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Journal of Magnetism and Magnetic Materials 211 (2000) 28–34

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Substrate influence on the magnetoresistance and magnetic order in $La_{0.6}Sr_{0.4}MnO_3$ films

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Abstract

We report structural, magnetic and transport measurements on $La_{0.6}Sr_{0.4}MnO_3$ thin films grown on MgO and $TiSrO_3$ substrates with thickness varying from 5 to 500 nm. We find that the lattice mismatch between substrates and films affects the morphology and induced-strains of the films. We show that these two different effects strongly influence the ferromagnetic order, the metal–insulator transition, the localization of the current carriers and the magnetoresistance of these materials. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Colossal magnetoresistance; Magnetic order; Manganite films

1. Introduction

The study of $A_{1-x}A'_xMnO_3$ (A: La, A′: Sr, Ba, Ca) manganites has been intensified due to the observation of a "colossal magnetoresistance" effect (CMR) in thin films of these materials. [1] In the $0.2 < x < 0.5$ doping range where the CMR effect is observed, the materials are ferromagnetic and metallic at low temperatures while they undergo a transition to a paramagnetic and insulator phase at high temperature. The importance of the crystal structure and lattice distortions in the magnetic and transport properties of these materials has been outlined by Goodenough [2] and other authors. More recently, Millis et al. [3] have studied theoretically the effect of uniform compression pressure and biaxial strains in the magnetic order of manganite films. Uniform compression, produced for example by hydrostatic pressure or cations substitution have also been investigated from an experimental point of view [4]. Biaxial stresses arise mainly from the lattice mismatch between the deposited material and the substrate. An important advance in this field has been made in the last years, by the experimental study of structural, transport and magnetic properties of thin films. Ju et al. [5] have studied the thickness dependence of the metal–insulator transition (MI) in relation to structural properties in La–Sr–Mn–O thin films finding a correlation between the strained lattice parameters and the shift of MI. Thin films have also been studied through transverse TEM microscopy [6], observing that lattice distortions persist up to the film surface in La–Ca–Mn–O films grown on SrTiO substrates (small lattice mismatch). A thickness-dependent shift of the metal–insulator transition with respect to the Curie temperature is also reported in Ref. [6]. There is an important

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PII: S0304-8853(99)00709-X

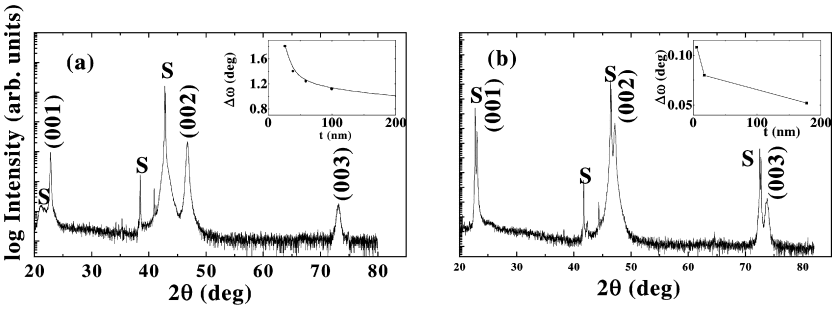

Fig. 1. X-ray diffraction patterns of $La_{0.6}Sr_{0.4}MnO_3$ thin films grown on (a) MgO and (b) $SrTiO_3$ substrates. The insets show the film dependence of the rocking curve width, $\Delta\omega$. Substrate-related peaks are labelled as S.

controversy about the origin of the MI shift. It has been associated by some authors to a grain size effect [7] while others claim that it is independent of this parameter [8]. The broad dispersion of experimental results indicates that growth conditions are a critical factor in determining the magnetic and transport properties of manganite thin films. In fact, slight distortions of the crystal structure can alter Mn–Mn magnetic interactions and thus lead to a change of the material transport properties. In order to contribute to the understanding of CMR and magnetism in thin films, we have studied the correlation between their structural, magnetic and transport properties.

