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Thickness dependence of the properties of $La_{0.6}Sr_{0.4}MnO_3$ thin films

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We have studied the thickness dependence of the transport and magnetic properties of strongly textured $La_{0.6}Sr_{0.4}MnO_3$ thin films grown on MgO and $SrTiO_3$, for thickness between 5 and 500 nm. While the resistivity and the magnetoresistance are strongly affected, the magnetization is only moderately changed. The effect on the metal-insulator transition, the low field magnetoresistance and carrier localization is dependent on the substrate, evidencing the effect of the induced defects and strains.

Pacs: 75.30.Vn, 75.70.-i, 71.30.+h

1. Introduction

The existence of colossal magnetoresistance (CMR) in the perovskite compounds $T_{1-x}D_xMnO_3$, with T a trivalent lanthanide cation and D a divalent cation, was discovered as early as 1950

These materials have attracted considerable attention over the last years due to the variety of phenomena present in them. These include, besides CMR, metal-insulator transition and magnetic and charge ordering. The CMR has motivated intensive research on the area given it's potential for use in devices.

The interrelation between the crystalline structure and the physical properties is one of the reasons for the richness in behavior. The importance of the double exchange mechanism (DEM) in charge carrier movement, and the influence over it of structural defects or strains impacts directly on the physical properties of the material. Recent experimental and theoretical work have stressed the importance of substrate induced strains in thin films. In this context it is interesting to study the properties of films grown on different single crystalline substrates, providing thus different biaxial strains and, possibly, growth mechanisms.

We have studied the thickness evolution of the properties of $La_{1-x}Sr_xMnO_3$ (LSMO) films grown on single crystalline MgO (MGO) and $SrTiO_3$ (STO) These materials have larger lattice constants than LSMO presenting lattice mismatches of 9% for MGO and 0.6% for STO.

2. Experimental details

The $La_{1-x}Sr_xMnO_3$ films were grown by DC magnetron sputtering from a stoichiometric ceramic target of nominal composition x=0.4 in an $Ar(90\%)/O_2(10\%)$ atmosphere at a total pressure of 200 mbar. During deposition the substrate temperature was kept at 660ºC or 700 C in an off-axis geometry in order to avoid resputtering effects.After growth the samples were cooled down to room temperature in an O_2 atmosphere at a total pressure of either 10 or 100 Torr. Films with thickness, *t*, ranging from 5 nm to 500 nm were grown both on (100) MGO and (100) STO single crystalline substrates.

The film thickness was determined by contact profilometry and x-ray diffraction size effect through Scherrer's formula, with agreement within 10%. The chemical composition of the films was determined by energy dispersive x-ray spectroscopy, EDX, and by x-ray photoemission spectroscopy, XPS, and found to be that of the target within the experimental error, 10%. The XPS analysis shows also full surface coverage without pinholes down to a thickness of 5nm. The surface topography was studied with atomic force microscopy, AFM. For the LSMO-MGO series small features of 50nm diameter and rms height of 14nm were observed in thin films (t<30nm), while for thicker films these features have an average size of 300nm and rms height of 35nm. The LSMO-STO films present a sharper size distribution but follow a similar tendency.

3. Results and discussion

The crystalline structure of the bulk compound is an hexagonal-rhombohedral $R\bar{3}C$ system, with lattice parameters a_h = 0.5473 nm and c_h = 1.336 nm (pseudo-cubic a_c = 0.3866nm)

The x-ray diffraction patterns (Cu K_α radiation) for the films only show LSMO pseudocubic $[001]_c$ and substrate related diffraction peaks, indicating a good texturation. The rocking curve width is found to be the same for all diffraction orders, indicating a mosaic spread origin. This width has a value of around 0.8º for the LSMO-MGO films and 0.1º for the LSMO-STO films.

