

Tunnel conduction in epitaxial bilayers of ferromagnetic $\text{LaCoO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ deposited by a chemical solution method

Irene Lucas,^{*,†,||} Jose Manuel Vila-Funqueiriño,[¶] Pilar Jimenez-Cavero,^{§,⊥}
Beatriz Rivas-Murias,[¶] Cesar Magen,[†] Luis Morellon,^{‡,||} and Francisco Rivadulla[¶]

*Fundación ARAID, 50018 Zaragoza, Spain, Dpto. Física de la Materia Condensada,
Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain, Centro de
Investigación en Química Biológica y Materiales Moleculares (CIQUS), Universidad de
Santiago de Compostela, 15782-Santiago de Compostela, Spain, and Instituto de
Nanociencia de Aragón (INA), Universidad de Zaragoza, Mariano Esquillor, Edificio I+D,
50018 Zaragoza, Spain*

E-mail: ilucas@unizar.es

*To whom correspondence should be addressed

†Fundación ARAID, 50018 Zaragoza, Spain

‡Dpto. Física de la Materia Condensada, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

¶Centro de Investigación en Química Biológica y Materiales Moleculares (CIQUS), Universidad de Santiago de Compostela, 15782-Santiago de Compostela, Spain

§Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, Mariano Esquillor, Edificio I+D, 50018 Zaragoza, Spain

||Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, Mariano Esquillor, Edificio I+D, 50018 Zaragoza, Spain

⊥Dpto. Física de la Materia Condensada, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

Abstract

We report magnetic and electronic transport measurements across epitaxial bilayers of ferromagnetic insulator LaCoO_3 and half-metallic ferromagnet $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LCO/LSMO: 3.5 nm / 20 nm) fabricated by a chemical solution method. The I - V curves at room temperature and 4K measured with Conducting Atomic Force Microscopy (CAFM) on well defined patterned areas exhibit the typical features of a tunneling process. The curves have been fitted to the Simmons model to determine the height (φ) and width (s) of the insulating LCO barrier. The results show a $\varphi=0.40 \pm 0.05$ eV (0.50 ± 0.01 eV) at room temperature (4K) and a $s= 3$ nm, in good agreement with the structural analysis. Our results demonstrate that this chemical method is able to produce epitaxial heterostructures with the quality required for this type of fundamental studies and applications.

Introduction

The large Hund exchange energy in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) produces a complete splitting of the majority and minority spin bands,¹ therefore making this material a good source of spin-polarized electrons.² Having a T_C well above room temperature (≈ 360 K), LSMO is therefore an ideal candidate to be used as an electrode in heterostructures for spin tunneling applications.³⁻⁶ On the other hand, the quality of the tunnel barrier in these heterostructures is the main and most critical step to success in the fabrication of a high quality magnetic tunnel junction. Spinel ferrites as NiFe_2O_4 (NFO) and CoFe_2O_4 (CFO) have been reported to show spin-filtering effects,⁷⁻¹¹ acting not only as insulating barrier but selecting the spin orientation due to their ferrimagnetic nature. However, despite their predicted high spin-filtering efficiency at room temperature, all the reports indicate a much lower performance than expected.^{12,13} Unfortunately, there are not many intrinsic ferromagnetic oxides that are also good insulators, and therefore alternative strategies for materials design must be developed to advance in this line.

In this regard, bulk magnetic and electric properties of certain perovskite oxides may be engineered on demand by epitaxial growth on a substrate. In particular, it has been shown that LaCoO_3 (LCO), which is a diamagnetic insulator in bulk at low temperatures, exhibits a ferromagnetic order under epitaxial tensile-strain below $T < 85$ K,¹⁴⁻¹⁸ combined with a high electrical resistivity.²¹ The origin of the ferromagnetism in strained LCO is still under debate:^{14,22,23} a complex relaxation mechanism of the epitaxial strain involving ordered stripe patterns of oxygen vacancies was proposed by Bišcup *et al.*¹⁴ In addition, it is well known that the close proximity between the crystal-field splitting of Co^{3+} in a octahedral oxygen environment and the exchange coupling, produces an activated population of the higher spin states at the expense of the low spin state (LS) in bulk LaCoO_3 .²⁴⁻²⁶ Therefore, other authors^{22,23} proposed a novel strain-relaxation mechanism which results in an ordered pattern of locally tetragonal and monoclinic distortions. These produce the coexistence of LS-HS Co^{3+} , and introduces the possibility of a ferromagnetic interaction.^{17,18} In this direction, Choi *et al.*²² reported the existence of a fully strained thin layer of the film of ≈ 2 nm close to the substrate. Therefore, it is not clear whether thin films of LCO of just a few nanometers compatible with the thicknesses required for the fabrication of tunneling barriers will retain the FM properties. Moreover, different growth methods could differ in the way of relaxing the epitaxial strain. In particular, chemical solution deposition methods imply a growth close to thermodynamic equilibrium, very different from the conditions in Pulsed Laser Deposition (PLD) or sputtering, and therefore the possibility of studying the magnetism in very thin films and heterostructures prepared by chemical methods becomes interesting. Moreover, chemical methods compared to physical methods as PLD or sputtering are cheaper methods since they do not need vacuum systems.