2. Results and discussion

The $La_{1-x}Sr_xMnO_3$ films were grown on single crystal substrates by DC magnetron sputtering from a stoichiometric ceramic target of nominal composition $x = 0.4$. The deposition was made in an Ar(90%)/O_2(10%) atmosphere at a total pressure of 200 mbar. During deposition the substrate temperature was kept at 660^0C. After deposition the samples were cooled down to room temperature in an O_2 atmosphere at a total pressure of 10 or 100 Torr. Films with thickness, t, ranging from 5 to 500 nm were grown both on (100) MgO and (100) $SrTiO_3$. In the rest of the paper these will be referred to as the f-MGO and f-STO, respectively. The film composition was measured by EDAX analysis on the films which were thick enough for the substrate signal not to be observed. The results show that the composition was equal to the target one, within the experimental resolution (10%). The morphology of the samples were observed by AFM. Small features of 50 nm diameter and rms height of 14 nm were observed in thin films ($t < 30$ nm), while for thicker films they have an average size of 300 nm and rms height of 35 nm. f-STO films present a sharper size distribution but follow a similar tendency. X-ray diffraction patterns always show (0 0 1) textured growth, as is shown in Fig. 1. The crystalline structure of the bulk compound has been indexed in an hexagonal–rhombohedral R3C system, with lattice parameters $a_h = 0.547315$ nm and $c_h = 1.3358$ nm (pseudo-cubic $a_c = 0.3866$ nm). The lattice parameter of the films were obtained indexing a pseudo-cubic structure. For the f-MGO films $a_c = 0.3882(4)$ nm with negligible thickness dependence. For the f-STO films, a_c increases smoothly with thickness from 0.384 nm to 0.385 nm. Both substrates, MgO and $SrTiO_3$, have cubic structures but with very different lattice mismatch, namely 9% between the manganite and MgO, and only 0.9% for $SrTiO_3$. This difference is evidenced in the rocking curve width, $\Delta\omega$, of the (0 0 2) diffraction peak, plotted as inset in Fig. 1. A monotonic decrease of $\Delta\omega$ with film thickness is observed for both f-MGO and f-STO, but the average value is markedly smaller for $SrTiO_3$ substrates, indicating a smaller mosaic spread. These results suggest that the growth mode of manganite films is different for the two substrates. For films grown on MgO, the invariance of a_c together with the thickness dependence of $\Delta\omega$ suggest that the

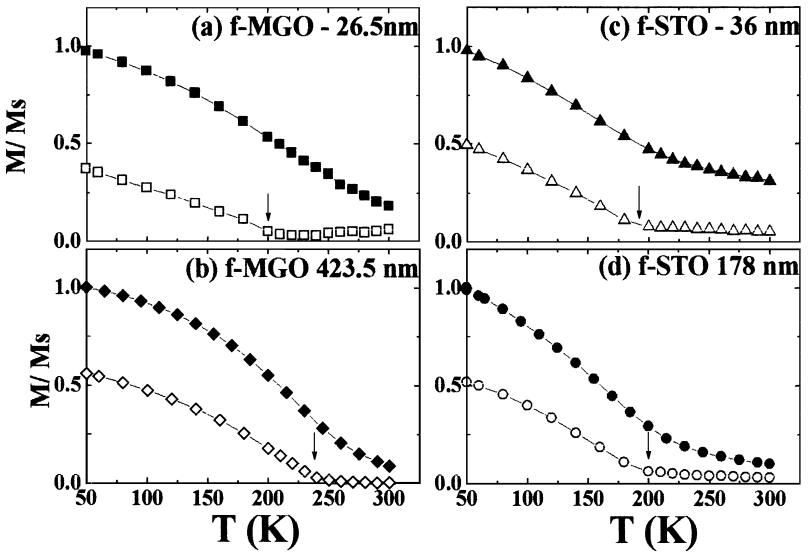

Fig. 2. Temperature dependence of the magnetization at 0.25 T (solid symbols) and at 0T (open symbols): (a) 26.5 nm- f- MGO; (b) 423.5 nm f-MGO; (c) 36 nm f-STO and (d) 178 nm f-STO.

