Strong interfacial magnetic coupling in epitaxial bilayers of $LaCoO_3/LaMnO_3$ prepared by chemical solution deposition.

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ABSTRACT

We report the synthesis of high quality epitaxial bilayers of $LaMnO_3/LaCoO_3$ (LCO/LMO) on (001) $LaAlO_3$, by spin-coating of a polymeric aqueous solutions. The bilayer shows a very large increase of the magnetization coercive field (≈ 3000%) with respect to the isolated LMO or LCO films. We suggest that the origin of this effect is a strong Mn^{4+}-O-Co^{2+} exchange interaction at the interface. Our results demonstrate that a simple chemical method is able to produce high quality epitaxial heterostructures in which interfacial effects can modify substantially the properties of the individual layers.

1. Introduction

Thin films, multilayers and the phenomena associated to their interfaces have attracted the interest of the scientific community due to the possibility of tuning their magnetic/electronic properties by epitaxial strain or by the electronic reconstruction induced at the contact between two different materials. For example, the ferromagnetic (FM) ordering exhibited below 85 K in a biaxially strained $LaCoO_3$ thin film [1,2] is surprising given the diamagnetic behavior observed in bulk. Another example is the extrinsic magnetocaloric effect in $La_{0.7}Ca_{0.3}MnO_3$ films due to the strain produced by the $BaTiO_3$ substrate [3]. A well-known phenomenon characteristic of magnetic heterostructures is the exchange bias (EB) effect [4,5]. In general, this interfacial effect involves a ferromagnetic and antiferromagnetic material [6,7], although it has been also reported at the interface between two different ferromagnets [8].

On the other hand, preparation of high quality thin-films and multilayers requires the use of physical deposition techniques (sputtering, Pulsed Laser Deposition, Molecular Beam Epitaxy, etc) that demand high cost equipments.

Chemical methods, although most cost-effective, do not produce the quality of layers and interfaces required for this kind of advanced studies. However, some authors recently reported the preparation of high-quality epitaxial thin-films of different oxides by spin-coating of a chemical precursor solution, using polyethyleneimine (PEI) as a cation-binder (Polymer Assisted Deposition, PAD) [2,9,10].

In this paper, we report the synthesis of an epitaxial bilayer film of $LaMnO_3/LaCoO_3$ (LMO/LCO) on $LaAlO_3$ (001) by PAD. The structure and morphology is comparable to that obtained by physical deposition techniques. The most relevant finding is an increase of the coercive field of the bilayer of 3000% with respect to the individual LCO and LMO layers. We discuss this observation as the result of an exchange between Mn^{4+}-O-Co^{2+} due to a redox process at the interface.

2. Experimental details

Nitrates of the cations (La, Mn, and Co) were dissolved in water, along with polyethyleneimine (PEI, Mw≈200000, Supelco Analytical) and ethylenediaminetetraacetic acid (EDTA). The relative molar concentrations in the solutions were metal:EDTA 1:1. For EDTA:PEI, a 1:2 (for La an Co) or 1:1 (for Mn) mass ratio was employed. PEI provides stability to the complex of $[EDTA\text{-}M^{n+}]^{(4-n)-}$, allows an homogeneous cation distribution and controls the viscosity of the solutions. All solutions were filtered using Amicon ultrafiltration unit with 10 kDa cellulose filters to remove uncoordinated cations, counter anions, and PEI of low molecular weight. The retained portions were analyzed by Inductively Coupled Plasma (ICP) to determine their cationic concentration. Solutions of the desired cations were mixed in stoichiometric proportions to obtain the composition of the final films and subsequently concentrated by evaporation up to 0.20 M and 0.06 M for lanthanum-manganese and lanthanum-cobalt solutions, respectively. Finally, the mixture was spun-coated at 4500 rpm (lanthanum-manganese layer, LMO) and 3000 rpm (lanthanum-cobalt layer, LCO) during 20 s on (001) $LaAlO_3$ (LAO) substrates. The precursor spun-coated films were annealed at 1223 K in air during 2 hours. It should be noted that the layer of LCO deposited on top of LMO was spun-coated after annealing the film of LMO at 1223 K.