In this work we report the fabrication of STO:Nb/LCO/LSMO epitaxial heterostructures by a chemical solution method. Tunneling current between the conducting top electrode LSMO and the conducting substrate of Nb doped SrTiO_3 (STO:Nb), was measured across an insulating barrier of LCO ≈ 3.5 nm by conductig tip AFM. Nanostencil lithography

technique has been used to define Au nanocontacts of different areas on top of the LSMO surface. The LCO barrier has been structurally characterized showing an epitaxial strained growth along the whole thickness and a sharp interface with the substrate and the LSMO top film. Magnetization measurements confirmed the magnetic nature of the thin barrier. The width (s) and height (φ) of the tunneling barrier between LSMO and LCO have been determined using the Simmons model and are consistent with reported values for insulating barriers used in similar heterostructures.

Experimental

For the deposition of the LCO/LSMO bilayers, an epitaxial layer of LCO was first crystallized on top of TiO₂-terminated Nb:STO (001).^{19-21,27} For this, individual solutions of the cations were prepared by dissolving the corresponding nitrates in water with ethylenediaminetetraacetic acid (EDTA, 1:1 molar ratio) and Polyethylenimine (PEI) (1:1 mass ratio to EDTA). Each individual solution was filtrated using Amicon filtration units (10 kDalton), and retained portions were analyzed by Inductively Coupled Plasma (ICP). The solutions were mixed according to the desired final stoichiometry and spin-coated at 3500 rpm (LCO) and 4000 rpm (LSMO) on the STO:Nb substrates using an acceleration and deceleration ramp of 250 rpm/s². The solutions were concentrated to 60 mM and 120 mM for LCO and LSMO respectively. Viscosity of solutions was measured in a DMA 4100M (Anton Paar) densimeter, with a microviscometer module (Lovis 2000 ME) resulting in values of 2.5-4 mPa.s. Under these conditions a polymeric film typically of 200 nm is obtained. This polymeric film was annealed in air at 950°C for 2 h. The samples were ramped to the final annealing temperature and cooled down at 1C/min to avoid cracks. Then, the polymeric precursor of the second layer is subsequently deposited and annealed under the same conditions. There is no preheating temperature. Controlling the cationic concentration of the initial solutions we were able to produce bilayers of LCO (3.5 nm) and LSMO (20 nm). The films cover the

whole surface of the substrates ($5 \times 5 \text{ mm}^2$), with only small imperfections at the corners. Scanning Transmission Electron Microscopy (STEM) characterization of the LCO/LSMO bilayer has been performed in an FEI Titan 60-300 operated at 300 kV and equipped with a high brightness Schottky field emission gun, a CETCOR probe aberration corrector from CEOS to provide a spatial resolution better than 1 Å in STEM mode, and a Gatan Imaging Filter 866 ERS for spectroscopic analysis. Z contrast imaging has been carried out in High Angle Annular Dark Field (HAADF) with a probe convergence angle of 25 mrad and an inner collection angle of approximately 58 mrad. HAADF imaging was combined with Electron Energy Loss Spectroscopy (EELS) to analyze chemically the heterostructures by Spectrum Imaging (SI). In this case, both the inner angle for the HAADF detector and the spectrometer collection angle were 60 mrad. SI has been performed with an energy dispersion of 0.5 eV and the dwell time around 0.04 sec. The specimen analyzed is a lamella extracted from the sample by Focused Ion Beam milling in an FEI Helios Nanolab 600 using a 5 kV ion beam for the final thinning to reduce the surface amorphization layer. LCO thin films have been reported to show pinholes at the surface to release epitaxial strain.²⁸ Therefore, conventional Van der Pauw geometry is not a valid method to measure the electric response. To overcome this problem nanostencil lithography has been used to deposit Au nanocontacts of different diameters using shadow masks patterned by focused ion-beam (FIB) lithography. CAFM measurements at room temperature were performed using a commercial Veeco-Brucker MultiMode system whereas an Attocube system was used for low temperature measurements. Both systems can be used in conductive mode and the Attocube AFM can be used at temperatures down to 1.5K and allows to apply in-plane magnetic fields up to 2T.

Results and discussion

The high-resolution X-ray reciprocal space map of the LCO/LSMO bilayer around the (-103) is shown in figure 1(a). The peak of the thin LCO layer can be clearly appreciated. There is a perfect in plane matching of the LCO and LSMO layers to the substrate, confirming the epitaxial growth of the films. This implies a tensile strain of +2.63% for LCO and +0.62% for LSMO, while the out of plane lattice parameter reflects a compression of 2.4% for LCO and 1.4% for LSMO. Moreover, only the (00l) peaks are observed between 10° and 120° in the 2Θ - ω scans (Fig.1(b)), indicating the oriented growth and absence of any spurious phase. Also, the observation of Kiessig fringes in the reflectivity analysis (Fig. 1(c)) confirms the low surface and interface roughness of the layers, and the continuous growth of the films over the substrate. This smoothness over the whole area is exceptional for layers grown by a chemical method, and particularly for a case like this in which a second layer of LSMO is deposited on top of a previously grown film of LCO. The values of the roughness derived from the fitting of the x-ray reflectivity curves and from topography AFM images are respectively 0.7(1)nm and 0.5(1.3) for all the interfaces and the top surface of LSMO. These values are perfectly comparable to typical values obtained by physical deposition techniques.