For *t* thinner than 50 nm this value increases, fact that could be due to thickness broadening of the diffraction peaks. For deposition temperatures different from 660 ºC a small $(110)_h(104)_h$ diffraction is observed for the LSMO-MGO series.

This result is in contrast to that of reference, where the growth on MgO substrates is found independent of deposition temperature, and no pure textured growth is found. For the LSMO-STO series good texturation is found for deposition temperatures in the studied range between 660 ºC and 700 ºC, in agreement with the results of references on STO and $LaAlO_3$ substrates.

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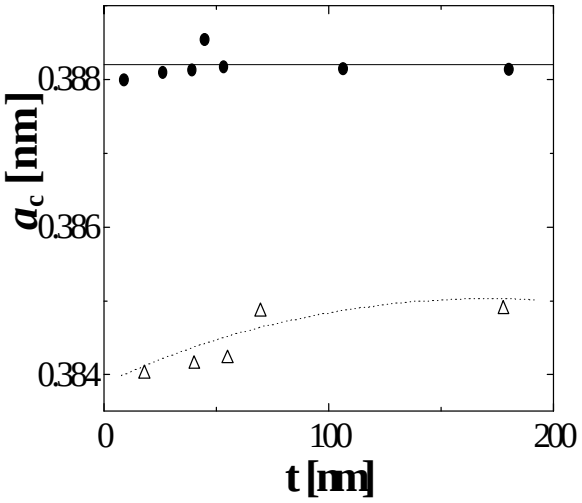

Fig. 1. Thickness dependence of the pseudocubic lattice parameter, a_c. Full circles, LSMO-MGO series; open triangles, LSMO-STO series. For the LSMO-MGO series the line indicates the average value. For the LSMO-STO series the line is drawn as a guide to the eye.

The lattice parameter of the films was determined indexing in the pseudo-cubic structure. Figure 1 shows the thickness dependence of this parameter, a_c, for both series of films. For the LSMO-MGO films a_c=0.3882(4) nm with negligible thickness dependence. For the LSMO-STO films a smooth increase with thickness from 0.384 nm to 0.385nm is apparent.

These structural results suggest that the growth mode of the two series of films is different. For the severely lattice mismatched LSMO-MGO system, we interpret the thickness independent lattice parameter and the increased rocking curve width as originating in a film which has relaxed the stresses in an "accommodation layer" of a few nanometers, probably through structural defects like dislocations or point defects, and which has an in-plane polycrystalline structure.For the LSMO-STO series, on the contrary, the thickness dependence of the lattice parameter and the smaller mosaic spread indicate the possibility of epitaxial growth.

In effect, if epitaxial growth were present, the expansive biaxial stress introduced by the STO substrate would produce a thickness dependent out of plane contraction, as observed. More structural characterization is under way to check on this hypothesis.

The electrical resistivity, r, of the films was measured as a function of temperature, T, and magnetic field parallel to the film surface, H, in a standard four probe configuration. Figure 2 shows the thickness evolution of the zero field resistivity for LSMO-MGO and LSMO-STO films. For the thicker films in both series, the maximum usually associated to the metal-insulator transition is observed. As the thickness is reduced, however, r(T) evolves towards an insulator-like dependence and the maximum reduces to a small feature superimposed in a monotonically decreasing curve.