In order to determine the cation stoichiometry and the thickness the films and bilayers were grown on $SrTiO_3$ substrates in the identical conditions and analyzed by Energy-dispersive X-ray spectroscopy (EDX) and X-ray reflectivity (note that $LaAlO_3$ will prevent the definition of the

La/Mn ratio in the film). The EDX analysis of cations for the LMO layer shows a ratio La:Mn = 1.04 very close to nominal composition, but this semicuantitative technique is not sensitive enough for the cationic ratio La:Co of the thinner layer. X-Ray Diffraction (XRD) measurements were carried out on a PANalytical Empyrean diffractometer in 10-120º range using Cu K_α radiation. Surface morphology was studied by Scanning Electron Microscopy (SEM) using a FESEM ULTRA Plus Zeiss and operating at 3 kV. This equipment also enables semi-quantitative EDX analysis (EVO LS 15) of the cations. Atomic Force Microscopy (AFM) images were obtained using an AFM/STM NEXT from NT-MDT in non-contact and conducting modes.

The electrical resistance was measured as a function of temperature in the range $150 < T$ (K) < 350, using a standard dc four-point probe. Before measuring the electrical properties, a Hall bar was defined using ion etching and a stencil mask. Cr/Au (5 nm/100 nm) was deposited to ensure Ohmic contacts.

Magnetic hysteresis loops, M(H), were measured in a Magnetic Property Measurement System from Quantum Design, with the magnetic field applied parallel to the film surface.

3. Results and Discussion

$LaMnO_3$ is an antiferromagnetic insulator with an O´-type orthorhombic structure (space group Pbnm) and a = 5.54 Å, b=5.72 Å, and c =7.70 Å [11] (with a pseudocubic lattice parameter a_c~3.98 Å). Cation deficient $La_{1-x}MnO_3$ show a rhombohedral distortion (space group R-3c) [12] and ferromagnetic behavior, with a metal-insulator transition which depends on the actual value of x [13]. On the other hand, bulk $LaCoO_3$ presents a rhombohedral distortion (space group R-3c) with lattice parameters a=b=5.44 Å, and c=13.09 Å (with a pseudocubic lattice parameter a_c~3.80 Å), and shows insulator-diamagnetic behavior. Synthesizing well ordered and smooth interfaces of $LaMn^{3+}O_3/LaCo^{3+}O_3$ provides an opportunity to study the exchange interaction Mn^{3+}-O-Co^{3+}, and the possible redox reactions that were suggested to be at the origin of the large coercive field observed in cation-ordered La_2MnCoO_6 [14].

The XRD patterns of the LMO and LCO/LMO bilayer films grown by PAD are shown in Figure 1. Only the (00*l*) reflections are observed, demonstrating the oriented growth of the films; no secondary reflections of impurities or missorientations are observed. These symmetric reflections are fitted in a pseudocubic indexation to obtain the out-of-plane pseudocubic *c*-axis parameter of the films. We observe that the LMO film is under compressive strain with a *c* value of 3.87 Å (in all these analysis we show the values for the pseudocubic structure). For the LCO/LMO bilayer, the LCO layer is under tensile strain induced by LMO, with a *c* value of 3.83 Å. The c value for the LMO layer changes slightly, to 3.88 Å, with respect to the isolated film of LMO. The epitaxial growth of the films is confirmed by means of a phi scan in (1 0 1) reflection. We observe that there is a good matching between the LMO film and the LAO substrate, see inset Figure 1.

From the analysis of the x-ray reflectivity curves, a total thickness of 26 nm is obtained for the bilayer, with a ≈ 20 nm thick film of LMO and ≈ 6 nm top layer of LCO.