The HAADF image of a cross sectional specimen of the bilayer shown in Fig. 2(a) evidences locally the good crystal quality of the bilayer. Both layers grow epitaxial and coherent onto the STO:Nb substrate. They are fully strained with no presence of structural defects, such as misfit dislocations, to accommodate the epitaxial strain. The 3.5-nm-thick LCO film can be clearly identified on top of the STO:Nb by the slightly higher intensity with respect to the 20-nm-thick LSMO top layer, which is related to the higher average Z number of the La-richer LCO. Over a series of images we have observed that the thickness of the LCO layer apparently decreases to 2-3 nm. This suggests that the LCO layer presents significant steps at the top surface. Geometrical Phase Analysis (GPA) has been carried out to probe locally the deformation state of the LCO and LSMO layers. The in-plane lattice parameter,

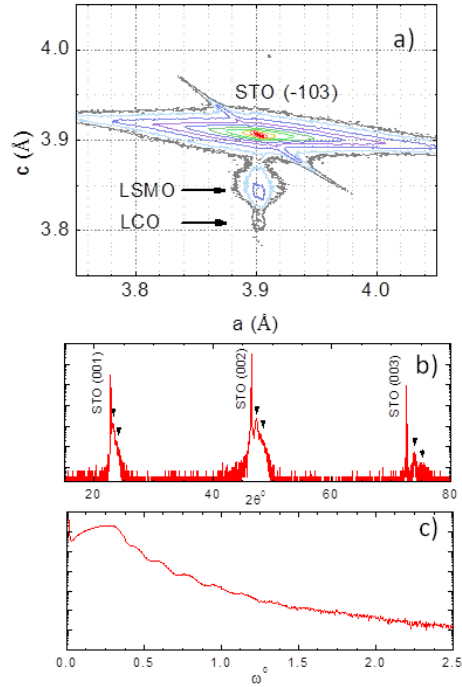


Figure 1: (a) High-resolution X-ray reciprocal space map of the LCO/LSMO bilayer, around the (-103) peak. (b) X-ray diffraction pattern of the LCO/LSMO bilayer. The arrows indicate the position of the (00l) peaks of LSMO and LCO. (c) X-ray reflectivity curve of the LCO/LSMO bilayer.

Fig. 2(b), is thoroughly homogeneous as expected from a fully strained film, whereas the out-of-plane lattice parameter, Fig. 2(c), shows an average out-of-plane lattice parameter for the LCO layer 3.0(5)% smaller than the substrate, whereas the LSMO is 1.3(3)% reduced with respect to the STO:Nb. These values are in very good agreement with the values obtained from X-ray diffraction. It is important to note that these values are consistent with a fully elastic deformation of LSMO, which conserves the volume of the system. However, for LCO the volume in the tensile strained film increases $\approx 5\%$ with respect to the bulk. This change must be related to a variation in the stoichiometry of the sample, most probably by the generation of oxygen vacancies. The oxygen deficiency of the LCO layer is evidenced in the HAADF image. It presents the typical structure of dark stripes perpendicular to the substrate plane which are a common feature due to the ordering of oxygen vacancies.²⁹

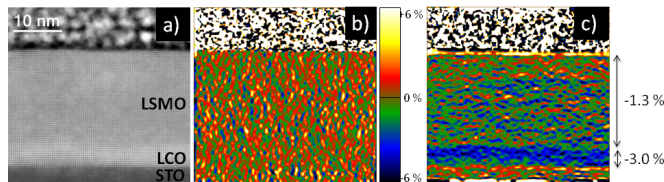


Figure 2: HAADF imaging of the LCO/LSMO bilayer grown on Nb:STO. (a) HAADF image. (b) In-plane and (c) Out-of-plane deformation of the lattice parameter with respect to the substrate obtained by GPA. The strong compression of the out plane lattice parameter in LCO is homogeneous through the film.

The chemical composition of the layers and their interfaces has been explored by STEM-EELS spectrum imaging. The result of a two dimensional chemical map across the two interfaces is presented in Figure 3. This atomic resolution map shows the atomic structure of the heterostructure with chemical sensitivity. La in A positions forms a square lattice which intermixes with the B-type Co (Mn) columns following the typical perovskite structure. It shows a region where STO:Nb-LCO interface is extremely sharp, with a thickness in the range of a single lattice cell, and no significant chemical diffusion is observed. Some diffusion of Co into the first layers of the manganite can be appreciated at the LCO-LSMO interface.