films relax the lattice mismatch through point defects, dislocations, or different grain structures in a layer of around 40 nm from the interface, leaving an almost non-strained film above. It has been reported [9] that also La–Ca–Mn–O films grown on MgO present a thickness independent lattice parameter, although these films were not completely textured. In the case of films grown on $SrTiO_3$ substrates, a_c slowly relaxes to the bulk value as the thickness increases, but is still strained at a thickness of 500 nm. This may be an indicator of epitaxy and not textured growth alone. These results are comparable to those of Rao et al. [10] in La–Ca–Mn–O films, where a fast relaxation for the in-plane lattice parameters was observed together with a slow variation of the out-of-plane lattice parameter to the bulk value, not conserving the lattice volume.

The temperature and field dependence of the magnetization have been studied using a SQUID magnetometer. In Fig. 2 magnetization curves of f-MGO and f-STO films are shown. The magnetization at 0.25 T saturates at low temperature at the expected value 580 emu/cm^3 in all the samples. The temperature dependence is thickness independent, scaling in a general curve characteristic of each substrate type, down to 30 nm. Below this thickness an enhanced field-induced magnetization is observed at high temperature, being more pronounced in the f-STO films. This effect is probably related to the increased disorder and strains in the structure.

The remanent magnetization, M_{REM}, (Fig. 2) measured after having saturated the sample with a 5T magnetic field gives complementary information about the system. The onset of the remanent magnetization is a marker of the magnetic order of the system. The characteristic temperature, T_{REM}, defined as the maximum slope of dM_{REM}/dT, is plotted in Fig. 3(a). A decrease of T_{REM} is observed in f-MGO and f-STO samples, when the film thickness is decreased from 500 to 10 nm. The thickness dependence of T_{REM} can be fitted by a power law, $T(\infty)(1 - At^{-\alpha})$. The α parameter is similar for the two series but $T(\infty)$ is smaller for the f-STO series. In both the cases, the films ordering temperatures lay below room temperature, far from that of the bulk compound (T_C (bulk) ≈ 374 K). The influence of substrate-induced strains on T_C has been studied theoretically by Millis et al. [3], who found

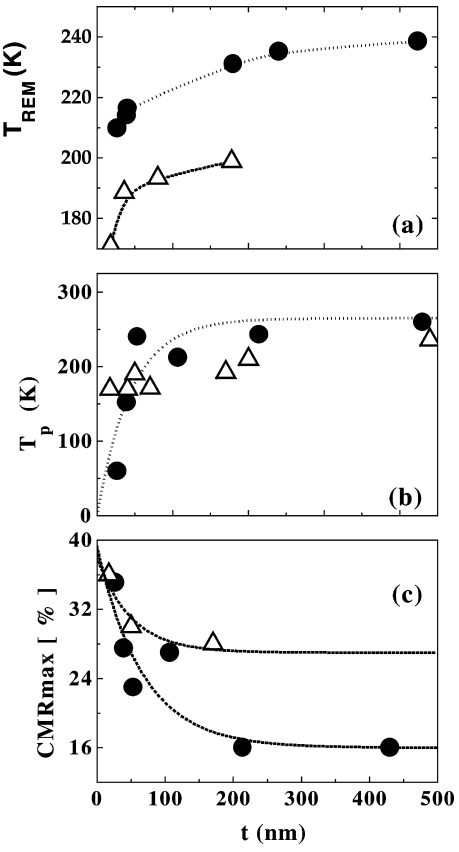

Fig. 3. Thickness dependence of (a) T_{REM}, (b) T_P and (c) Maximum CMR. Open triangles correspond to f-STO films and full circles to f-MGO ones, respectively. The lines are guides to the eyes.

an important reduction of T_c due to lattice mismatch between substrate and films. In this picture, the smaller ordering temperature found in f-STO samples can be understood as a consequence of more strained films, compatible with their possible epitaxial growth.