High-resolution x-ray reciprocal space maps (RSM) were performed around the (-1 0 3) reflection of the perovskite structure (Figure 2), to study the epitaxial growth of the films. Q_x and Q_y are calculated as $Q_x = \sin\theta \sin(\theta - \omega) = h\,\lambda/2a$ and $Q_x = \sin\theta \cos(\theta - \omega) = l\,\lambda/2c$. The LMO film shows an in-plane lattice parameter a = 3.87 Å. In the case of the bilayer, the addition of the

LCO over the first layer increases slightly the in-plane lattice parameter of LMO to a =3.88 Å (out-plane c = 3.88 Å). These results are in good agreement with those obtained by XRD. In the RSM, we observed that the films are partially relaxed due to the large mismatch between LAO (a = 3.79 Å) and LMO (a_c (bulk) = 3.98 Å) and between LMO and LCO layers (a_c (bulk) = 3.80 Å). The relative mismatch, defined as $\varepsilon = \left(a_{Film} - a_{Substrate}\right) / a_{Substrate} \times 100$, is +5.01 % (compressive), for the LMO film and -1.81 % (tensile), for the LCO layer with respect to the LMO layer (a_c = 3.87 Å).

LMO film shows a surface roughness lower than 1 nm, as determined by AFM (Figure 3a, left). This is important because it is a crucial point to obtain an epitaxial growth of the top LCO film in the bilayer. It is interesting to point out that black spots in the conductivity map (Figure 3a, right) correspond to non-conductive La_2O_3 particles that remain after the synthesis, also confirmed by EDX analysis. The surface of the LCO layer presents many rectangular holes, which probably help releasing the epitaxial stress of this layer (Figure 3b).

The temperature dependence of the electrical resistivity is shown is Figure 4. Both individual LMO and LCO show a semiconductor behavior above 150 K, although LCO is much more resistive than the manganite. Even though the sample is lanthanum deficient a metal-insulator transition is not observed in this range as occurs in other La-deficient films deposited on STO [13]. This ensures that the LMO film must be very close to its stoichiometric composition. The more resistive behavior of LCO layer is consistent with the observation of a higher resistivity of the bilayer, with respect to the LMO film. Therefore, although the top layer of LCO shows some holes, the coverage is still good enough so that transport properties are dominated by the insulating top layer.

The magnetization response as a function of the temperature of the films is shown in Figure 5 left. The LMO film shows an magnetic transition at T=140 K which is close to the antiferromagnetic transition temperature reported for the stoichiometric bulk sample [15,16] and for PLD growth films [17]. In the bilayer we observed two different magnetic transitions: one at ≈80 K, corresponding to the ferromagnetic transition of the LCO layer, in agreement with previous works [2,18], and another one at 185 K, which is substantially larger than the magnetic transition temperature of LMO.

The magnetic hysteresis loops at 10 K for both films is displayed in Figure 5 (right). The LMO film, which is La-deficient, shows a narrow ferromagmetic loop with H_C about 12 kA/m and 2.88 μB/Mn for the saturation magnetization. This FM behavior in lanthanum-deficient films was already reported by Gupta et al. [13]. A huge increase in the coercive field of the bilayer with respect to the LMO film (≈ 3000%) is observed, H_C~365 kA/m.

At first sight this could be related to an interfacial FM coupling of the LMO and LCO layer. However, the coercivity remains very high above the Curie temperature of LCO (see hysteresis loop at 120 K in Figure 5, right), suggesting that the effect comes from a direct atomic coupling between Mn-O-Co at the interface.

High values of coercive field and T_C close to 200 K has been reported for La_2MnCoO_6 [14,19]. It is known that Co^{2+} in an octahedral environment still shows a pronounced orbital magnetic moment, and a large magnetic anisotropy due to spin-orbit coupling.

At the interface, Mn^{3+} ions will be in contact with Co^{3+}. Due to the relative positions of the Mn^{4+}/Mn^{3+} and Co^{3+}/Co^{2+} redox pairs in an oxide, this situation is unstable against a redox reaction to give Mn^{4+}/Co^{2+}. Therefore, we suggest that there would be a few unit cells across the interface in which a strong ferromagnetic interaction e_g^2-2p:O-e_g^0 and is expected as a result of a redox process of the form Mn^{3+}-O-Co^{3+} ⇆ Mn^{4+}-O-Co^{2+}. This is indeed observed in our M(H) curves shown in Figure 5 right.

The length of this interfacial region could probably go beyond a single unit cell, and extend over a wider area due to interfacial cationic mixing. However, the observation of the T_C = 85 K, characteristic of the LCO film, confirms the most of the top film retain the Co^{3+} stoichiometry. Therefore, we are in front of a phenomenon occurring mostly at the interface between LMO and LCO.

