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Electrical and magnetoresistivity studies in chemical solution deposited $La_{(1-x)}Ca_xMnO_3$ thin films

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High quality magnetoresistive $La_{(1-x)}Ca_xMnO_3$ thin films have been prepared by the chemical solution deposition technique. A solution of propionate precursors of lanthanum, calcium, and manganese in propionic acid was used for this purpose. Films of varying compositions (x varying from 0.1 to 0.4) were spin coated on to $LaAlO_3(100)$ and $SrTiO_3(100)$ substrates at room temperature and pyrolyzed in the temperature range 600–850 °C. For fixed compositions, annealing at higher temperatures shifts the insulator–metal transition temperature (T_{I-M}) to higher values accompanied by a reduction in the resistivity values. The T_{I-M} variation for different x values was found to be less pronounced in the compositions $x=0.2$, 0.3, and 0.4. Typical T_{I-M} values of 283 K and 290 K were obtained for $La_{0.7}Ca_{0.3}MnO_3$ coated on $LaAlO_3$ and $SrTiO_3$ substrates, respectively, when annealed at 850 °C. The substrate effect was found to be more pronounced for the x value 0.1 which showed two peaks (one at 271 K and another at 122 K) in the ρ-T curve. The roles of substrate mismatch, composition variation, and annealing temperatures are discussed.
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INTRODUCTION

The recent discovery of colossal magnetoresistance (CMR) in doped perovskite manganites such as $R_{(1-x)}A_xMnO_3$ (R=La, Nd, Sm, and Pr, A=Ca, Sr, Ba, and Pb) near the phase transition from a paramagnetic insulator at high temperatures to a ferromagnetic metal at low temperatures has rekindled interest in these materials from both a fundamental and an applications point of view.[1,2] However, the need for a high magnetic field of the order of a Tesla is an impediment to practical applications. The half-metallic nature of the electronic structure[3] of these compounds implies a 100% spin polarization, which is of significance in magnetic tunnel junctions. Values as high as 86% have been measured experimentally in thin film tunnel magnetoresistance junctions.[4] It is therefore important to fabricate and characterize high quality epitaxial films using a simple, inexpensive, and reproducible method in which the stoichiometry can be accurately predetermined and controlled. The technique of solution spin coating/chemical solution deposition[5] has been found to be attractive in comparison with dc magnetron sputtering, pulsed laser deposition, and chemical vapor deposition. In this article we present preliminary electrical resistivity and magnetoresistivity measurements on chemical solution deposition (CSD) films of $La_{(1-x)}Ca_xMnO_3$ (LCMO) on $LaAlO_3$ (100) (LAO) and $SrTiO_3$ (100) (STO) single crystal substrates.

EXPERIMENTAL DETAILS

A precursor solution containing various metal propionates in stoichiometric proportion was prepared and dissolved in a definite amount of propionic acid to obtain 0.3 molar solution. For this purpose, metal propionates were prepared by double decomposition reaction of the commercially available high purity metal acetates, i.e., $La(OOCH_3)_2$ (CDH), $Ca(OOCH_3)_2$ (CDH), and $Mn(OOCH_3)_2$ (CDH) in propionic acid.

Fourier transform infrared (FTIR) studies were carried out on Ca/Mn/La propionates using a Bruker IFS 66 V FTIR spectrometer. The spectrum confirms the formation of the required compound. The IR spectra also revealed the OH stretching frequencies indicating the presence of water of hydration in these compounds.

Thermogravimetric-differential thermal analysis (TGDTA) measurements of these propionates were performed using a STA-409C NETZSCH, Germany. The TGDTA tracings obtained for propionates show that the pyrolysis above 600 °C completely removes the organic constituents.

Thin films were coated on commercially available $LaAlO_3$ (100) (LAO) and $SrTiO_3$ (100) (STO) substrates. These precursor films thus obtained were pyrolyzed at 600 °C in a preheated furnace for about 30 min. Coating process was repeated several times to obtain the desired film thickness. Later, the films were annealed at 850 °C. The x-ray diffraction (XRD) patterns of these films were obtained using a STOE x-ray diffractometer. Scanning electron microscopic (SEM) investigations of the surface and the interface of these films were carried out using Leo Stereo Scan 400,