The magnetic properties of the bilayer are summarized in figure 4. The magnetization of the thin LCO layer is very small, and the diamagnetism of STO dominates the signal at

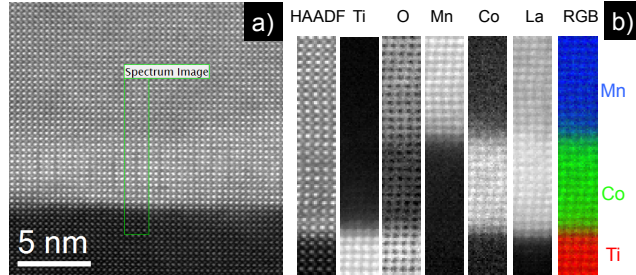


Figure 3: Spectrum imaging of the LCO/LSMO bilayer grown on STO. (a) HAADF reference image. (b) Integrated intensity maps of the simultaneously acquired HAADF, Ti $L_{2,3}$, O K, Mn $L_{2,3}$, Co $L_{2,3}$ and La $M_{4,5}$ signals.

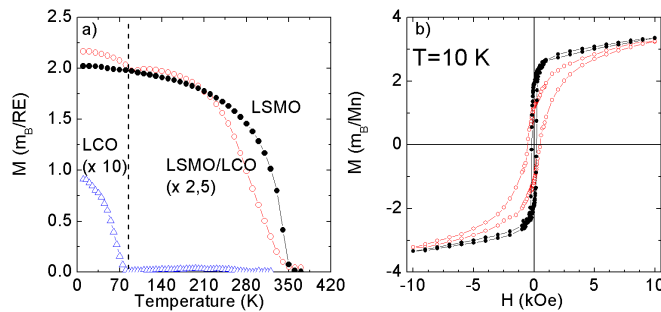


Figure 4: (a) Temperature dependence of the magnetization of a 20 nm thick film of LSMO, a $\simeq 3.5$ nm thick layer of LCO, and the LCO/LSMO bilayer, at $H = 100$ Oe. The FM contribution of LCO is visible in the bilayer below the $T_C = 85$ K. (b) Field dependence of the magnetization at 10 K for a single layer of LSMO (black circles) and for the LCO/LSMO bilayer (red open circles).

fields larger than ≈ 100 Oe. For that reason the $M(H)$ loop for the single layer of LCO is not presented in figure 4(b). In any case, the magnetic transition at $T_C \approx 85$ K is clearly visible, both in the single layer of LCO and in the bilayer, on top of the magnetization of LSMO. These results demonstrate that ≈ 3.5 nm thick strained films of LCO deposited by this chemical method are still ferromagnetic. On the other hand, the increase in the coercive field of the bilayer with respect to pure LSMO as well as the higher saturation field (Fig. 4(b)), points to an increase in the anisotropy that might be related to an AF coupling of the LCO and LSMO layers at the interface.

The transport properties at room temperature have been determined by CAFM using a silicon tip coated with boron-doped conducting diamond. To obtain well defined contact areas for CAFM measurements, Au nanocontacts have been defined on the surface of LSMO using square silicon nitride (Si_3N_4) membranes ($250 \mu\text{m} \times 250 \mu\text{m}$, 200 nm thick) as shadow masks. The membranes have been patterned by FIB defining triangles to deposit nanocontacts ranging between 750 nm and $5 \mu\text{m}$, as shown in figure 5(a). Figure 5(b) shows a topography image (left) and the corresponding current map (right) for nanocontacts of different diameters. Well defined sharp Au dots were obtained showing higher conductivity than LSMO surface, as expected. The procedure to perform CAFM measurements is well established and is based on the current flow from the AFM ground to the upper layer of the sample and through the tip effective contact area. This effective AFM tip contact area can be difficult to determine due to the shape of the tip and given that it depends on the applied force. This problem is overcome using the nanostructured contact geometry so that injected current depends only on the size of the Au dots. Conductive AFM measurements using contact geometry have been achieved so far in Au/LCMO interfaces fabricated by sputtering.³⁰⁻³²

AFM topography of the LCO surface prior to the deposition of the LSMO layer showed a large number of pinholes $\approx 1 \mu\text{m}$ diameter, with an average distance between them around $5 \mu\text{m}$. Thus, the larger contacts can easily cover part of these pinholes and give Ohmic

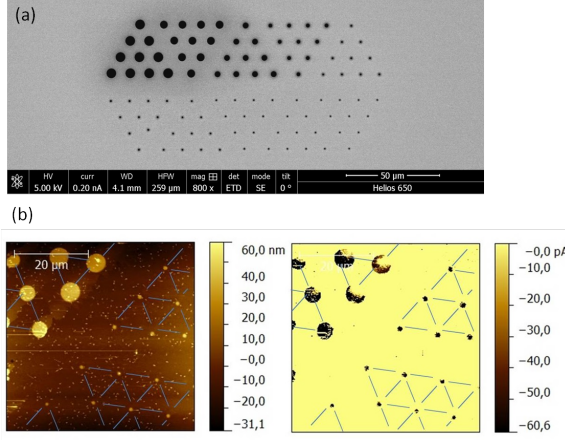


Figure 5: (a) Silicon nitride membrane to be used as shadow mask patterned using FIB lithography. Every triangle allows to deposit a group of 10 Au contacts with same diameter, ranging from $5 \mu\text{m}$ to 750 nm . (b) Topography image (left) and corresponding current map (right) of Au nanocontacts of different diameters ($5 \mu\text{m}$, $4 \mu\text{m}$, 900 nm , 850 nm and 800 nm) evaporated on the LSMO surface.

