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Surface behavior of $La_{2/3}Ca_{1/3}MnO_3$ epitaxial thin films

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The role of the surface layers in $La_{2/3}Ca_{1/3}MnO_3$ magnetic oxide epitaxial thin films is analyzed. We show that the topmost layers do play a very relevant role on the transport properties acting as an insulating barrier. Atomic force microscopy (AFM) measurements in the current sensing mode exhibit typical features of tunneling conduction. The analysis of the *I*-*V* curves by using the Simmons model give values of barrier thickness in good agreement with nonmagnetic layer thickness estimates from magnetic measurements. *Ex situ* annealing in air at high temperature clearly improve the magnetotransport properties of the films reducing the surface insulating barrier. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2133925]

During the last decade manganese perovskites have been the subject of permanent activity due to their very promising properties for the development of magnetic and magnetoresistive devices. Most of these applications require the use of thin films and heterostructures in which interfaces and surfaces do play a very active role on their final performances. In fact, it has been shown that the magnetic and electronic properties of oxide based superlattices can be tuned through interfacial effects, such as strain, charge transfer, and spin exchange interactions.[1] In most practical devices the final step implies the deposition of conventional metal, such as Au, on top of the heterostructure in order to make the contacts with the metallic wiring. However the contact resistance and the transport mechanism across these oxide-normal metal interfaces are not well known in detail, even they are of major relevance for the development of magnetoresistive devices, such as magnetic tunnel junctions (MTJ's) and spin injectors.

Across a manganite/normal metal union a large interfacial resistance is usually found; nevertheless the origin of this contribution remains elusive. Nonmetallicity of the oxide interface or depletion of the density of states and spin polarization close to the interface[2] are only some of the possible explanations offered so far. On the other hand, it has been found that composition may be altered close to the surface due to surface segregation of the dopant atoms[3–5] and that these surface layers are likely to be insulating and nonmagnetic. These surface segregation effects have been detected in LCMO (Ref. 3) as well as in LSMO (Ref. 4) leading to an alteration of the Mn^{3+}/Mn^{4+} balance. Therefore, a change of the magnetic and transport properties with respect to that of the bulklike material should also be expected. In fact, the alteration of magnetic and transport properties of manganite interfaces with vacuum[2,6] or with an insulating layer[7] has been clearly shown. On the other hand, it has also been observed that very thin films exhibit magnetic and transport properties substantially different from that of thicker bulklike films.[8] These features are generally attributed to the existence of a nonmagnetic layer.[9–11] The existence of a nonmagnetic layer effect has also been observed at the grain surfaces in granular manganite samples.[12] For obvious reasons the control of this surface or interfacial layer with degraded magnetic and transport properties is of great technological importance to enhance the performance of manganite-based devices.

Some results regarding the transport properties across a ferromagnetic oxide/insulating barrier bilayers were reported by Bibes *et al.*[13] by using atomic force microscope (AFM) working on the current-sensing mode (CS). Nevertheless, we should mention that the method used was strongly dependent on the tip, the applied force, and the roughness. On the other hand, similar experiments, with macroscopic contacts (400 μm^2) made by lithography, between different magnetic oxides and metals have been reported by Mieville *et al.*[14]

In this work we present results of contact resistance measurements in the $La_{1/3}Ca_{2/3}MnO_3$ (LCMO)/Pt system. LCMO epitaxial thin films of about 80 nm thick have been grown by rf sputtering on top of the $LaAlO_3$ (LAO) substrate [T_D=800 °C and a pressure of 330 mTorr (Ar+20% O_2)] (as-grown samples). Some samples were *ex situ* annealed in air at 1000 °C for 2 h (annealed samples). The contacts between the manganite film and the metal have been prepared by *ex situ* deposition of a 30 nm thick Pt layer on top of the manganite film by e-beam evaporation at room temperature. Different nanostructured contact geometries have been defined by using a focus ion beam system (FIB) (FEI with Ga^{3+} ions and with a current of 10 pA) and then transport properties have been tested by means of an AFM system working on the CS mode with a doped diamond tip. The I/V characteristics measured across the LCMO/Pt interface exhibit the typical features of a tunneling process. The analysis of the I/V curves by using the Simmons model at the intermediate voltage[15] allows us to estimate the energy (φ_0) and the thickness (S) of the barrier, obtaining values of S in good agreement with the estimate of the nonmagnetic layer derived from magnetic measurements.

