

Proximity effects induced by a gold layer on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin films

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The authors report about $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ single crystal manganite thin films in interaction with a gold capping layer. With respect to uncoated manganite layers of the same thickness, Au-capped 4 nm thick manganite films reveal a dramatic reduction (≈ 185 K) of the Curie temperature T_C and a lower saturation low temperature magnetization M_0 . A sizable T_C reduction (≈ 60 K) is observed even when an inert SrTiO_3 layer is inserted between the gold film and the 4 nm thick manganite layer, suggesting that this effect might have an electrostatic origin. © 2007 American Institute of Physics. [DOI: 10.1063/1.2778353]

The perovskite manganites of composition $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($A=\text{Ca}, \text{Sr}, \text{Ba}$) have attracted a considerable interest because of the interplay between spin, charge, orbital, and lattice degrees of freedom in these materials, leading to a large variety of magnetic and electronic properties, such as colossal magnetoresistance.¹ The half-metallic character of manganites with $A=\text{Sr}, \text{Ca}$ is particularly relevant for applications in spin electronics where sources and detectors of highly polarized electron currents are required.

The electric and magnetic properties of manganites are extremely sensitive to the concentration of free carriers. These properties can be varied not only by hole doping the material but also by designing a heterostructure where light or an externally applied electric field might effectively modulate the carrier concentration.² Attempts to incorporate p -doped manganites in heterostructures with n -type conductors have demonstrated the possibility to control the carrier concentration and tune the intrinsic magnetic properties of the manganite layer through the modulation of interfacial electronic bands either with external bias voltages or carrier injection.^{3,4} Modulation of the transport and magnetic properties of epitaxial manganite films has also been obtained in field effect devices, where a voltage is applied to a metal^{5,6} or ferroelectric⁷⁻⁹ gate electrode.

The presence of an interface represents, by itself, a significant perturbation of the electronic properties of perovskite manganites.² The interface with a metal is known to affect the chemical and electronic environments of strongly correlated oxides (a wide group of materials where electron-electron correlations play a fundamental role and that includes manganites), and can change basic electronic parameters such as the Hubbard energy U , the electronic bandwidths, or the exchange energies.¹⁰ Nevertheless, the impact of the creation of a manganite/metal interface has been scarcely investigated,¹¹ although its understanding is a fundamental step in the study of the effects taking place when other perturbations, such as electric fields, are applied to the heterostructure.

In the following, we report about the dramatic effects that depositing a metal layer on a $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) thin film has on the manganite magnetic properties. Since

bulk LSMO is metallic at the $x=0.33$ Sr doping concentration, band bending cannot take place throughout an extensive space charge region, contrary to what happens in the insulating manganite phases. Therefore, the interface with a different material is expected to influence the LSMO electronic and magnetic properties only over a very short length scale. It is thus essential to grow high quality thin LSMO layers forming very sharp interfaces with the metal. A noble metal is the most obvious choice as a partnering material, in the attempt to reduce chemical interdiffusion and interface reactions. Aluminium, for instance, drains oxygen from the manganite, altering its stoichiometry and strongly affecting the junction resistance versus temperature dependence.¹²

Thin single crystal LSMO films (thickness t_{LSMO} between 4 and 12 nm) were deposited on SrTiO_3 (STO) by pulsed laser deposition using a tripled neodymium doped yttrium aluminum garnet laser (wavelength=355 nm). The laser fluence was 1.4 J/cm^2 with a repetition rate equal to 2 Hz. The sample temperature and oxygen pressure were 973 K and 0.29 mbar, respectively. The surface roughness was characterized by atomic force microscopy (AFM) and proved to be ≈ 0.2 nm root-mean-square, with a very small number of droplets covering less than 1% of the sample area. The LSMO deposition rate was calibrated by x-ray reflectometry, so that the estimated error in the thickness is lower than 0.2 nm.

All the LSMO thin films reproduce the characteristic metal-to-insulator transition [see Fig. 1(a)] typical of bulk LSMO. The temperature T_p at which the resistivity maximum is observed decreases with the LSMO film thickness, as discussed in Ref. 7. From the thickness dependence of the LSMO layer conductance [Fig. 1(b)], one can see that LSMO becomes electrically insulating below a critical thickness of the order of ≈ 3 nm, in agreement with Ref. 7. Anyway, the presence of a maximum in the resistivity versus temperature dependence in Fig. 1(a) ensures that even the LSMO thin films with $t_{\text{LSMO}}=4$ nm cannot be considered as electrically dead.⁷

The sample magnetization M as a function of the temperature T has been determined by a superconducting quantum-interference device (SQUID) and is reported in Fig. 2 for LSMO thin films with thicknesses $t_{\text{LSMO}}=4$ nm [Fig. 2(a)] and $t_{\text{LSMO}}=8$ nm [Fig. 2(b)]. The Curie temperature T_C