curves by direct contact between LSMO and the substrate. On the other hand, contact diameters below $5 \mu\text{m}$ give consistent results showing only some small dispersion associated with experimental fluctuations of the tunnel current through an insulating barrier between two conducting layers. These fluctuations follow a log-normal distribution³³ and therefore a logarithmic average was performed for every series of $I-V$ experimental curves measured for every contact size. Figure 6(a) shows $I-V$ averaged curves characteristic of tunnel current corresponding to the LSMO/LCO bilayer for different Au contact sizes. The intensity measured for every voltage value scales with the contact size, as expected.

To prove the quality of the tunneling barrier, the value of resistivity for the volume of LCO through we have performed the measurements can be calculated from the reported $I-V$ curves. Taking into account the values of current for a voltage of 0.1V at room temperature and at 4K , the resistivity obtained at room temperature is $0.45 \text{ M}\Omega\text{cm}$ and $14.5 \text{ M}\Omega\text{cm}$ at 4K . This proves the good insulating behavior of the tunneling barrier.

To determine the width and height of the tunnel barrier, the $I-V$ curves have been fitted to the Simmons model³⁴ in the intermediate voltage range, assuming an isotropic barrier (equation 1). Furthermore, the robustness of the results was tested by the Brickman model

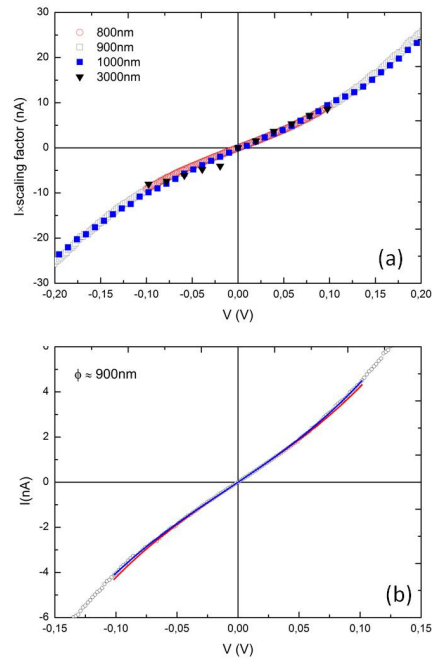


Figure 6: (a) Scaling of the I - V averaged curves as a function of the Au contact diameter measured at room temperature by direct contact of the conducting AFM tip on contacts with diameter ranging from $3 \mu\text{m}$ to 800 nm . (b) Averaged I - V curve corresponding to a 900 nm Au contact showing the fit to the Simmons model (red line) and to the Brinkman model (blue line).

(equation 2) to evaluate the case of an anisotropic barrier.³⁵ A representative example is shown in figure 6(b). The height and width of the barrier obtained from the fitting are $\varphi = 0.46 \pm 0.01$ eV and $s = 2.7 \pm 0.1$ nm, respectively in the case of Simmons model and $\varphi_{av} = 0.46 \pm 0.02$ eV and $s = 2.7 \pm 0.2$ nm in the case of Brinkman model. The same fits were repeated for the different contact sizes using Simmons model, resulting in an average height $\varphi = 0.40 \pm 0.05$ eV and width $s = 3.2 \pm 0.4$ nm. This value of s is very close to the thickness of the LCO layer extracted from STEM images ($t = 3.5 \pm 0.2$ nm). Also, the value obtained for φ in the LCO barrier is comparable to previously reported in a LSMO/STO(3-5 nm)/LSMO heterostructures ($\varphi \approx 0.5-0.7$ eV),³⁶ and LCMO/STO(3 nm) ($\varphi \approx 0.6$ eV).^{31,32}

$$J = \frac{e}{2\pi\hbar s^2} \left\{ \begin{array}{l} \left(\frac{2\varphi - eV}{2} \right) \exp \left[-(2m)^{1/2} \frac{4\pi s}{\hbar} \left(\frac{2\varphi - eV}{2} \right)^{1/2} \right] \\ - \left(\frac{2\varphi + eV}{2} \right) \exp \left[-(2m)^{1/2} \frac{4\pi s}{\hbar} \left(\frac{2\varphi + eV}{2} \right)^{1/2} \right] \end{array} \right\} \quad (1)$$

$$J = G(0) \left(V - \frac{4\sqrt{2ms}}{3\hbar} \frac{\Delta\varphi}{16\bar{\varphi}^{3/2}} eV^2 + \frac{9}{128\bar{\varphi}} \left(\frac{4\sqrt{2ms}}{3\hbar} \right)^2 e^2 V^3 \right) \quad (2)$$

Therefore, these results demonstrate that thin layers of LCO fabricated by this chemical method retain a good insulator character and can be used as tunneling barriers with LSMO at room temperature.

