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Magnetic and electrical properties of $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ epitaxial layers by pulsed laser deposition

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Abstract

Epitaxial $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ (LCMCO) thin films were prepared on (1 0 0) $LaAlO_3$ single-crystal substrates by pulsed laser deposition (PLD). We have been studied using X-ray diffraction (XRD), electrical transport magneto-transport and dc magnetization. XRD pattern reflects that all films have c-axis epitaxial growth on $LaAlO_3$ substrates. The decrease in out-of-plane cell parameter specifies a progressive relaxation of in the plane compressive strain as the thickness film is increases. From the dc magnetization measurements, it is observed that ferromagnetic to paramagnetic transition temperature increases with increase in the film thickness. Magneto-resistance and temperature coefficient of resistance increases with thickness of film and have maximum value near its metal to insulator transition temperature.

Keywords: C. Magnetic properties; C. Electrical properties; $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$; Curie temperature

1. Introduction

During the last many decades the colossal magnetoresistance (CMR) effect in hole-doped manganites has attracted the significant interest due to their potential applications such as magnetic random access memory, disk-drive read heads, bolometers and magnetic field sensors and so on [1]. However, among manganite the increased attention has been given to the compound $La_{1-x}Ca_xMnO_3$(LCMO) because the ionic radii of the La^{3+} and Ca^{2+} are very similar (e.g., 1.38 Å and 1.38 Å, respectively). The doping of the divalent cations in $LaMnO_3$, tune the valance state of Mn (Mn^{3+}/Mn^{4+}) with the configuration $(t_{2g})^3$ $(e_{g1})^1$ for Mn^{3+} and $(t_{2g})^3$ for Mn^{4+}. Therefore, by changing the valency of the Mn ions, the transport and magnetic property of the LCMO materials can be engineered from insulating to metallic state and paramagnetic to ferromagnetic state [2]. The electronic and magnetic properties of these materials are explained using the double exchange (DE) of electron between neighboring Mn^{3+} and Mn^{4+} ions as proposed by Zener [3] and strong electron phonon interaction arising from the Jahn-Tellor splitting of outer *d* levels [4].

Since the double exchange mechanism is related to the Mn^{3+}–O–Mn^{4+} bond distance and angle [5]. Therefore, the doping of transition metal ions at Mn site is an interesting way to modify the key Mn^{3+}–O–Mn^{4+} network which may leads significant effect on the transport and magnetic properties of manganites. In the last few years, lots of studies have been carried out by many research groups by doping of transition metal ion at Mn site. The substitution of Co at Mn site is particularly interesting because Co ions has three type of spin states, i.e., low spin, intermediate spin and high spin. These different spin states results from the facts that the crystal field splitting (10Dq) of the Co 3d states and Hund's rule coupling energy are comparable for the cobaltites.

In this paper, we study $La_{0.70}Ca_{0.30}Mn_{0.95}Co_{0.05}O_3$ (LCMCO) thin films prepared $LaAlO_3$ (0 0 1) substrate using pulsed laser deposition (PLD) [6]. Effect of film thickness on structural, magnetic and transport properties have studied thin using high resolution X-ray diffraction (HRXRD), field cooled magnetization and transport measurements.

2. Experimental

The bulk target of LCMCO was synthesized by standard solid state reaction technique. The stoichiometric amounts of

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highly pure La_2O_3 (99.99%), Mn_2O_3 (99.99%), $CaCO_3$ (99.99%) and CoO (99.99%) powders were mixed thoroughly using ball milling and then pre-calcinated for 12 h at 1000 °C. The pre-calcinated materials were again ground and calcinated at 1200 °C for 24 h. Finally, the samples were ground to fine powder, pressed into pellet form, and sintered at 1300 °C for 24 h. At the end of each heat treatment the samples are allowed to cool slowly to room temperature. LCMCO films were deposited on (0 0 1) $LaAlO_3$ substrates suing PLD using a KrF pulsed eximer laser (λ = 248 nm) with a laser energy of 2–3 J/cm^2 and a laser frequency of 10 Hz. During the deposition, the substrate temperature was from 700 °C. The heating was performed with an average heating time of 20 °C/min and a cooling was applied after the deposition in a vacuum chamber. During the deposition process, the oxygen partial pressure in the chamber was maintained at 300 mTorr.

The thickness of the thin films was checked by a JSM 5610 scanning electron microscope (SEM, Japan). The structural properties of the LCMCO films is studied using a HRXRD (Philips X'pert (MPD 3040) with a CuK_α (λ = 0.15406 nm), Netherlands) measurements and the scans were performed with 0.02θ step size in the 2θ range of 20–80°. The *M–T* curves and resistance was measured using a Quantum Design Physical Properties Measurement System Model 6000 (PPMS, USA) over a temperature range of 20–320 K.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the LCMCO thin films deposited on $LaAlO_3$ (0 0 1) substrate using PLD. All the peaks in the XRD spectra reveals that the (0 0 1) plane of the film is oriented parallel to the substrate surface. The out-of-plane lattice spacing of the LCMCO films can be simply estimated from the (0 0 2) Bragg reflection, using $c = L\lambda/2\sin\theta_i$, where L is the location of the Bragg reflection in r.l.u.; θ_i is the measured Bragg angle; and λ is the wavelength of the X-rays [7]. Fig. 1(b) shows the high resolution X-ray diffraction patter close to (0 0 2) reflection of LCMO thin film with different thickness. It can be clearly seen from the HRXRD spectra that peak position of (0 0 2) reflection shift toward the higher 2θ value as film thickness increases. This shift toward the higher angles corresponds to a variation of out-of-plane cell parameter from 3.913 Å (300 nm) to 3.8904 Å (1 μm). The FWHM calculated from peak (0 0 2) plane is found to decrease from 0.25178 to 0.12902 whereas the intensity increases as film thickness increases which indicates that the film thickness affects the crystallinity of the LCMO thin films. Therefore, XRD measurements signify that the film grown on (0 0 1) $LaAlO_3$ substrates are under in-plane compressive strain and are highly *c*-axis oriented single phase epitaxial films. The decrease in out-of-plane cell parameter indicates a progressive relaxation of in the plane compressive strain as the thickness film is increases.