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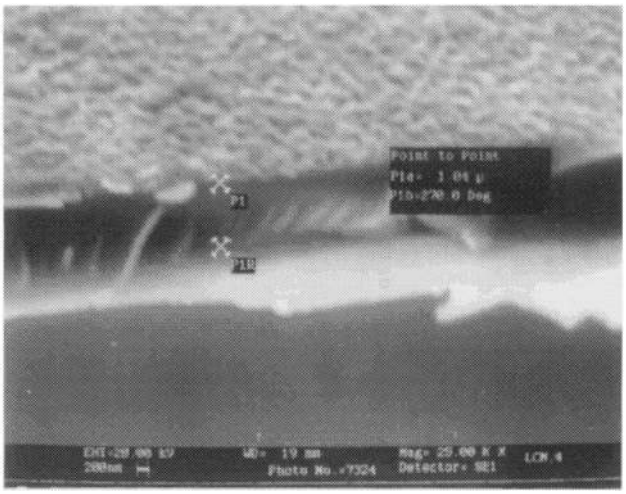

FIG. 1. SEM photograph of a cross section of $La_{0.6}Ca_{0.4}MnO_3/LaAlO_3$ thin film.

UK. Low temperature resistivity measurements were made by the conventional four probe method down to 20 K using a Janis closed cycle refrigerator and magnetoresistance was measured in a field of 1.5 T down to liquid nitrogen temperature using a bath type cryostat and a Varian electromagnet.

RESULTS AND DISCUSSION

From the sectional SEM image of a typical LCMO (0.4) film on the LAO substrate it can be seen that the film thickness is of the order 0.5 μm and its adherence to the substrate is good (Fig. 1). On the top surface of the film, granularity is observed to a small extent and is due to insufficient high temperature annealing of the film. However, even these grains on the top layer are highly oriented as verified by the absence of XRD peaks other than (h00). Annealing the films at higher temperatures for a longer time should allow the grains to merge and form a smooth surface.[6]

Figure 2 shows the XRD pattern of LCMO thin films coated on LAO substrates with compositions in the range

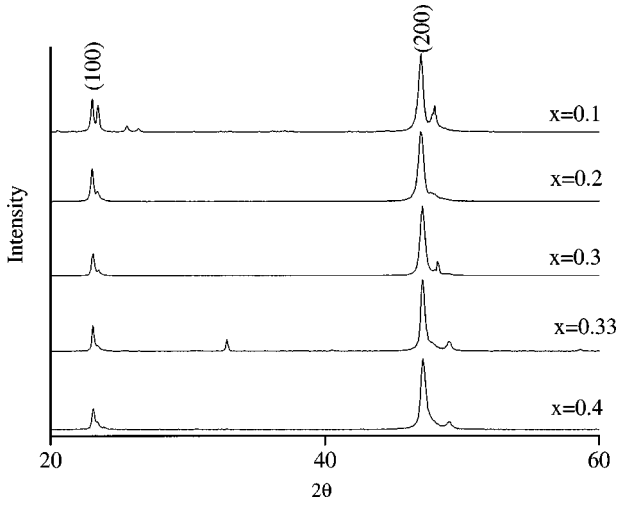

FIG. 2. XRD pattern of $La_{(1-x)}Ca_{(x)}MnO_3$ ($x=0.1$, 0.2, 0.3, 0.33, and 0.4) thin films coated on $LaAlO_3$ substrate.

TABLE I. The values of the $I-M$ transition temperature of LCMO on LAO substrates.

Substrate	Composition	a (Å)	T_p (K)	MR % at T_p	ρ_{max} (mΩ m)
LAO	0.1	3.864	271	25	2.76
LAO	0.2	3.863	287	40	3.16
LAO	0.3	3.858	283	42	2.26
LAO	0.33	3.856	279	46.5	2.81
LAO	0.4	3.852	280	40	3.91
STO	0.3	3.856	290	28	4.03

from $x=0.1$ to $x=0.4$. Since the thickness of these films is of the order of micron, the peaks due to the films are more prominent than those of the substrate. For all these films, the major XRD peaks were indexed corresponding to the (100) and (200) planes of a cubic perovskite cell. The peak positions shift to higher angles as the Ca^{2+} content increases, indicating a decrease in the lattice constant from 3.864 Å (for $x=0.10$) to 3.852 Å (for $x=0.40$) (Table I). The LCMO (0.3) films coated on LAO and STO substrates have a lattice constant of 3.858 and 3.856 Å, respectively. These values are slightly less than that of the bulk materials.[7] The prepared films are thick enough that the substrate misfit is considerably reduced. The shrinkage of the rare earth (RE) manganate lattice is expected when a small sized Ca ion substitutes for a RE ion at the dodecahedral site. LCMO (0.1) shows the existence of a cubic phase with a lattice constant of 3.864 Å coexisting with some minor phase, which is yet to be identified and is also reflected in the electrical resistivity data.

