REVISTA COLOMBIANA DE FÍSICA, VOL. 34, No. 2. 2002

MAGNETIC AND MAGNETOTRANSPORT PROPERTIES OF $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ THIN FILMS

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ABSTRACT

$La_{0.67}Ca_{0.33}MnO_{3-\delta}$ manganites thin films were deposited *In Situ* using a high-pressure dc-sputtering process. Pure oxygen at a pressure of 3.5 mbar was used as sputtering gas. The films were grown on different single crystal substrates. Electrical characterization showed a metal-insulating transition between 150 K and 280 K dependent of the substrate. The films exhibit a strong substrate dependence of the Curie temperature T_C and ΔT_C the Curie temperature distributuion width. We observe that the T_C distribution can be described sufficiently well by a Gaussian distribution function. The upper cut-off value of the distribution, which is ~ $\overline{T}_C + 2\Delta T_C$, appears to be identical in all samples.

INTRODUCTION

The manganites $Ln_{1-x}A_xMnO_3$ (x<0.5) exhibit a conventional FM to PM transition [1]. These oxides exhibit semiconducting and metallic behaviors in the paramagnetic and ferromagnetic states, respectively, and magnetoresistance of up to several hundred percent in a field of only a few Tesla near the Curie temperature is observed. The magnetic and electric properties in these materials have been examined the framework of "Double Exchange", which considered the magnetic coupling between Mn^{3+} and Mn^{4+} that results from the motion of an electron between the two partially filled *d*-shells with strong on-site Hund's coupling[1]. Few studies of the structural and magnetotransport properties in thin epitaxial $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ films have been reported without an additional annealing process [2]. In this work, we report the *In Situ* growth of epitaxial of $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ thin films onto different substrates using a high pressure dc-sputtering process. In this paper, we investigate the magnetic and transport properties of the epitaxial $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ films of constant composition and thickness, but grown onto $LaAlO_3$(001) $SrTiO_3$(001), MgO(001), $NgGaO_3$(001) and Si(111) single crystal substrates.

EXPERIMENT

Manganites $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ (LCMO) films were deposited using a high-pressure dc-sputtering process with a sintered LCMO sputtering target of 35 mm diameter [3]. The sintered disk was then attached to one of sputtering system electrode using a special silver bonding. Pure oxygen at a pressure of 3.5 mbar was used as sputtering gas, the target voltage was 380 V with a current of 100 mA flowing between the electrodes. The heater temperature where is located the substrate was kept constant during deposition with a precision of $\pm 0.1^oC$. The deposition rate was kept constant at approximately 1.5 nm/min for all films. The films were grown onto substrates at heater temperatures of 850^oC. No post-deposition annealing of the films was necessary. X-ray diffraction (XRD) measurements θ-2θ were performed using a Rigaku diffractometer (Cu $K\alpha 1$-line: λ=1.5406 Å) and showed our films to have (002) orientation with bulk-like lattice parameters [3]. Resistivity was measured by the conventional four-probe method in the range from 10K to 300K. Magnetization measurements were performed as function of temperature using a Quantum Design extraction magnetometer, equipped with a 7-T superconducting solenoid.

RESULTS AND DISCUSSION

Fig. 1a shows a typical zero-field resistivity and its derivative ($d\rho/dT$) as function of the temperature of a 200 nm thick LCMO film grown on $LaAlO_3$. The ρ vs T curve shows the high-temperature activated, and low-temperature metallic behavior in agreement with other reports. [2] Here, the temperature at curve maximum correspond to the metal-insulator transition T_{MI}=276K of the LCMO film grown on $LaAlO_3$. The ρ vs T measurements of the samples grown on the other substrates showed a T_{MI} transition in the range of 150K (MgO) and 280K ($SrTiO_3$). The T_{MI} value suggests a magnetic ordering temperature that corresponds to PM-FM transition in the inflection point of ρ-T curve. The $d\rho/dT$ vs T curve, Fig. 1a, shows the maximum where the PM-FM transition occur. Fig.1b shows the magnetization dependent of temperature M(T), for LCMO/$LaAlO_3$ with a magnetic field of 100 Oe applied within the plane of the film. The transition is not truly abrupt, as one would expect for an ideal ferromagnet. We can see from Fig. 1b, that there is a tail in the magnetization curve that extends several Kelvin around T_C. Similar broadening effects of the transition have been observed previously in ultrathin magnetic films, and were attributed to sample inhomogeneity in particular to a distribution of T_C values. The aspect of sample inhomogeneity is of particular significance in the manganites, because ferromagnetic samples are randomly doped mixed valence systems. We have investigated the sample homogeneity of sputter LCMO films deposited onto $SrTiO_3$(001), MgO(001), $NgGaO_3$(001) and Si(111). The M(T) measurements for the different films showed the same broadening effect than Fig. 1b, however, significant quantitative differences were found depending on the substrate used [3]. We found it is possible to describe the average temperature-dependent magnetization M(T) by a superposition of individual