Several authors claim that manganites films [7,11,12] behave as superparamagnetic systems and that T_{REM} is related to the blocking temperature. Voogt et al. [13] have reported similar results in ultrathin Fe_3O_4 films ($t < 6$ nm). It is important to remark that superparamagnetic effects are observed in systems where typical magnetic grain sizes are smaller than 10 nm. For this reason caution should be exerted in analysing manganite film magnetization in terms of superparamagnetism. Energy barriers arising from dipole–dipole interactions or anisotropy fields, which are proportional to the grain volume and the distance between them in the former case, would be smaller than the temperature range usually studied only when grain size is smaller than 10 nm for manganite films.

F-STO and f-MGO thin films of $t < 10$ nm present a remanent magnetization that slowly decreases to zero with increasing temperature, following an exponential dependence. In these films, lateral dimensions of the grains are of the order of the thickness, a few tens of nanometers, near the limit of single-domain behaviour. However, the characteristic relaxation time measured in our samples are much smaller than those of superparamagnetic systems [13].

A non-negligible remanence is still observed above T_{REM} for $t < 30$ nm thick samples, increasing with decreasing thickness. The remanent magnetization measured above T_{REM} for thinner films suggest the existence of short-range ordered regions. An image of distorted regions coupled by different effective constants (due to defects or strains), could lead to a progressive ordering by developing a ferromagnetic long-range order as the inter-grain coupling becomes of the order of the measuring temperature. These distorted regions would be mainly located at the substrate interface, and their weight would be smaller for thicker films.

A rapid growth of the 0 K extrapolated M_{REM} is observed with increasing film thickness, saturating above 40 nm around 0.5 M_S for f-MGO and f-STO films. The remanent value for thick films can be interpreted in terms of biaxial anisotropy or random oriented anisotropy axis. This kind of behaviour has been also observed in Fe_3O_4 thin films [13] and has been again attributed to the remanent magnetization of a blocked state of superparamagnetic clusters. The reduction of remanence could also be due to a change in the magnetic anisotropy within the films: In thin films both the lateral size of grains is usually of the order of the film thickness changing notably the magnetotastic fields in the sample [13] and surface anisotropy becomes more important.

The resistivity of the samples was measured using a standard four-probe method. Typical

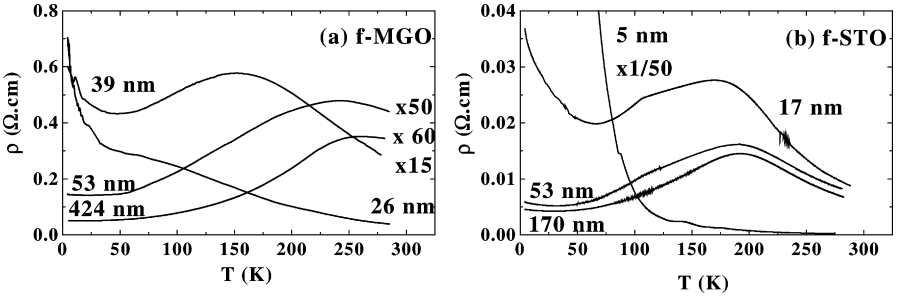

Fig. 4. Temperature dependence of the resistivity for (a) f-MGO and (b) f-STO films.

resistivity versus temperature curves of f-MGO and f-STO are shown in Fig. 4. The resistivity shows a maximum at T_P, usually assigned to the MI transition which is expected to occur at the Curie temperature in manganite compounds as has been explained by Zenner in terms of double exchange interactions. However, in f-MGO and f-STO films this transition is shifted to lower temperatures as film thickness decreases. In Fig. 3(b) the thickness dependence of T_P is plotted together with the magnetic ordering temperature in order to compare both values. As the film thickness decreases several features are observed: (a) T_{REM} and T_P progressively decouple; (b) the "metallic" phase at low temperatures evolves towards a " localized" phase and (c) the maximum at T_P becomes less important until the very thin films become unobservable. It is interesting to remark that T_P of f-STO samples shows less variation with thickness than that of f-MGO. The lower T_P of f-STO films for $t > 40$ nm is consistent with the lower magnetic ordering temperature of these material with respect to f-MGO films.