Structural characterization of as-grown and annealed samples has been performed by x-ray diffraction and atomic force microscopy (AFM). Magnetic properties were measured with a commercial SQUID magnetometer (Quantum Design). A complete report of the structural, magnetic, and transport properties will be published elsewhere.[16]

Magnetic properties of as-grown films are clearly depressed as the thickness t, diminish (see Fig. 1). Nevertheless, the saturation magnetization M_S, strongly improves af-

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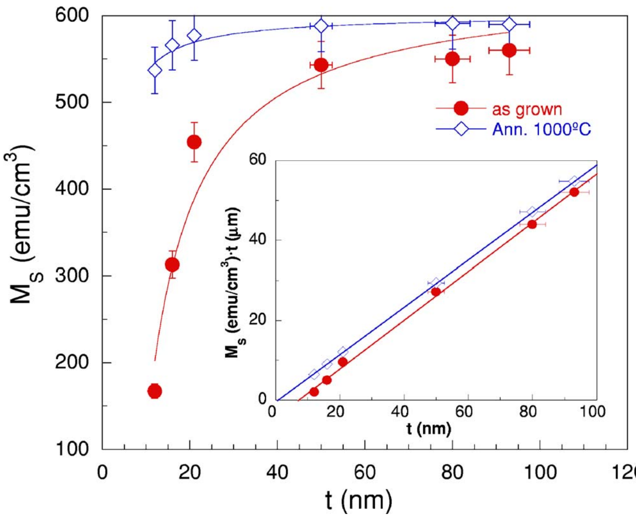

FIG. 1. (Color online) Saturation magnetization (M_S) of LCMO films as a function of the thickness (t). Inset: Fit of M_St product to estimate the nonmagnetic layer.

ter annealing samples in air at high temperature (see Fig. 1). The thickness of the nonmagnetic layer, obtained from the extrapolation of the M_St product to zero (see inset of Fig. 1), is reduced from ≈6 nm for the as-grown films to ≈1 nm for the annealed ones.

Circles in the range of a few μm diameter (⊘) have been defined by rings of about 50 nm thick to avoid metallic contact between the regions inside and outside of the rings [Figs. 2(a) and 2(b)], and to ensure that the current between the inside and outside regions must go through the manganite. A macroscopic contact between the LCMO film and the AFM ground was done, and then the current circulating through the tip was measured [see Fig. 2(c)]. Outside the patterned contact regions the current saturates and the resistance was not measurable (see Fig. 3). We estimate that this resistance was smaller than $10^4\ \Omega$ and we take this value as the lower limit of our measurements. On the other hand, when measur-

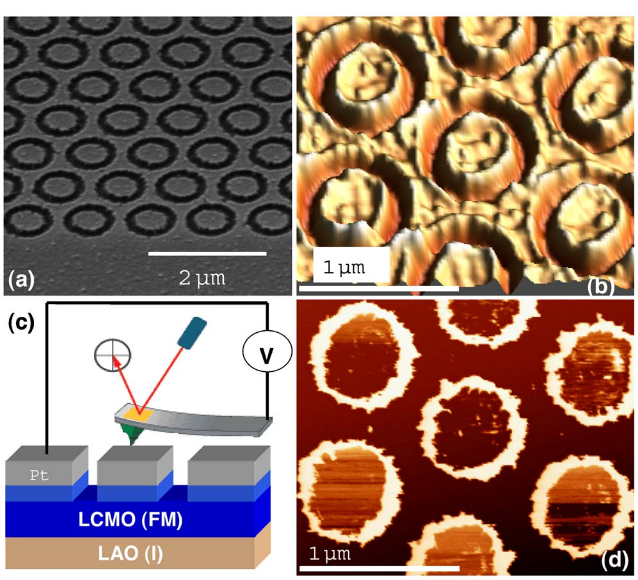

FIG. 2. (Color online) (a) SEM image of 500 nm circles patterned film by using the focus ion beam (FIB) technique, (b) AFM topography, (c) setup for the transport measurements, and (d) resistance mapping of some patterned circles showing the saturation current outside the circles, nonconductance in the rings, and small conductance inside the circles.

