challenging using conventional laboratory XRD equipment.

To avoid this difficulty, the evolution of the structural parameters with thickness was studied indirectly by ferromagnetic resonance. FMR is a technique very sensitive to small variations in the magnitude of the different magnetic anisotropy terms. Different rotation patterns of the MnO$_6$ octahedra along different directions of the crystal will change the orbital overlap and, through spin–orbit coupling also change the magnetocrystalline anisotropy of the films. We will show that these changes measured by FMR can be correlated with the structural distortions in the films.

The angular dependence of the resonance field ($H_R$) in a FMR experiment can be evaluated at the magnetization equilibrium angles, $\theta_0$ and $\phi_0$ for the different orientation of the magnetic field $[19]$

$$\left( \frac{\omega}{\gamma} \right)^2 = \frac{1}{M^2 \sin^2 \theta} \left[ \frac{\partial^2 F}{\partial \theta^2} \frac{\partial^2 F}{\partial \phi^2} - \left( \frac{\partial^2 F}{\partial \theta \partial \phi} \right)^2 \right]_{\theta_0, \phi_0}$$

(1)

where $\omega$ is the angular frequency, $M$ is the saturation magnetization, $F$ is the free energy of the system and $\gamma = g \mu_B / h$, where $g$ is the gyromagnetic factor and $\mu_B$ is the Bohr magneton. Based on the structural results, three different anisotropy terms were included in the free energy expression: a biaxial in-plane anisotropy constant $K_4^{IP}$, an in-plane uniaxial...
anisotropy constant $K_u$, and a perpendicular out-of-plane anisotropy constant $K_{\text{out}}$ along [0 0 1] [20], to account for possible contribution from the magnetocrystalline anisotropy [20, 21], interface effects [22], domain shape [23], or interfacial stress [24]:

$$F = -\mathbf{H} \cdot \mathbf{M} + 2\pi M^2 \cos^2 \theta - \frac{K_{\text{IP}}}{4} \sin^4 \theta \sin^2 2\phi$$

$$+ K_{\text{out}} \cos^2 \theta + K_u \sin^2 \theta \cos^2 (\phi - \frac{\pi}{4})$$

(2)

where the first and second terms correspond to the Zeeman and demagnetization energy, respectively. The $\theta$ and $\phi$ are the polar and azimuthal angles of the magnetization vector, according to the scheme of figure 5. In this way the values of $K_{\text{IP}}$, $K_u$, and $K_{\text{out}}$ can be determined from fittings of experimental $H_r(\theta, \phi)$ curves by solving self-consistently equations (1) and (2) [25].

Following the formalism explained above, the thickness dependence of the magnetocrystalline anisotropy in our films was obtained from FMR experiments with $H$ rotating in the plane of the films, i.e. $\phi_H = 0$–360°, $\theta_H = 90°$ and also perpendicular to the film, i.e. $\theta_H = 0°$. The experiments were performed at 200 K, except for the thinner samples, which were taken at 150 K to ensure that the samples are completely magnetized at the resonance field. The FMR spectra show a single Lorentzian line in all cases, except for thinner CSD films (see figure 5). In this case two broad overimposed lines precludes the accurate analysis of their resonance field, so we excluded these samples from the discussion.

The angular dependence of $H_r(\phi_H, \theta_H = 90°)$ is shown in figures 6 and 7. The resonance condition in this configuration is also a function of the perpendicular magnetic anisotropy with respect to the applied field at saturation. Therefore, the different in-plane and out-of-plane contributions to the magnetocrystalline anisotropy can be obtained from the in-plane measurements reported in these figures. All samples show a clear biaxial anisotropy with the easy axis along the (1 1 0) direction of STO (the diagonal directions of the (0 0 1) substrate), and the hard axis coinciding with the (1 0 0) directions of STO (the sides of the substrates), which is in agreement with previous reports [26, 27]. Note that contrary to magnetization, in a FMR experiment the maximum and minimum of $H_r$ mark the hard and easy magnetization axis directions, respectively.

Previous FMR and torque magnetization experiments in single crystals of LSMO showed a uniaxial in-plane magnetic anisotropy [28, 29]. These experiments are not influenced by any external stress, and therefore they reflect the pure magnetocrystalline anisotropy in LSMO. On the other hand, the crystalline anisotropy depends on the interatomic distance, and therefore the magnetoelastic contribution to the anisotropy is expected to be important in thin films due to epitaxial matching to the substrate. If the magnetostriction, $\lambda$, is assumed to be isotropic, the free energy per unit volume as a function of the tension, $\sigma$, is [30]:

$$F_\sigma = -\frac{3}{2} \lambda \sigma \cos^2 \Theta$$
where Θ is the angle between the spontaneous magnetization and the direction where the stress is applied. For LSMO the average λ is positive [31], and therefore the easy axis (minimum $E_0$) occurs when the magnetization is parallel to the stress axis. The positive (tensile) epitaxial stress induced by STO on the film of LSMO results in a tetragonal symmetry [1], which is in agreement with the observation of a fourfold anisotropy in figures 6 and 7, with the easy axis along (1 1 0). Therefore, the fourfold in-plane magnetic anisotropy on films on STO is very much determined by the epitaxial strain.