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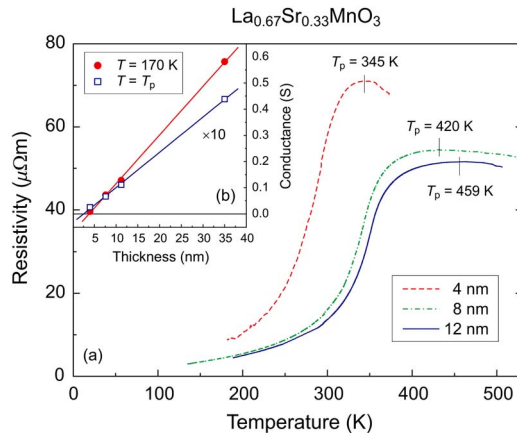


FIG. 1. (Color online) (a) Temperature dependence of the resistivity in thin LSMO films with thicknesses equal to 4, 8, and 12 nm, measured in the four-probe configuration. (b) LSMO conductance as a function of the LSMO film thickness, at $T=170$ K and at $T=T_p$. The lines in the inset are linear fits to the data points.

is obtained as the temperature corresponding to the higher temperature inflection point of $M(T)$. In agreement with the observed trend of T_p , T_C is lower than the bulk value and decreases with the film thickness. We also note that the T_p reduction we observe by varying t_{LSMO} from 8 to 4 nm is more pronounced than the reduction of T_C . This indicates that the magnetic and electric transitions do not coincide, as highlighted in Ref. 13, and suggests that in thin LSMO films the transport properties are more affected than the magnetic ones.

Subsequently, we have studied the effect of depositing a thin (2 nm thick) gold layer on top of LSMO films prepared, as described above. Au has been evaporated from a Knudsen cell (pressure during deposition $\approx 10^{-9}$ mbar). AFM does not measure any degradation of the surface roughness after Au deposition. Transport measurements across the Au/LSMO interfaces evidence an Ohmic (nonrectifying) behavior.

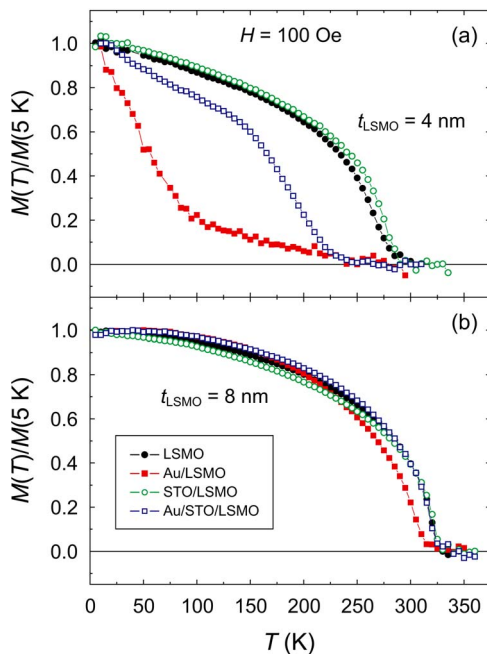


FIG. 2. (Color online) Normalized magnetization vs temperature curves measured by SQUID for different heterostructures: (a) LSMO thickness $t_{\text{LSMO}}=4$ nm or (b) $t_{\text{LSMO}}=8$ nm. The STO and Au thickness is 2 nm.

TABLE I. Curie temperature T_C , Curie temperature shift ΔT_C , and low temperature magnetization M_0 in LSMO thin films with and without Au and/or STO capping.

Sample	t_{LSMO} (nm)	T_C (K)	ΔT_C (K)	M_0 (emu/cm ³)
LSMO	4±0.1	280±5		420±70
Au/LSMO	4±0.1	95±10	185±11	150±100
STO/LSMO	4±0.1	285±5	-5±7	500±70
Au/STO/LSMO	4±0.1	220±10	60±11	420±70
LSMO	8±0.1	325±2		590±65
Au/LSMO	8±0.1	315±2	10±3	420±65
STO/LSMO	8±0.1	325±2	0±3	480±65
Au/STO/LSMO	8±0.1	325±2	0±3	520±65
LSMO	12±0.1	345±2		490±50
Au/LSMO	12±0.1	340±2	5±3	450±50

The effects of the Au capping on both the LSMO Curie temperature and the saturation magnetization M_0 at low temperature ($T=5$ K) are noteworthy, as seen from Fig. 2 and Table I, where values of T_C , M_0 , and ΔT_C (the shift of the Au-capped LSMO layer Curie temperature with respect to the same thickness uncapped layer) are listed. A sizable reduction of T_C and M_0 is observed for $t_{\text{LSMO}}=4$ nm, while for $t_{\text{LSMO}}=8$ nm the T_C and M_0 reduction is much smaller but still evident (see Fig. 2). No significant modifications are evidenced between uncapped and Au-capped LSMO thin films with $t_{\text{LSMO}}=12$ nm.

