Influence of the microstructure on the magnetoresistance of manganite thin films

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We present magnetic and electric transport studies on several series of $La_{0.7}Ca_{0.3}MnO_3$ polycrystalline pellets and thin films. The thin films were obtained by DC magnetron sputtering on several substrates and by sol-gel deposition technique on Si (100). The diffraction patterns show the polycrystalline character of films grown on Si by both techniques. The morphology was studied by AFM and the mean grain sizes were obtained. The steady decrease of the low temperature magnetoresistance (MR) at high fields is explained by the increase of the effective section for conduction by the orientation of pinned Mn magnetic moments at the surface of the grains and, therefore, depend strongly on the connectivity between grains. On the contrary, the low field MR is related to the magnetic behavior of the ferromagnetic domains of the grains. Low and high field MR characteristics of thin films deposited on different substrates are correlated to their microstructure.

1-Introduction

Manganese perovskites $La_{1-x}A_xMnO_3$ (A= Ca, Sr, Ba...) have recently attracted much interest because of their potential magnetic applications using their high (up to colossal) magnetoresistance effect [1]. Ca compounds with $0.15 < x < 0.5$ present an insulator to metal transition, at T_{IM}, and para to ferromagnetic (FM) ordering, at T_c, both about 265K for x=0.33.

The metallic FM state is quite well described by the double-exchange model but polaronic effects due to strong electron-phonon coupling have also to be invoked in the insulator regime where the conduction is achieved by hopping of small polarons. The effect of grain boundaries, grain size, artificially induced boundaries, or films with microcracks [2-6] have been extensively studied since the large values of low temperature low field magnetoresistance is now established to be a spin dependent scattering process at the boundaries [2,7,8].

A comprehension of the detailed mechanisms for the high field magnetoresistance of polycrystalline perovskite oxides is still lacking. Nevertheless, it is now clear that spin polarized scattering at grain boundaries together with the magnetic state of their surface are crucial points in this problem. We have rise the evidence that the connectivity between the grains is of special relevance in the conductivity of the metallic ferromagnetic state of 33% Ca doped manganites [9] as well as in the low temperature high field magnetoresistance [10].

A poor connectivity can lead to the suppression of the metallic behavior in the ferromagnetic phase. Therefore part of the phenomenology observed in polycrystalline pellets or thin films of mangetoresistive manganites is, in fact, related to extrinsic characteristics as the quality of the surface or the degree of compactation of the grains.

In this work we have performed magnetic and magneto-transport measurements as a function of temperature of $La_{0.67}Ca_{0.33}MnO_3$ thin films, that present different morphology depending on the substrate and compare them to bulk ceramic pellets.

2. Experimental details

Several sets of samples were prepared in order to check the effect, of connectivity between grains, grain size, chemical disorder and morphology of the films on the magnetic and transport properties of these systems.

$La_{0.7}Ca_{0.3}MnO_3$ powder was obtained by standard ceramic process. This powder was pressed into 1 cm pellets to be used as samples and also into in a 2” pellet to be used as a sputtering target. The samples were sintered at different temperatures whose effect is to "glue" one grain to the other, starting with a “cleaned” powder (extra annealing at 1200C for 24h) or a “dirty” powder, both, the sintering temperature and the quality of the surface of the grains, vary the connectivity between grains.

The number used to label the samples indicates its sintering temperature and the letters “C” or “D” stands for “cleaned” or “dirty” powder. The effect of the grain size is checked by comparing these ceramic samples to a series of polycrystalline thin films with different grain sizes. This series of thin films was grown by dc sputtering on Si (100) substrates at room temperature in a mixed Ar and O_2 atmosphere (ratio 4:1) and then annealed at 850 ºC for 10 minutes. The films atomic force microscopy (AFM) images show grains of rather spherical shape with mean diameters between 12 nm and 80 nm depending on the film thickness which lie between 100 nm and 1200 nm.

Another series consists in thin films obtained by DC sputtering deposited on different substrates but under identical conditions and with the same thickness. At last, several thin films obtained by a sol-gel technique on Si (100) substrates were also obtained. Grazing incidence and standard X-ray diffraction of the sputtered thin films on all substrates except on SrTiO3 and LaAlO3, revealed their polycrystalline character and expected lattice parameters for Ca concentration of about 28\%. In the text the sputtered thin films are identified by their substrate

The magnetization measurements were performed either in a SQUID magnetometer (for the thin films) or in a "Physical Properties Measurement System" (PPMS) from Quantum Design (pellets). The transport measurements were all performed in the PPMS with a standard four-probe configuration.