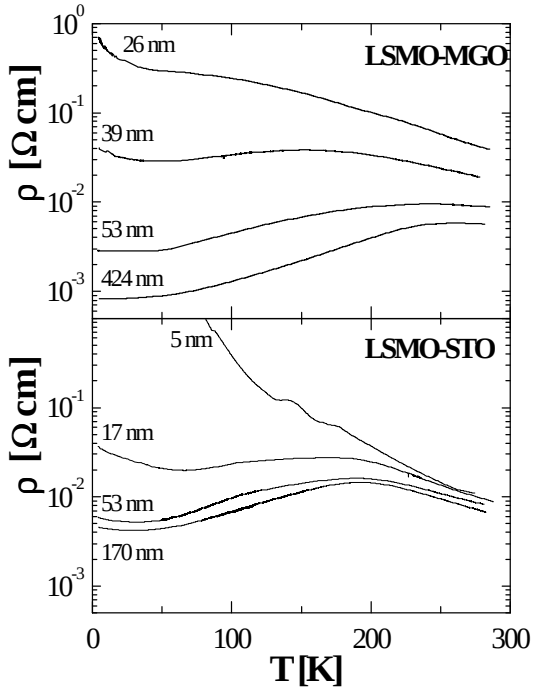

Fig. 2.- Temperature dependence of the resistivity, r. Thickness is indicated for each sample.

Also the temperature at which the maximum is located, T_p, decreases for smaller thickness. At low temperatures, a negative slope is observed in r(T) for all films. The data in this range is well adjusted by a variable range hopping law $r(T) = A\exp\left(Q/T^{1/4}\right)$ where Q^{-1} is proportional to the carrier's localization volume

As is shown in figure 3 this localization volume increases rapidly with thickness for both series, although it increases faster and is larger for the LSMO-MGO series. This behavior can be understood as a consequence of the structural disorder induced by the substrate mismatch. In our interpretation of the growth mode of the films, the epitaxial LSMO-STO series is expected to be strained throughout the thickness of the film.

This will distort the Mn-O-Mn angles and distances and the DEM coupling will be affected, giving origin to carrier localization. On the contrary the LSMO-MGO series is expected to relax the substrate induced stresses in a layer near the substrate interface. Above this layer the structure will be relatively undistorted and the localization effects will be smaller. For total thickness comparable or thinner than this layer, the structural disorder will be dominant.The behavior at temperatures higher than T_p follows a thermally activated regime $r(T) = B\exp\left(\Delta/T\right)$. This dependence is again interpreted as localization of carriers due to both structural and magnetic disorder.

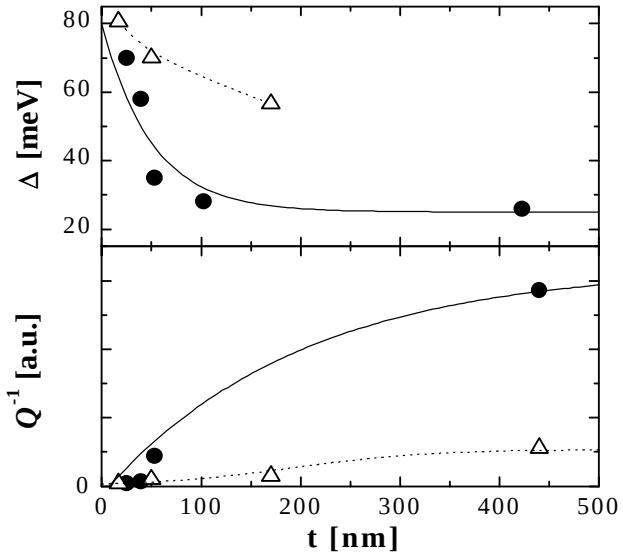

Fig. 3.- Thickness dependence of the adjusted gap, Δ, at the high temperature thermally activated resistivity regime, and of the low temperature localization volume, Q^{-1}. Full circles, LSMO-MGO series; open triangles, LSMO-STO series. Lines are drawn as guides to the eye.

In this high temperature regime the Mn3+ and Mn4+ ions are randomly oriented originating localization through the DEM mechanism.The gap, Δ, is determined by the distance between the Fermi energy and the mobility edge. The adjusted values for Δ are included in figure 3 and are of the same order of magnitude as usually reported. It is observed that Δ is larger for the LSMO-STO series and has a weaker thickness dependence.