We have performed an x-ray photoemission spectroscopy (XPS) study of Au-capped LSMO samples as a function of the gold layer thickness, to check for interdiffusion of chemical species at the interface by monitoring the core photoemission lines and/or Auger peaks.¹⁴ The shape and position of the characteristic peaks from LSMO are essentially unchanged upon Au deposition, indicating the absence of relevant chemical reactions at the interface, at variance with what observed for Al on LSMO.¹² Our results are consistent with recent x-ray absorption and circular dichroism spectroscopy data, demonstrating that the deposition of Au on LSMO has no effect on the shape of the spectra collected at the Mn $L_{2,3}$ edges.¹⁵ No sizable interdiffusion of chemical species was detected beyond the instrumental sensitivity (about 10%) from the XPS peak intensity trend versus Au coverage. However, it must be noticed that the Curie temperature in LSMO is extremely sensitive to even small variations (a few percent) of the oxygen concentration,¹⁶ so chemical effects on T_C or M_0 cannot be completely ruled out by our XPS analysis.

In order to suppress interdiffusion and interface chemical reactions, we have inserted a thin (2 nm thick) STO film between the Au capping and the LSMO layer. Since epitaxial LSMO/STO assume the same STO in-plane lattice constant, a STO layer does not introduce further strain in the underlying manganite film. Strain, in fact, is known to significantly alter the electronic properties of perovskite manganites.¹⁷ As one can see from Fig. 2 and Table I, the effects induced on both T_C and M_0 by a STO overlayer without gold capping are negligible. Therefore, the STO overlayer, which is insulating, can be considered as inert.

The magnetic characterization performed by SQUID reveals that the Au/STO/LSMO multilayer with $t_{\text{LSMO}}=8$ nm and the corresponding uncapped LSMO film with the same

thickness have, within the experimental uncertainty, the same T_C and M_0 values (see Table I). Conversely, the Au/STO/LSMO heterostructure with $t_{\text{LSMO}}=4$ nm surprisingly still presents a large reduction (≈ 60 K) of T_C .

As mentioned above, the manganite T_C reduction induced by the Au capping through the STO spacer at $t_{\text{LSMO}}=4$ nm is not likely to be due to interdiffusion. Strain effects can also be reasonably ruled out since the Au film is thin and not epitaxial, and any strain would be partially released by the STO spacer. In any case, by extrapolating the linear dependence of T_C versus in-plane strain¹⁷ to the (unreasonably high) value corresponding to the Au-STO lattice mismatch ($\approx 4\%$), one can estimate a maximum T_C reduction of less than 40 K. Therefore, strain cannot explain the observed T_C decrease, at least for $t_{\text{LSMO}}=4$ nm. This conclusion is corroborated by the fact that, in this sample, M_0 is unaltered with respect to the value measured on uncapped LSMO layers.

Apparently, magnetism in LSMO is an extremely sensitive probe of local charge variations and the presence of the STO spacer does not exclude space charge effects very close to the interface, although it may attenuate them. Due to the high concentration of free carriers (10^{21} cm⁻³), the Thomas-Fermi screening length of LSMO is very short (0.2–1.9 nm) but higher than that of Au (0.07 nm),¹⁸ so that the difference in the work function of Au and LSMO would mainly drop in a thin accumulation region of the LSMO film. This can easily explain why the effects of the Au capping layer are reduced in the samples with $t_{\text{LSMO}}=8$ nm. The insertion of the dielectric STO spacer is estimated to reduce the voltage drop in the LSMO film by 30% (assuming a STO dielectric constant equal to 30, as expected in ultrathin films), as a fraction of the difference between the Au and LSMO work functions drops on the STO layer. An alternative explanation could be that the electrostatic screening of charge fluctuations¹⁰ in the LSMO layer provided by image charges in the Au film might hinder the double exchange interaction responsible of ferromagnetic ordering in LSMO, leading to a T_C reduction in the thinner films. The screening would be less effective as the Au-LSMO separation is increased by inserting a dielectric layer. In order to disentangle pure proximity effects due to electrostatic screening from true field effects inducing charge depletion/accumulation in the manganite, $M(T)$ measurements in applied electric field would be needed.

We would like to underline that the T_C reduction in Au- and Au/STO-capped LSMO thin films is very high compared to the field-induced T_C shifts (a few kelvins) typically observed in field effect devices,⁸ and of the same order of magnitude of the T_p shifts (up to 130 K) induced by charge injection in p - n structures.⁵ This suggests that thin manganite films might be particularly suitable for devices where trans-

port and magnetic properties could be tuned by the externally applied electric fields.

In summary, we have observed that capping La_{0.67}Sr_{0.33}MnO₃ thin films with gold has sizable effects on the manganite Curie temperature and saturation magnetization at low temperature. These effects consist in a strong reduction of T_C and M_0 in Au-capped LSMO thin films with respect to uncoated LSMO films of the same thickness. For the thinnest (4 nm thick) investigated LSMO film, a smaller but significant T_C reduction (≈ 60 K) is observed even when an inert SrTiO₃ spacer is inserted between the gold film and the manganite layer. This finding suggests that the proximity effects induced by gold on the LSMO layer magnetic properties might have, at least partially, an electrostatic origin.

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