In order to prove the possibility of the LCO barrier to act as a spin-filter, CAFM measurements were performed below the Curie temperature of LCO under different applied fields. The results obtained at low temperature are much more reproducible, and the value of the barrier s and φ is practically the same for every contact size. Figure 7(a) shows tunnel current curves obtained at low temperature under fields ranging from -500 Oe to 500 Oe. No field dependence was observed, therefore the system does not act as an efficient spin filter. The values of s and φ from the fit to Simmons model show no change in the barrier width with respect to room temperature, as expected. However, there is an increment of

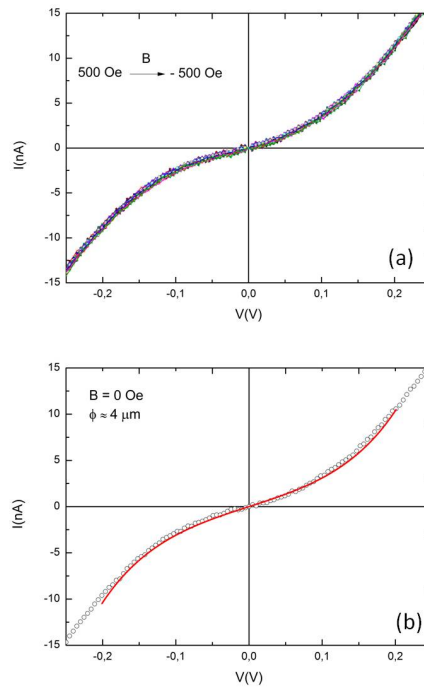


Figure 7: (a) I - V curves measured on a $4 \mu\text{m}$ contact at 4K applying magnetic field in-plane ranging between -500 to 500 Oe. (b) Averaged I - V curve for a $4 \mu\text{m}$ contact showing the fit to Simmons model (red line).

0.1 eV in the barrier height. It is worth to mention that room temperature measurements were repeated using the second AFM system before cooling the sample to confirm the reproducibility of the measurement. The same value of φ and s were obtained in both AFM at room temperature.

Given the possibility of Co to diffuse into the LSMO layer, the formation of a Co/Mn spinel of the type CoMn_2O_4 could be a possibility to explain the increase of φ . However, in this case the size of the barrier should be also modified. Alternatively, a favorable redox reaction between Co^{+3} and Mn^{+3} to produce Co^{+2} and Mn^{+4} , will introduce a $\text{Co}^{+2}\text{-O-Co}^{+2}$ AF interaction at the interface. Looking at the magnetic data of figure 4, the decrease of the T_C of LSMO observed in the bilayer with respect to isolated LSMO films, and the decrease of its volume magnetization, makes this possibility very probable.

Conclusions

In summary, we have demonstrated that tunnel heterostructures of LCO/LSMO can be fabricated by a simple chemical method. Our results show that ≈ 3.5 nm thick strained films of LCO still show ferromagnetic behavior. An increase in the coercive field of the bilayer with respect to pure LSMO is observed, as well as a higher saturation field, pointing to an increase in the anisotropy that could be related to an AF coupling of the LCO and LSMO layers at the interface. The I - V curves measured across the tunneling barrier with a CAFM scale with the contact size, and were correctly fitted to Simmons model. The room temperature value of $\varphi = 0.40 \pm 0.05$ eV is in good agreement with previous reports for insulating barriers used in similar heterostructures, while the value estimated for $s = 3.2 \pm 0.4$ nm is confirmed by the thickness of the LCO barrier measured by STEM. These results enhance the possibility of using LCO as a suitable insulating barrier in oxide-based magnetic tunnel junctions.

Aknowledgements

The authors aknowledge the support to this work from Spanish Ministry of Science through projects No. MAT2011-28532-C03-02 and MAT2011-27553-C02 including FEDER funding, the Aragón Regional Government (Project No. E26), ERC-StG-259082(2DOTHERMS) and Xunta de Galicia (2012-CP071). Jose Manuel Vila-Fungueiriño aknowledges MINECO of Spain for support through the FPI program and Irene Lucas and Cesar Magen aknowledge Fundación Aragonesa para la I+D from support through ARAID program.

References

References

- (1) Park, J. H.; Vescovo, E.; Kim, H. J.; Kwon, C.; Ramesh, R.; Venkatesan, T. Direct Evidence for a Half-Metallic Ferromagnet. *Nature*. **1998**, 392, 794-796.
- (2) Owen, M.; Bibes, M.; Barthélémy, A.; Contour, J. P.; Anane, A.; Lemaitre, Y.; Fert, A. Nearly Total Spin Polarization in La₂/3Sr₁/3MnO₃ from Tunneling Experiments. *Appl. Phys. Lett.*. **2003**, 82(2), 233-235.
- (3) Bibes, M.; Barthélémy, A. Oxide Spintronics. *IEEE Trans. Electron Devices*.. **2007**, 54(5), 1003-1023.
- (4) Opel, M. Spintronic Oxides grown by Laser-MBE. *J. Phys. D: Appl. Phys.*.. **2012**, 45(3), 033001.
- (5) Bibes, M.; Villegas, J. E.; Barthélémy, A. Ultrathin Oxide Films and Interfaces for Electronics and Spintronics. *Adv. Phys.*.. **2011**, 60(1), 5-84.
- (6) Hueso, L. E.; Pruneda, J. M.; Ferrari, V.; Burnell, G.; Valdes-Herrera, J. P.; Simons, B. D.; Littlewood, P. B.; Artacho, E.; Fert, A.; Mathur, N.