The fitting to equations (1) and (2) is shown as continuous lines over the experimental data in figures 6 and 7. From the experiments it is not possible to separate the demagnetizing energy and $K_{\text{out}}$ term of equation (2). Then in order to fit this energy contribution we define $K_{\text{eff}} = 2\pi M^2 + K_{\text{out}}$. For obtaining a better determination of $K_{\text{eff}}$ we perform in-plane and out-of-plane measurements. The results obtained for both configurations are within the error bars and are reported in table 1. It is important to note that it is not straightforward to use the magnetization obtained by magnetometry to fit the FMR angular variation. As it is usually observed, the measured saturation magnetization by the SQUID magnetometer diminishes with the film thickness due to the presence of points defects and surface effects such as dead layers and deficiency at the surface stoichiometry. When the thickness is comparable or smaller that the exchange length, $l_{\text{ex}} \sim 10$ nm [32], the scale of microstructure is smaller than $l_{\text{ex}}$ and the magnetic properties are averaged [33–35]. In our system for the thicker films ($t \geq 20$ nm) the SQUID magnetization agree with the bulk value and it is considerably smaller for thinner films ($t \lesssim l_{\text{ex}}$). Therefore, the saturation magnetization values, measured for each sample at the corresponding temperature of the FMR experiments, were an input in our calculation of the magnetic anisotropy. Also the $g-$factor was set to $g = 2.0$, as generally observed in bulk La$_{0.7}$Sr$_{0.3}$MnO$_3$ [36, 37].

The anisotropy constants obtained from the fittings are listed in table 1. All PLD films, irrespective of their thickness, are characterized by a biaxial anisotropy constant $K^B \approx 2$ J m$^{-3}$, plus an order of magnitude smaller uniaxial anisotropy $K_u$. The existence of these two anisotropy terms was previously reported from magnetization measurements in LSMO under tensile strain by several authors [1, 26, 38, 39]. The mono-clinically distorted unit cell of LSMO results from a different rotation pattern of the MnO$_6$ octahedra along the (1 1 0) axis ($a^* a^* c^0$), which produces an important difference in the magnitude of the orbital overlap along the equivalent (1 1 0) easy axis directions, introducing the extra uniaxial anisotropy term.

On the other hand, the situation is completely different in the films synthesized by CSD: the value of $K^B$ is much larger in these films compared to PLD, and most importantly, the uniaxial anisotropy term vanishes, $K_u \approx 0$. A larger in-plane fourfold anisotropy is in qualitative agreement with larger in-plane coercivity, as observed in figure 4. However, the estimated $H_c \approx 2K^B_{\text{IP}}/M$ for these films is in the 80–200 Oe range, smaller than observed values, which calls for further relevant effect of magnetic inhomogeneities which could act as pinning centers for domain walls [33]. This is also consistent with the much wider FMR lines observed in CSD with respect to PLD films.

The arrangements of MnO$_6$ octahedra compatible with the analysis of the experimental FMR and XRD in epitaxial films of LSMO synthesized by PLD and CSD are shown in figure 8. Following the argument before, the absence of $K_u$ in CSD films indicates a similar orbital overlap along the (1 1 0) axis, which in turn requires an equivalent rotation of the MnO$_6$ octahedra along the $a$ and $b$ axis. The most plausible possibility is $a^* a^* c^0$ (Glazer tilt system number 16), compatible with unit cell parameters $a = b > c$ under tensile stress (tetragonal, space group $I4/mmm$) and our previous x-ray analysis (see figure 2). The results of CSD are then consistent with an elastic deformation of LSMO, without any significant anisotropy in the octahedral tilting along the direction of the easy axis.

The arrangements of MnO$_6$ octahedra compatible with the analysis of the experimental FMR and XRD in epitaxial films of LSMO synthesized by PLD and CSD are shown in figure 8. In summary, we have demonstrated that the characteristic in-plane uniaxial component of the magnetic anisotropy can be completely suppressed in chemically prepared thin films of LSMO. This implies different mechanisms of octahedral rotation to accommodate the biaxial tensile stress, depending on the growth conditions. Magnetic anisotropy determines the

| $t$ (nm) | $K^B_{\text{IP}}$ $10^4$ erg cm$^{-3}$ | $K_u$ $10^4$ erg cm$^{-3}$ | $K_{\text{eff}}$ $10^4$ erg cm$^{-3}$ | $M$ (emu cm$^{-3}$) |
|---------|---------------------------------|-----------------|-----------------|-----------------|
| 3       | 2.0 (2)                         | 0.10 (1)        | 55 (0)          | 200             |
| 6       | 1.3 (1)                         | 0.25 (3)        | 110 (10)        | 260             |
| 20      | 2.3 (2)                         | 0.10 (1)        | 250 (20)        | 580             |
| CSD     | 10                              | 3.5 (3)         | 0               | 140 (10)        | 440             |
|         | 22                              | 4.5 (5)         | 0               | 230 (20)        | 590             |
switching and relaxation of magnetization, and therefore the results presented here are not only interesting from a fundamental point of view, but they must be considered for applications of half-metallic ferromagnet LSMO in different types of devices. Advances in microscopy techniques now permit to measure precisely the amplitude of individual atomic displacements in epitaxial oxides [40]. It will be certainly important to obtain a direct image of these displacements and to correlate them with local changes in the magnetization of the film, depending on the growth method. Finally, we would like to remark the enormous possibilities offered by the sensitivity of FMR for the indirect study of subtle structural changes in ultrathin films, using conventional laboratory equipment.

Acknowledgments

This work was supported by the European Research Council (ERC StG-259082, 2DTHERM), Xunta de Galicia (2012-Proyecto No. CP072) and by the Ministry of Science of Spain (Project No. MAT2013-44673-R). JMVF also acknowledges the same organization for an FPI grant. EW and JM thank UNCuyo Argentina for Grant No C011.

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