The resistivity versus temperature plots of all the films show an insulator to metal ($I-M$) transition, which is the characteristic of perovskite CMR manganates when cooling down to 20 K. For LCMO (0.3), film on LAO substrate with a transition temperature of 283 K is observed. This is the highest value reported so far in the sol-gel/CSD derived thin films of this composition on LAO substrate.[8] The values of the $I-M$ transition temperature of LCMO ($x=0.2$, 0.3, 0.33, and 0.4) on LAO substrates are given in Table I. The highest value of $T_{I-M}=287$ K is observed for LCMO (0.2) in the films on LAO. This is higher than the bulk value of 195 K for this composition.[9] Sreekala *et al.*[10] had seen a similar behavior for T_{I-M}(290 K) in LCMO (0.2) thin films on LAO prepared by pulsed laser deposition and annealed at 850 °C for 10 h in continuous flowing oxygen. This may be attributed to several factors such as lattice mismatch-induced strains, cationic vacancies and compression of the c-axis lattice parameter resulting in a decrease in the unit cell volume. The substrate effect in the case of our CSD derived thin films is more prominent in the low calcium containing compositions. This was evidenced by the anomalous behavior of the LCMO (0.1) film. From the reported phase diagram for the LCMO system, the bulk compound with $x=0.1$ does not show any $I-M$ transition down to 20 K. When a thin film of this composition was prepared by the CSD technique, the resistivity behavior was surprisingly different. Two peaks in the ρ-T plot are observed at 122 and 271 K indicating the coexistence of two possible phases undergoing $I-M$ transitions at two different temperatures. The formation and stabi-

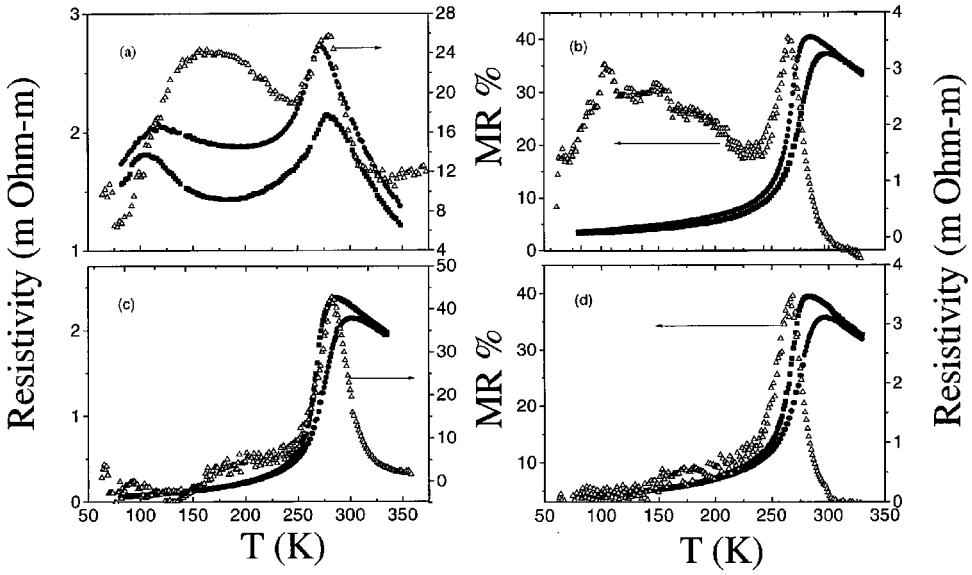

FIG. 3. Plot of resistivity: at 0 T and 1.5 T, and MR% versus temperature for $La_{1-x}Ca_xMnO_3$ [(a) $x=0.1$, (b) $x=0.2$, (c) $x=0.3$, (d) $x=0.4$] thin films coated on $LaAlO_3$.

lization of such phases in this low Ca composition may be directly related to the epitaxial formation of the LCMO film with cubic structure as opposed to orthorhombic structure, when prepared in bulk. This in turn can induce corresponding modifications in the electronic structure of the system favoring the $I-M$ transition to occur in these films. Annealing at 850 °C shifted the peak position towards the high temperature side and simultaneous decrease in ρ_{max} which is due to the reduction of the defects, strains, etc.[11] In the as-prepared films the broken bonds inhibit charge transfer and hence ferromagnetism. Annealing replenishes the oxygen sublattice and enhances the conductivity.