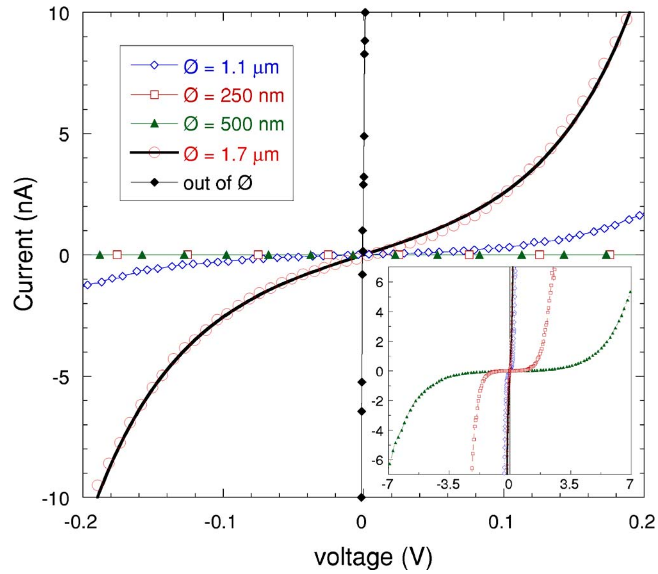

FIG. 3. (Color online) Zoom of the I/V curves measured inside (circles) and outside of the patterned areas for an as-grown LCMO film with a capping layer of 30 nm of Pt. The lines through the experimental points correspond to fits using the Simmons model. Inset: I/V curves in the extended range.

ing inside the patterned areas a higher resistance, containing the contribution across the LCMO/Pt interface from the patterned contact area, is measured.

In patterned less as-grown films contact resistance between the LCMO layer and the tip was so high that it was impossible to measure even by applying 10 V between the film and the tip. In contrast, patterned less annealed samples exhibit tunneling conduction with tip currents of about 10^{-8} A at 1 V. On the other hand, a measurable resistance inside the patterned circles is found in as-grown samples. Figure 2(d) shows a current mapping for 500 nm ⊘ circles, showing saturation of the measuring current outside the circles, nonconductance in the rings and small conductance inside the circles.

In Fig. 3 we show some I/V characteristic curves obtained when the tip was positioned on top of one circle. In all the cases (circles with different ⊘) I/V curves exhibit the typical features of a tunneling conduction mechanism. On the other hand, I/V curves measured in different positions inside the circles are very similar between them, as well as in circles of similar size. Nevertheless, we should mention that I/V curves obtained in circles with clearly different sizes do not scale with area.

We have analyzed I/V curves by using the Simmons model at the intermediate-voltage range to estimate φ_0 and S,[15]

$$J=\left(\frac{e}{2\pi h s^2}\right)\left\{\left(\frac{2\varphi_0-eV}{2}\right)\times\exp\left[-(2m)^{1/2}\frac{4\pi s}{h}\left(\frac{2\varphi_0-eV}{2}\right)^{1/2}\right]-\left(\frac{2\varphi_0+eV}{2}\right)\times\exp\left[-(2m)^{1/2}\frac{4\pi s}{h}\left(\frac{2\varphi_0+eV}{2}\right)^{1/2}\right]\right\}. \quad (1)$$

The values of S obtained in circles bigger than 1 μm in ϕ are in very good agreement with the estimates of the nonmagnetic layer thickness from magnetic measurements. For instance, for the circle with ⊘=1.7 μm,

$S = 3.3$ nm, and $\varphi_0 = 0.5$ eV. Note that $S = 3.3$ nm is very similar to the nonmagnetic layer (3 nm for the as grown film) assuming that half of the nonmagnetic layer corresponds to the top interface (LCMO/vacuum) and the other half to the bottom interface (LCMO/LAO).

The same procedure has been used with annealed films but, in this case the resistance measured inside and outside of the patterned areas was very similar. A contact resistance between 1 and 2 $M\Omega/\mu m^2$ was measured in the case of the smaller circles. This result reflects the strong reduction of the non-magnetic layer in annealed samples (0.5 nm) and clearly indicates that, as expected, not only magnetic but also transport properties are strongly improved in annealed samples. Our results show that the surface layer in as-grown LCMO sample has an insulating nature exhibiting the typical features of a tunneling conduction mechanism. However, high temperature annealing in air strongly reduce the insulating character of this surface layer.

In summary, we have measured the interfacial resistance across a LCMO/Pt interface showing that a thin insolating layer exist at the surface of as-grown LCMO films. The conduction mechanism exhibits the typical features of a tunneling process and the barrier thickness, derived from fitting of the experimental data by using the Symons model, is in very good agreement with estimates of the nonmagnetic layer derived from magnetic measurements. The insulating character of the LCMO surface layer can be strongly reduced by high temperature annealing in air. These results are of major interest for the development of manganite based magnetoresistive devices. We also believe that the new method we have described could be very helpful in the implementation of oxide-based magnetoresistive devices.

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