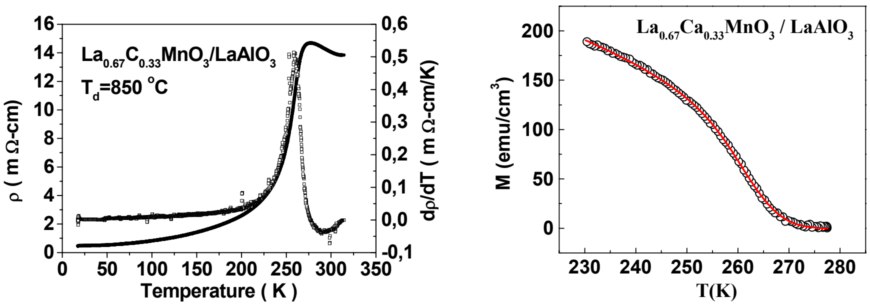

Fig. 1: (a) ρ vs T and dρ/dT for LCMO/$LaAlO_3$..(b) Comparison of experimental M(T) data and the least-squares fitting result(line) for the same sample.

power low functions according to [3]:

$$M(T) = m_0 \int_{T_C} \left(\frac{T_C - T}{T_C} \right)^{\beta} \theta(T_C - T) \cdot \rho(T_C) dT_C \qquad (1)$$

Where m_0 is a factor proportional to the saturation magnetization and β is the temperature critical exponent of the magnetization. θ(x) is the heavyside function, which insures that the magnetization vanishes for $T > T_C$. For our LCMO films, the distribution function $\rho(T_C)$ is taken to be a Gaussian. The Gaussian distribution is characterized by $\overline{T}_C$, average Curie temperature, and the Curie temperature distribution width ΔT_C. Fig. 1b shows a set of experimental data, measured on the film grown on $LaAlO_3$, in comparison to the least-squares fit in the critical region according to Eq. (1). The quality of the fittings for samples grown onto $SrTiO_3$(001), MgO(001), $NgGaO_3$(001) and Si(111) is comparable to the one shown in Fig. 1b. In a previous study, we investigated if the broadening effect, shown in the Fig. 1b is intrinsic or field induced [3]. The Fig. 2a shows the resulting ΔT_C values for the film grown on $SrTiO_3$, as a function of field in the range from 20 to 2 kOe. Each data set was analyzed according Eq. (1). We can see two regimes of transition broadening. For small fields (region I), ΔT_C is constant, and above 200 Oe (region II) ΔT_C increase due to high applied field. All samples investigated show the same characteristic. If we compare all samples for small fields (region I), we find the intrinsic distribution width. The inset from the Fig. 2a, shows ΔT_C vs $\overline{T}_C$, for *H*=100 Oe. We find that as $\overline{T}_C$ increases ΔT_C decreases, and the linear fit exhibits a slope ~−1/2. This implies that the part from the material with highest *T* value have the same value or identical cut-off in all samples. This value is $\overline{T}_C + 2\Delta T_C$. If we make a plot of T_C distribution versus $\overline{T}_C$ for all samples, Fig. 2b, we can see that the Gaussians contains all parts of the sample. However, ΔT_C and $\overline{T}_C$ depend of the substrate used. Finally, all Gaussians have an identical cut-off on the high temperature side. The interval from 0 to $\overline{T}_C + 2\Delta T_C$ contains 98% of the weight for the Gaussian distribution, which seems to be a good choice for the transition temperature cut-off, that correspond to optimal doping composition.

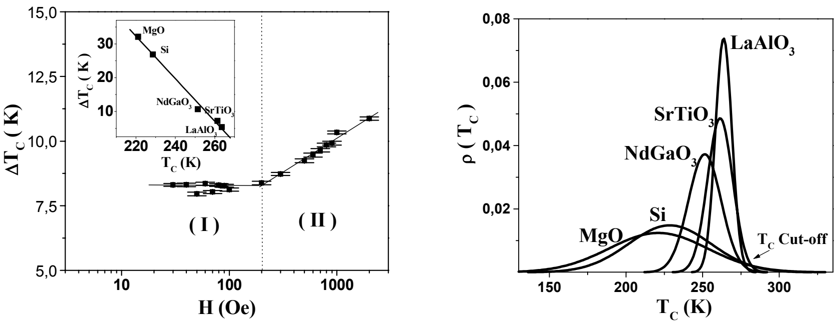

Fig. 2: (a) ΔT_C vs H_{app} for LCMO/$SrTiO_3$. The inset shows the linear fit of ΔT_C vs $\overline{T}_C$ for all samples at H=100 Oe. (b) The gaussian distribution for all films. All T_C distributions have approximately the same $\overline{T}_C + 2\Delta T_C$ value.

In summary, we have prepared epitaxial $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ films grown on different substrates. The films exhibit a strong substrate dependence of the magnetotransport properties. In particular, a upper cut-off value for the $T_C = \overline{T}_C + 2\Delta T_C$ identical for all samples was observed.

ACKNOWLEDGMENTS: This work was support by COLCIENCIAS under Contract No. 361-97. Work at Argonne has been supported by the U. S. Department of Energy, Basic Energy Sciences - Materials Sciences under Contract W-31-109-ENG-38.

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