3. Results and discussion

3.1 Magnetic behavior

Fig. 1 shows the magnetic susceptibility (inset) and its derivative, the ferromagnetic transition temperatures (T_c) are indicated with arrows, of a representative pellet (all pellets are identical from the magnetic point of view) as well as those of thin films deposited on $SrTiO_3$ and on Si(100). Fig.2 presents The magnetization curves at 5K of the same two thin films. Pellet's T_c, at 265K, corresponds well to the composition La0.67Ca0.33MnO3 while all the sputtered thin films present a lower Tc, at 247K. The thin films Ca content has been estimated to be 28%. The transition is less sharp for the Si thin film as expected for small grains. The thin films coercive fields, H_c, (SrTiO3: 240 Oe, Si (100): 580 Oe) are larger than the pellet one (80 Oe). In all cases the magnetization at 5K is practically

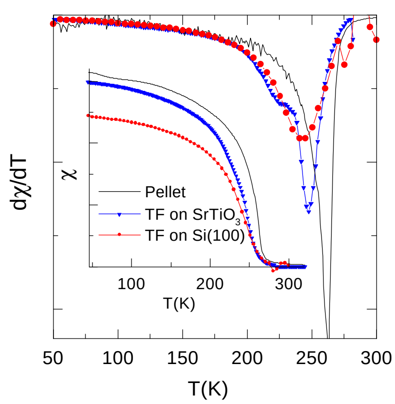

Fig.1- Susceptibility (inset) and its derivative of a ceramic pellet and two thin films of $La_{1-x}Ca_xMnO_3$

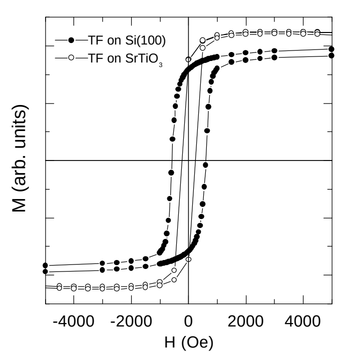

Fig. 2- Hysteresis loops at 5K of a polycrystalline thin films deposited on Si(100) and an epitaxial film on SrTiO3

saturated at about 1T The explanation for such large differences in H_c is the following: the pellet presents the behavior of a randomly oriented powder, the thin films on SrTiO3 are epitaxial and the observed H_c is dominated by the form anisotropy. On the contrary thin films on Si are polycrystalline samples with very small grains (below 80 nm) and the observed magnetization is very probably due to single domain grains where H_c is the field necessary to flip the magnetization of the whole domain, which is higher than the field necessary to propagate a domain.

3.2 Transport and Magnetoresistance

The samples were chosen so that it was possible to discriminate the effects of different types of defects, usualy present in this kind of compounds, on their magneto-transport properties.

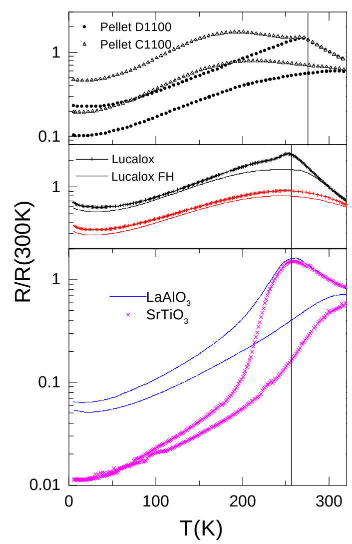

Fig. 3-. Resistance of several thin films and pellets at 0T and 9T, normalized by their value at 300 K and 0T. Vertical lines indicate their T_c.

Fig.3 presents the measured resistance of several thin films and pellets at 0T and 9T, normalized by their value at 300 K and 0T, their corresponding T_c are indicated as vertical lines. Note that the temperature for the insulator to metallic regimes transition temperatures, T_{IM}, is very similar to T_c except for D1100 pellet. It has been observed [10] that, as the sintering temperature of the pellets decreases, T_{IM} decreases, the resistance at 300K increases several orders of magnitude and R(T)/R(300K) dramatically increases at low temperatures.