Above the MI transition the resistivity shows a "localization"-like behaviour. This means that the mobility edge, E_B, is above the Fermi energy and so conduction occurs by hopping to an empty level above E_B [14]. Adjusting the temperature dependence by a thermally activated law, $\rho_m e_B^{(\Delta/kT)}$, gives a thickness dependence of the gap Δ, (Fig. 5(a)) which indicates a progressive localization of the carriers with decreasing t. The change is more abrupt in the f-MGO series. Films grown on $SrTiO_3$ present larger gaps than the ones grown on MgO in the whole thickness range, indicating that the mobility edge of the former films is farther from

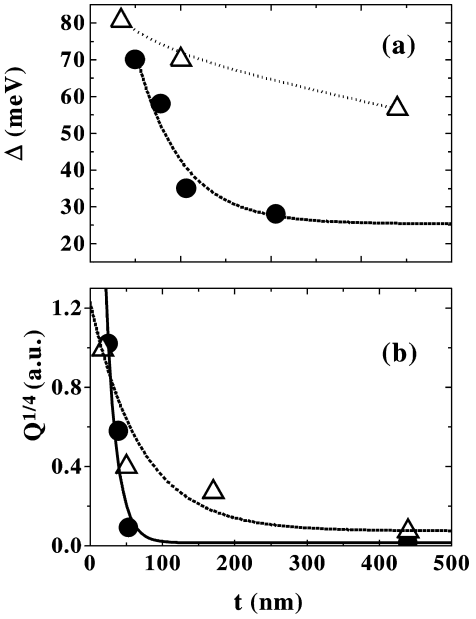

Fig. 5. Thickness dependence of: (a) gap Δ and (b) Variable range hopping exponent, $Q^{1/4}$ for f-MGO and f-STO samples. The lines are guides to the eyes.

the Fermi energy. The gap (is comparable with previously reported values [15].

Below a characteristic temperature, T_M, the films present a variable range hopping resistivity, i.e. the conductivity at low temperatures follows $\rho = Ae_B^{(Q/kT)1/4}$ where A is a constant that depends on the electron–phonon interactions and Q is inversely proportional to the electron's localization volume [14]. The localization volume increases with film thickness in both f-MGO and f-STO samples, as can be seen in Fig. 5(b). f-STO films

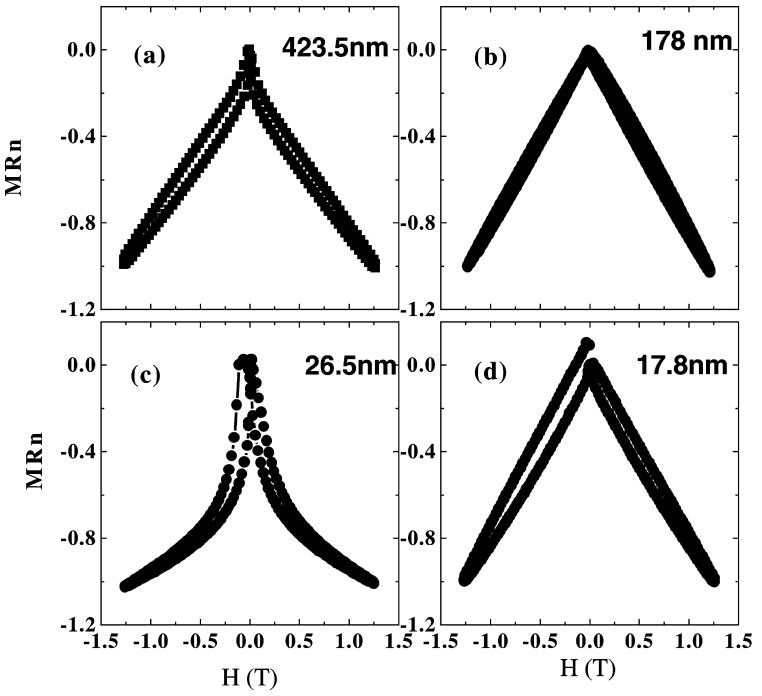

Fig. 6. Normalized magnetoresistance as a function of applied field for samples of different thickness grown on (a) MgO and (b) $SrTiO_3$, at 4.25 K.

with approximately the same thickness than f-MGO films show a smaller volume of localization.