The magnetoresistance (MR) for LCMO thin films coated on LAO (Fig. 3) shows the typical characteristics of the ideal epitaxial film for the composition $x=0.3$, 0.33, and 0.4. The LCMO (0.3) film on STO substrate also shows the same behavior. For a fixed composition and process parameters, the MR values of the films on LAO are found to be appreciably higher than that on STO (Table I) indicative of the role of substrates on the magnetoresistance of the deposited films. In contrast to the low temperature behavior of the epitaxial films with x values 0.3 and above, broadening of transition and separation of the MR peak were observed in the films with composition $x=0.1$ and 0.2. The broad MR in these latter films below the T_{I-M} is indicative of the presence of lattice defects and strain in the films with low Ca contents than those with high Ca contents ($x \geqslant 0.3$). In the literature, this broadening is explained as originating from lattice defect or the magnetic inhomogeneities due to composition fluctuations present in the samples. The magnetic inhomogeneities due to nonuniform distribution of Ca^{2+} ions are evidenced in sol-gel grown LCMO (0.33).[12] Further systematic study is in progress in order to get more insight into the behavior of these CSD deposited epitaxial thin films.

CONCLUSIONS

High quality epitaxial thin films of $La_{1-x}Ca_xMnO_3$ with different x values were fabricated on $LaAlO_3$ and $SrTiO_3$ substrates and characterized. The film with a composition having an x value of 0.1 showed insulator–metal transition at 270 K. In comparison, the bulk material with the same composition does not exhibit any such transition down to 20 K. This observation of an electronic transition in the film with an x value of 0.1 could be due to the substrate which has enabled this composition to crystallize in the cubic structure which would have otherwise crystallized in orthorhombic structure. For a fixed composition and process parameters, the MR values on LAO are found to be appreciably higher than that on STO which again indicates the role of substrates in deciding the MR behavior of the thin films.

[1] R. von Helmholt, J. Wecker, B. Holzapfel, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
[2] S. Jin, M. McCormack, T. H. Tiefel, and R. Ramesh, J. Appl. Phys. **76**, 6929 (1994).
[3] W. E. Pickett and D. J. Singh, Phys. Rev. B **53**, 1146 (1996).
[4] M.-H. Jo, N. D. Mathur, N. K. Todd, and M. G. Blamire, Phys. Rev. B **61**, R14905 (2000).
[5] U. Hasenkox, C. Mitze, and R. Waser, J. Am. Ceram. Soc. **80**, 2709 (1997).
[6] G. M. Gross, F. S. Razavi, R. B. Praus, and U.-U. Habermeier, J. Magn. Magn. Mater. **211**, 22 (2000).
[7] I. O. Troyanchuk, O. S. Mantytskaya, S. N. Pastushonok, E. F. Shapovalova, and V. A. Virchenko, Crystallogr. Rep. **41**, 797 (1996).
[8] S.-Y. Bae and S. X. Wang, Appl. Phys. Lett. **69**, 121 (1996).
[9] P. Schiffer, A. P. Ramirez, W. Bao, and S.-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
[10] R. Shreekala, M. Rajeshwari, R. C. Srivastava, K. Ghosh, A. Goyal, V. V. Srinivasu, S. E. Lofland, S. M. Bhagat, M. Downes, R. P. Sharma, S. B. Ogale, R. L. Greene, R. Ramesh, and T. Venkatesan, Appl. Phys. Lett. **47**, 1886 (1999).
[11] M. Pattabiraman, P. Murugaraj, G. Rangarajan, V. Prasad, S. V. Subramanyam, V. S. Sastry, S.-M. Koo, and K. V. Rao, Pramana, J. Phys. **55**, 1 (2000).
[12] I.-B. Shim, S.-Y. Bae, Y.-J. Oh, and S.-Y. Choi, Solid State Ionics **108**, 241 (1998).