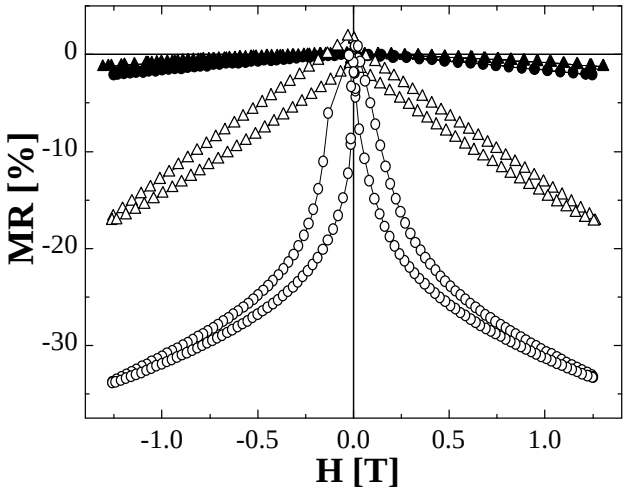

Fig. 4.-Magnetoresistance, MR, curves as a function of applied field, H, for a 17 nm thick LSMO-STO film, triangles, and a 25 nm thick LSMO-MGO film, circles, at 4.5K, open symbols, and 288K, full symbols.

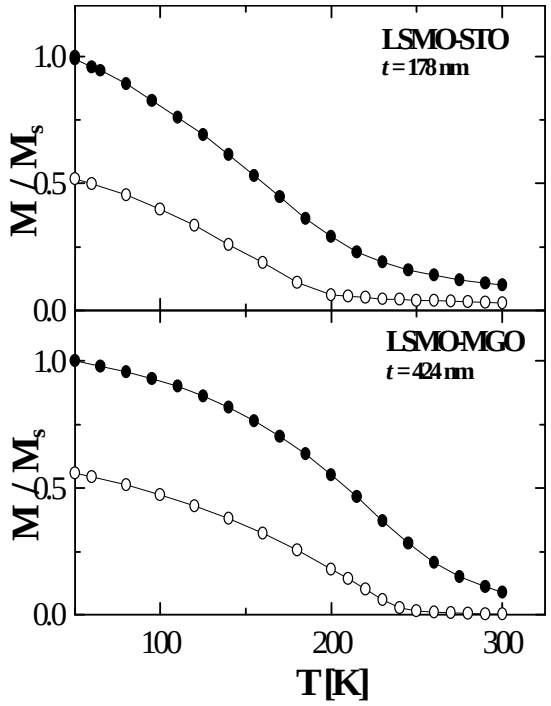

Fig. 5.- Temperature dependence of the magnetization, M, normalized by the saturation magnetization, M_s, for a 178 nm LSMO-STO and a 424 nm LSMO-MGO film. Full circles, M measured with an applied field of 0.25 T. Open circles, remnant magnetization measured after saturating the sample at 4.5K with 5T.

The structural disorder also reflects in the magneto-transport properties. Figure 4 shows the magnetoresistance, $MR = [r(H) - r(0)]/r(0)$, as a function of H for a LSMO-MGO and a LSMO-STO film at 4.5K and room temperature. At high temperature, where no magnetic order is present, MR is small and does not present an appreciable hysteresis. However, at low temperatures, the behavior of both series is markedly different.

The LSMO-STO series shows a linear dependence, while the LSMO-MGO series shows a low field steeper dependence. This low field behavior, which has been identified as inter-grain tunneling, reinforces our hypothesis about the LSMO-STO series being an epitaxial system and the LSMO-MGO series being a polycrystalline textured system.

The magnetization of the samples shows the expected ferromagnetic behavior. Hysteresis curves show that the magnetization, M, saturates at H of about 0.2 T and presents a coercitive field of the order of 200 Oe. Figure 5 shows typical M(T) data acquired with a SQUID magnetometer. The temperature dependence of the remnant magnetization, measured after saturating the sample at 4.5K with 5 T, shows a monotonic decrease, which extrapolates to zero at a temperature T_{rem}, which we take as an estimate of the Curie temperature.