4. Conclusions

In summary, we have shown that epitaxial bilayers of different oxides can be grown under tensile/compressive stress, by a simple chemical deposition method. We suggest that the magnetic properties of LMO/LCO bilayers are determined by a redox reaction and the subsequent exchange interaction occurring at the interface. This is an example of how interfacial phenomena can produce properties which depart from those of the original components.

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References

[1] D. Fuchs, C. Pinta, T. Schwarz, P. Schweiss,1 P. Nagel, S. Schuppler, R. Schneider, M. Merz, G. Roth, H. v. Löhneysen, Phys. Rev. B 75 (2007) 144402.

[2] F. Rivadulla, Z. Bi, E. Bauer, B. Rivas-Murias, J. M. Vila-Fungueiriño, Q. Jia, Chem. Mater. 25 (2013) 55.

[3] X. Moya, L. E. Hueso, F. Maccherozzi, A. I. Tovstolytkin, D. I. Podyalovskii, C. Ducati, L. C. Phillips, M. Ghidini, O. Hovorka, A. Berger, M. E. Vickers, E. Defay, S. S. Dhesi, N. D. Mathur, Nat. Mater. 12 (2013) 52.

[4] J. Nogués, Ivan K. Schuller, J. Magn. Magn. Mater. 192 (1999) 203.

[5] J. F. Ding, O. I. Lebedev, S. Turner, Y. F. Tian, W. J. Hu, J. W. Seo, C. Panagopoulos, W. Prellier, G. Van Tendeloo, T. Wu1, Phys. Rev. B 87 (2013) 054428.

[6] W.H. Meiklejohn, C.P. Bean, Phys. Rev. 102 (1956) 1413.

[7] A. E. Berkowitz, K. Takano, J. Magn. Magn. Mater. 200 (1999) 552.

[8] X. Ke, M. S. Rzchowskia, L. J. Belenky, C. B. Eom, Appl. Phys. Lett. 84 (2004) 5458.

[9] Q. Jia, T. M. McCleskey, A. K. Burrell, Y. Lin, G. E. Collins, H. Wang, D. Q. Li, S. R. Foltyn, Nat. Mat. 3 (2004) 529.

[10] A.K. Burrell, T. M. McCleskey, Q. X. Jia, Chem. Commun. (2008) 1271.

[11] C. Ritter, M. R. Ibarra, J. M. De Teresa, P. A. Algarabel, C. Marquina, J. Blasco, J. García, S. Oseroff, S-W. Cheong, Phys. Rev. B 56 (1997) 8902.

[12] M. Wołcyrz, R. Horyń, F. Bourée, E. Bukowska, J. Alloys Compd. 353 (2003) 170.

[13] A. Gupta, T. R. McGuire, P. R. Duncombe, M. Rupp, J. Z. Sun, W. J. Gallagher, G. Xiao, Appl. Phys. Lett. 67 (1995) 3494.

[14] R. I. Dass, J. B. Goodenough, Phys. Rev. B 67 (2003) 014401.

[15] B.C. Hauback, H. Fjellvåg, N. Sakai, J. Solid State Chem. 124 (1996) 43.

[16] S.-W. Cheong, C. H. Chen, Striped Charge & Orbital Ordering in Perovskites Manganites, Chapter: Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides, C. N. R. Rao & B. Raveau, eds., World Scientific, Singapore (1998).

[17] C. Aruta, M Angeloni, G. Balestrino, N. G. Boggio, P. G. Medaglia, A. Tebano, B. Davidson, M. Baldini, D. Di Castro, P. Postorino, P. Dore, A. Sidorenko, G. Allodi, R. De Renzi, J. Appl. Phys. 100 (2006) 023910.

[18] D. Fuchs, E. Arac, C. Pinta, S. Schupler, R. Schneider, H. v. Löhneysen, Phys. Rev. B 77 (2008) 14434.

[19] S. Yáñez-Vilar, M. Sánchez-Andújar, J. Rivas, M. A. Señarís-Rodríguez, J. Alloys Compd. 485 (2009) 82.