- D. Transformation of Spin Information into Large Electrical Signals using Carbon Nanotubes. *Nature*. **2007**, 445 (7126), 410-413.
- (7) Luders, U.; Bibes, M.; Bouzehouane, K.; Jacquet, E.; Contour, J. P.; Fusil, S.; Bobo, J. F.; Fontcuberta, J.; Barthelemy, A.; Fert, A. Spin Filtering through Ferrimagnetic NiFe₂O₄ Tunnel Barriers. *Appl. Phys. Lett.* **2006**, 88(8), 082505.
- (8) Luders, U.; Barthelemy, A.; Bibes, M.; Bouzehouane, K.; Fusil, S.; Jacquet, E.; Contour, J. P.; Bobo, J. F.; Fontcuberta, J.; Fert, A. NiFe₂O₄: A versatile Spinel Material brings new Opportunities for Spintronics. *Adv. Mater.* **2006**, 18(13), 1733-1736.
- (9) Chapline, M. G.; Wang, S. X. Room-Temperature Spin Filtering in a CoFe₂O₄/MgAl₂O₄/Fe₃O₄ Magnetic Tunnel Barrier. *Phys. Rev. B*. **2006**, 74(1), 014418.
- (10) Ramos, A. V.; Guittet, M.-J.; Moussy, J.-B.; Mattana, R.; Deranlot, C.; Petroff, F.; Gatel, C. Room Temperature Spin Filtering in Epitaxial Cobalt-Ferrite Tunnel Barriers. *Appl. Phys. Lett.* **2007**, 91(12), 122107.
- (11) Foerster, M.; Rigato, F.; Bouzehouane, K.; Fontcuberta, J. Tunnel Transport through CoFe₂O₄ Barriers investigated by Conducting Atomic Force Microscopy. *J. Phys. D: Appl. Phys.* **2010**, 43(29), 295001.
- (12) Chen, Y. F.; Ziese, M. Spin filtering in La_{0.7}Sr_{0.3}MnO₃/CoFe₂O₄/Nb(0.5%): SrTiO₃ Heterostructures. *Phys. Rev. B*. **2007**, 76(1), 014426.
- (13) Takahashi, Y. K.; Kasai, S.; Furubayashi, T.; Mitani, S.; Inomata, K.; Hono, K. High Spin-Filter Efficiency in a Co Ferrite Fabricated by a Thermal Oxidation. *Appl. Phys. Lett.* **2010**, 96(7), 072512.

- (14) Biskup, N.; Salafranca, J.; Mehta, V.; Oxley, M. P.; Suzuki, Y.; Pennycook, S. J.; Pantelides, S. T.; Varela, M. Insulating Ferromagnetic LaCoO₃-delta Films: A Phase Induced by Ordering of Oxygen Vacancies. *Phys. Rev. Lett.* **2014**, 112(8), 087202.
- (15) Fuchs, D.; Arac, E.; Pinta, C.; Schuppler, S.; Schneider, R.; von Löhneysen, H. V. Tuning the Magnetic Properties of LaCoO₃ Thin Films by Epitaxial Strain. *Phys. Rev. B.* **2008**, 77(1), 014434.
- (16) Park, S.; Ryan, P.; Karapetrova, E.; Kim, J. W.; Ma, J. X.; Shi, J.; Freeland, J. W.; Wu, W. D. Microscopic Evidence of a Strain-Enhanced Ferromagnetic State in LaCoO₃ Thin Films. *Appl. Phys. Lett.* **2009**, 95(7), 072508.
- (17) Sterbinsky, G. E.; Ryan, P. J.; Kim, J. -W.; Karapetrova, E.; Ma, J. X.; Shi, J.; Woicik, J. C. Local Atomic and Electronic Structures of Epitaxial Strained LaCoO₃ Thin Films. *Phys. Rev. B.* **2012**, 85, 020403.
- (18) Hsu, H.; Blaha, P.; Wentzcovitch, R. M. Ferromagnetic Insulating State in Tensile-Strained LaCoO₃ Thin Films from LDA+U Calculations. *Phys. Rev. B.* **2012**, 85(14), 140404.
- (19) Cobas, R.; Munoz-Perez, S.; Cadogan, J. M.; Puig, T.; Obradors, X. Magnetoresistance in Epitaxial Thin Films of La_{0.85}Ag_{0.15}MnO₃ produced by Polymer Assisted Deposition. *Appl. Phys. Lett.* **2013**, 99(8), 083113.
- (20) Jia, Q. X.; McCleskey, T. M.; Burrell, A. K.; Lin, Y.; Collis, G. E.; Wang, H.; Li, A. D. Q.; Foltyn, S. R. Polymer-assisted Deposition of Metal-oxide Films. *Nat. Mater.* **2004**, 3(8), 529-532.
- (21) Rivadulla, F.; Bi, Z. X.; Bauer, E.; Rivas-Murias, B.; Vila-Funqueiriño, J. M.; Jia, Q. X. Strain-Induced Ferromagnetism and Magnetoresistance in