At low temperatures, M at 0.25 T saturates at the expected value of 580 emu/cm^3 for all thickness and shows a dependence basically independent of thickness down to approximately 30 nm.

Below this value the data shows an enhanced field induced M at high temperatures, more pronounced for LSMO-STO films. This is also seen in the remanence data as a tail above T_{rem}. These effect is probably due to the increased relevance of strains and structural defects in this thickness range, which could lead to the existence of short range ordered regions mainly located at the substrate interface.

The thickness dependence of T_{rem} and T_p is shown in figure 6. It is clear that both temperatures do not follow the same trend, T_p decreasing more than T_{rem} on decreasing thickness. This effect is more pronounced for the LSMO-MGO series, where a difference as big as 100 K is found for the two characteristic temperatures. Within the DEM model this difference cannot be explained, T_p being completely correlated to T_c. This effect has to involve some other mechanism besides DEM. This mechanism could be either of structural origin, like grain boundary scattering, or of intrinsic origin. Until the structural effects are not completely understood further hypothesis cannot be ventured.

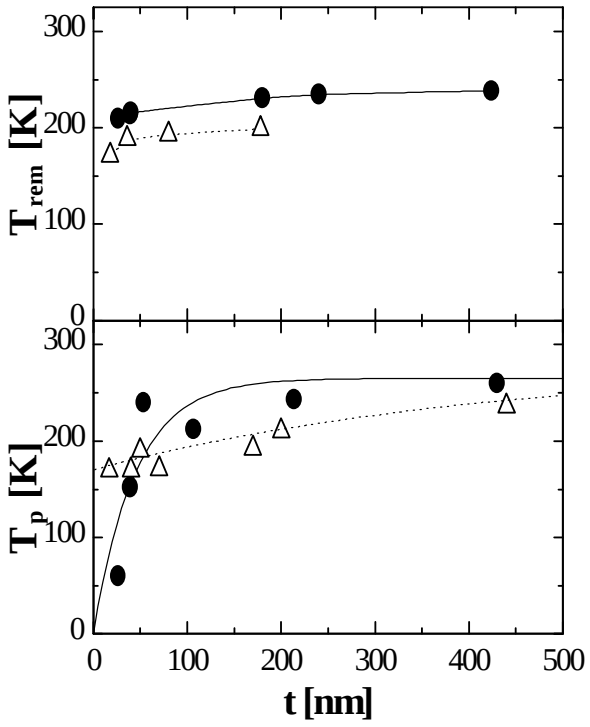

Fig. 6.- Thickness dependence of the temperature of the resistivity maximum, T_p, and of the temperature at which the remnant magnetization extrapolates to zero, T_{rem}. Full circles, LSMO-MGO series; open triangles, LSMO-STO series. Lines are drawn as guides to the eye.

4. Conclusion

In conclusion, we find that the growth mode and the properties of $La_{0.6}Sr_{0.4}MnO_3$ films are greatly influenced by the biaxial stress introduced by the substrate. The structural results indicate that for the large lattice mismatched MgO substrates the biaxial stresses relax in an layer of a few nanometers, probably through structural defects like dislocations or point defects.

On the contrary, for well lattice matched $SrTiO_3$ substrates, the films appear to be truly epitaxial and strained across the whole thickness. This difference correlates with the transport properties of the films, where localization due to structural disorder is observed at low temperatures.

The films grown on $SrTiO_3$ substrates show a smaller localization volume than those grown on MgO, possibly reflecting a more extended strain field. However, the localization gap is systematically larger for LSMO-STO, indicating that the effect of strains is more effective than morphological disorder to confine the carriers. Another correlation is seen in the magnetotransport, where grain boundary related low field magnetoresistance is found for films grown on MgO, but not for films grown on $SrTiO_3$.

A progressive decoupling between T_{rem} and T_p on decreasing thickness was observed, more pronounced for films grown on 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.

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