For temperatures higher than T_M the magnetization decreases with increasing temperature and, as predicted by the double exchange model, the resistivity increases. For temperatures below T_M, where the magnetization remains nearly constant, crystalline disorder and strains are mainly responsible for localization. T_M is thickness dependent, thinner films presenting higher T_M.

The magnetoresistance is defined as: $MR(H) = [R(H) - R(0)]/R(0) \times 100$. We define the CMR value as the magnetoresistance for the maximum applied field ($H_{MAX} = 1.25$ T). The temperature dependence of CMR usually shows a maximum at temperatures slightly below T_P. However, in very thin films ($t < 10$ nm for f-STO samples and $t < 25$ nm for f-MGO samples) the CMR increases monotonically with decreasing temperature down to 4.2 K. Fig. 3(c) shows the thickness dependence of the maximum CMR, which is larger for thinner films in both series of samples.

The shape of the magnetoresistance curves depends strongly on temperature and on the substrate. Above T_{REM}, MR is reversible and very small. Magnetoresistance curves, measured at 4.2 K, are shown in Fig. 6. For f-MGO samples a low-field magnetoresistance ($H < 0.3$ T) is observed, which increases with decreasing temperature and film thickness (Fig. 6(a) and (b)). This component has been associated to inter-grain tunneling transport [16]. This component amounts to as much as 60% of the total magnetoresistance, as seen in Fig. 6. A different behaviour is observed in f-STO where no low-field MR is observed. The normalized magnetoresistance (defined as: MR (H) / CMR) of all the f-STO samples scales on a single curve for temperatures lower than T_P. As stated before, the f-MGO samples have more morphological disorder than the f-STO samples due to the greater lattice mismatch.

Crystal defects and grain boundaries are pinning centers for magnetic domain walls, so magnetic domains can be identified to crystalline grains. The

samples grown on $SrTiO_3$ have a much smaller disorder so we do not expect a large grain contribution. This could explain the absence of low-field magnetoresistance in f-STO films. However, they show an increase in the magnetoresistance as the film thickness is decreased, which could be due to substrate-induced strains.

3. Conclusions

We can conclude that the structural, magnetic and transport properties of manganite thin films are strongly affected by the substrates. The lattice mismatch between the film and the substrate change the growth mode of the films. We have observed that the lattice parameters of films grown on MgO are thickness-independent, suggesting that the large mismatch with the substrate is overcome by the presence of defects and dislocations at the interface. On the other hand, lattice parameters of films grown on $SrTiO_3$ increase smoothly with thickness evidencing the presence of tensile strains.

The magnetic ordering temperature, T_{REM}, is lower in the last films suggesting an extreme sensitivity of the Mn–Mn interactions to strains, as could be expected.

A progressive decoupling between T_{REM} and the metal–insulator transition temperature, T_P, with decreasing thickness was observed, more pronounced in f-MGO. This fact suggests that magnetic and transport properties are not only correlated by double exchange interactions but that another mechanism has to be taken into account to explain these properties in thin films. The dependence of the grain boundary resistivity with the magnetization of the system or an intrinsic mechanism could be at the origin of this phenomena. Work is in progress to elucidate this aspect of the study.

An increase in the current carrier localization is observed in thinner films. The variation with thickness is more pronounced in f-MGO supporting the existence of an accommodation layer at the interface with the substrate, above which the films are less strained. However, the localization gap is systematically larger for f-STO, indicating that the effect of strains is more effective than the morphological disorder to confine the carriers. f-STO films present, at the same time, higher magnetoresistance effects.

An increasing low-field magnetoresistance component with decreasing thickness has been measured in f-MGO films, resulting from the spin-dependent tunneling across the misoriented grains of the accommodation layer.

Acknowledgements

We acknowledge B. Alascio for fruitful discussions. This work was partially supported by the CONICET (PEI N0 0123/97), by the ANPCYT (PICT 97 N0 03-00052-01025) and Fundación Balseiro. LBS and JG are members of CONICET, Argentina.

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