- Epitaxial Thin Films of LaCoO₃ Prepared by Polymer-Assisted Deposition. *Chem. Mater.* **2013**, 25(1), 55-58.
- (22) Choi, W. S.; Kwon, J. H.; Jeon, H.; Hamann-Borrero, J. E.; Radi, A.; Macke, S.; Sutarto, R.; He, F. Z.; Sawatzky, G. A.; Hinkov, V.; Kim, M.; Lee, H. N. Strain-Induced Spin States in Atomically Ordered Cobaltites. *Nano Lett.* **2012**, 12(9), 4966-4970.
- (23) Kwon, J. H.; Choi, W. S.; Kwon, Y. K.; Jung, R.; Zuo, J. M.; Lee, H. N.; Kim, M. Nanoscale Spin-State Ordering in LaCoO₃ Epitaxial Thin Films. *Chem. Mater.* **2014**, 26(8), 2496-2501.
- (24) Haverkort, M. W.; Hu, Z.; Cezar, J. C.; Burnus, T.; Hartmann, H.; Reuther, M.; Zobel, C.; Lorenz, T.; Tanaka, A.; Brookes, N. B.; Hsieh, H. H.; Lin, H. -J.; Chen, C. T.; Tjeng, L. H. Spin State Transition in LaCoO₃ Studied using Soft X-ray Absorption Spectroscopy and Magnetic Circular Dichroism. *Phys. Rev. Lett.* **2006**, 97(17), 176405.
- (25) Yan, J. Q.; Zhou, J. S.; Goodenough, J. B. Bond-Length Fluctuations and the Spin-State Transition in LCoO₃ (L=La, Pr, and Nd). *Phys. Rev. B.* **2004**, 69(13), 134409.
- (26) Goodenough in *Metallic Oxides*, Progress in Solid State Chemistry 5, (1971).
- (27) Vila-Funqueiriño, J. M.; Rivas-Murias, B.; Rodríguez González, B.; Rivadulla, F. Interface Magnetic Coupling in Epitaxial Bilayers of La_{0.92}MnO₃/LaCoO₃ Prepared by Polymer-Assisted Deposition. *Chem. Mater.* **2014**, 26(3), 1480-1484.
- (28) Vila-Funqueiriño, J. M.; Rivas-Murias, B.; Rivadulla, F. Strong Interfacial

- Magnetic Coupling in Epitaxial Bilayers of LaCoO₃/LaMnO₃ prepared by Chemical Solution Deposition. *Thin Solid Films*. **2014**, 553, 81-84.
- (29) Klenov, D. O.; Donner, W.; Foran, B.; Stemmer, S. Impact of Stress on Oxygen Vacancy Ordering in Epitaxial (La_{0.5}Sr_{0.5})CoO₃-partial Derivative Thin Films. *Appl. Phys. Lett.* **2003**, 82(20), 3427-3429.
- (30) Balcells, L. I.; Abad, L. I.; Rojas, H.; Martinez, B. Material Damage induced by Nanofabrication Processes in Manganite Thin Films. *Nanotechnology*. **2008**, 19(13), 135307.
- (31) Balcells, L. I.; Abad, L. I.; Rojas, H.; Del Pino, A. P.; Estrade, S.; Arbiol, J.; Peiro, F.; Martinez, B. Transport Properties across the La_{2/3}Ca_{1/3}MnO₃/SrTiO₃ Heterointerface. *J. Appl. Phys.* **2008**, 103(7), 07E303.
- (32) Balcells, L. I.; Abad, L. I.; Rojas, H.; Del Pino, A. P.; Estrade, S.; Arbiol, J.; Peiro, F.; Martinez, B. Electronic Effects in Manganite/Insulator Interfaces: Interfacial Enhancement of the Insulating Tunneling Barriers. *Small*. **2008**, 4(3), 365-371.
- (33) Da Costa, V.; Romeo, M.; Bardou, F. Statistical Properties of Currents flowing through Tunnel Junctions. *J. Magn. Magn. Mater.* **2003**, 258, 258-259.
- (34) Simmons, J. G. Electric Tunnel Effect between Dissimilar Electrodes separated by a Thin Insulating Film. *J. Appl. Phys.* **1963**, 34(9), 2581.
- (35) Brinkman, W. F.; Dynes, R. C.; Rowell, J. M. Tunneling Conductance of Asymmetrical Barriers. *J. Appl. Phys.* **1970**, 41(5), 1915-1921.

- (36) Sun, J. Z.; Krusin-Elbaum, L.; Duncombe, P. R.; Gupta, A.; Laibowitz, R. B. Temperature Dependent, Non-Ohmic Magnetoresistance in Doped Perovskite Manganate Trilayer Junctions. *Appl. Phys. Lett.* **1997**, 70(13), 1769-1771.