To explain the observed transport behavior in polycrystalline samples, we propose the existence of two kinds of conduction channels parallel connected. One kind is related to the transport properties of the system and is achieved through the contact areas between grains. The other shows energy barriers at all temperatures due to poor connectivity, disorder and contamination at the grain surface that inhibit metallic conduction.

The epitaxial (TF on SrTiO3) or quasi epitaxial (TF on LaAlO3) thin films present a very different behavior (lower part of Fig. 3) than all the polycrystalline samples (bulk and thin films) while their magnetic behavior is quite similar.

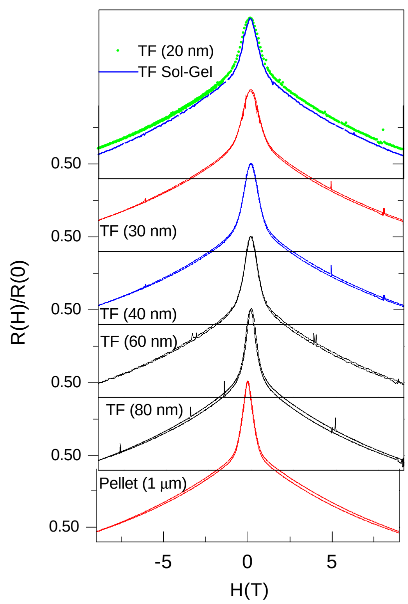

Fig.4- Measured resistance at 5K normalized by its maximum value (around H=0T) of thin films on Si(100) with different grain sizes and a pellet.

C1100 pellet (grains about 2000 nm) and all Si(100) thin film (grains between 80-20 nm) samples present T_{IM} similar to T_c, as expected from the double exchange mechanism, indicating a good connectivity between grains, and present identical high field magnetoresistance (MR) at 5K (Fig. 4). On the contrary, the low field MR, varies considerably showing a less steep decay of the resistance as the grain size decreases.

The decrease of the resistance at high fields can be explained by the following mechanism: At low temperature the metallic channels give rise to a MR which is determined by the spin polarized tunneling (SPT) between grains that depends on the angle formed by the magnetic moments of these grains. The variation of this angle with the external magnetic field is given by the measured magnetization M(H).

At the grain surface Mn spins can be blocked, for example, because their environment is unbalanced or because of magnetic anisotropy. Magnetic measurements are not sensitive to these disordered Mn spins because the fraction is very small, but the conduction at low temperature is drastically reduced because one distorted Mn closes that conduction channel.

Considering that the magnetic field (H) aligns Mn spins blocked at the surface in a linear way, opening new conduction channels, we can explain the steady decrease of the resistance at high fields by the linear increase of the effective section for metallic conduction by the alignment of the pinned Mn magnetic moments. The slope of the HFMR depends on the ratio between the metallic to non-metallic sections that, in turn, depends on the connectivity between grains and on the stiffness of the blocked Mn spins at the surface. Fig. 5 shows that this process is the dominant in the MR of thin films deposited on $SrTiO_3$ and $LaAlO_3$. These thin films do not show the steep decrease of resistance at low fields that corresponds to SPT but only the quasi linear behavior up to the highest measured fields.

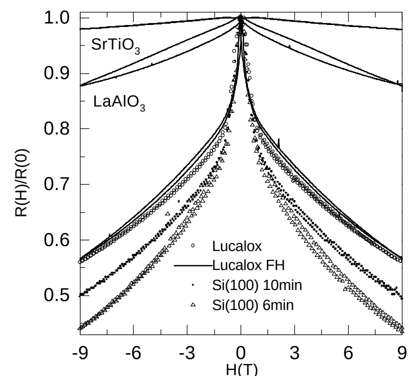

Fig. 5- MR at 5K normalized by its maximum value for thin films deposited on several substrates or annealing times.

4. Conclusions

We have shown that the conduction in maganese perovskites is achieved by parallel channels. The section for metallic channels is determined by the connectivity between grains. The effect of an external magnetic field is to align blocked spins at the surface of the grains in a linear way opening new conduction channels that were broken, decreasing considerably the resistance, while the magnetization remains nearly constant.

This effect is not related to the grain size of the grains but to the differences in the effective section for metallic conduction of the samples and on the stiffness of the blocked Mn spins at the grain surface. This process is the dominant in epitaxial or nearly epitaxial films while no SPT low field MR is present.

Acknowledgments

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