The magnetization, $M(T)$ is shown in Fig. 2, of the samples for 300, 500 nm and 1 μm film has been undertaken under field cooled (FC) condition. The sample was cooled from room temperature to 100 K in presence of 3 T applied magnetic field and then magnetization was measured in the warming cycle. All the film undergoes ferromagnetic to paramagnetic transition as temperature is increases. There are many factors which affects the structural and physical properties of the thin films in compare to their bulk properties. One of them is expected that increase in the film thickness may relieve lattice mismatch induced strain. Fig. 2 is clearly seen that the Curie temperature (T_C) is found to increase from 235 K of 300 nm to 245 K of 1 μm. There is a certain trend for an increase of (T_C) with increasing film thickness which is associated with the strain

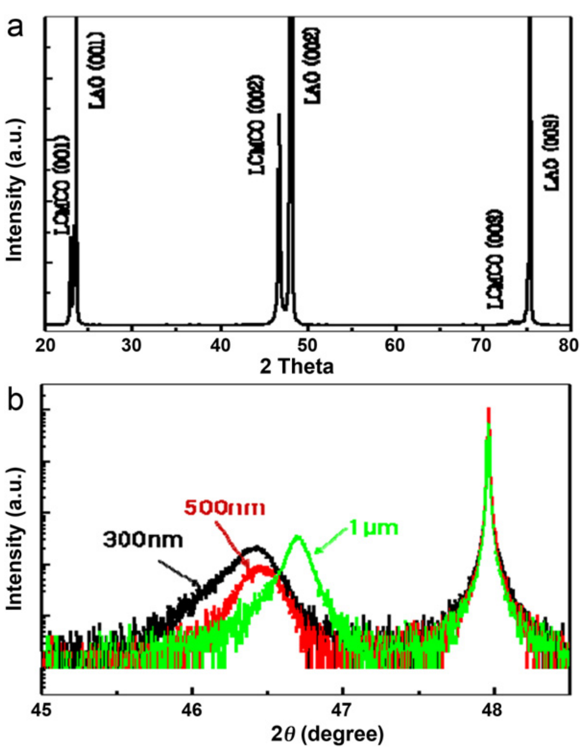

Fig. 1. (a) θ–2θ X-ray diffraction pattern of LCMCO thin film. (b) High resolution X-ray diffraction patter of LCMCO thin film with different thickness.

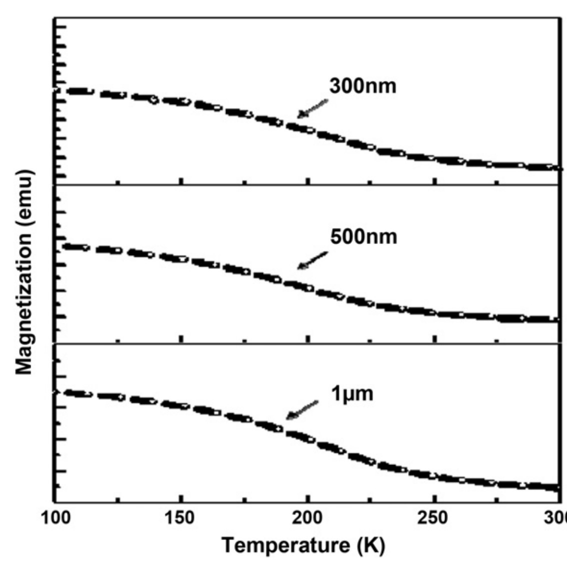

Fig. 2. Temperature dependent of magnetization at 3T of LCMCO thin films with different thickness (field cooled mode).

relaxation of the film. It should be noted that trend observed for the out of-plane lattice parameters of the films correlates well with the magnetization measurements. While epitaxial strain is relaxed and magnetization curves similar to the one for the bulk material [8] are obtained for thicker films, compressive epitaxial strain imposed by the $LaAlO_3$ substrate on thinner ones is relatively sustained and the charge-ordered phase is suppressed [9].

The magneto resistance (MR%) of the LCMCO thin films with different thickness was measured in the temperature range 100–300 K in the presence of 7 T magnetic fields and the corresponding data is plotted in Fig. 3. MR is defined by

$$\mathrm{MR} = \frac{[\boldsymbol{\rho}(0) - \boldsymbol{\rho}(\boldsymbol{H})]}{\boldsymbol{\rho}(0)} \tag{1}$$

where $\boldsymbol{\rho}$ ($\boldsymbol{H}$) and $\boldsymbol{\rho}$ (0) are resistance of the sample in applied field and without external applied field. It is observed at $H_{dc} = 7$ T MR value is maximum around T_C.

Fig. 3 shows the resistivity (Ω m) of the LCMO thin films and Fig. 4 indicates there MR ratio (%), it is clear that the MR increases with increase in the film thickness. The observed values of the MR are 1359% at 171K for 300 nm film and increases to 1525% at 180 K for 1 μm film. Many groups have been reported the thickness dependent properties of the manganite film [10], but a disagreement has been found concerning the origin of the observed phenomena. Some groups have claimed that the difference in the oxygen content is the most important factor responsible for the observed variation in physical properties and T_C of manganites while strain has less effect [11], whereas other groups stated that a change in

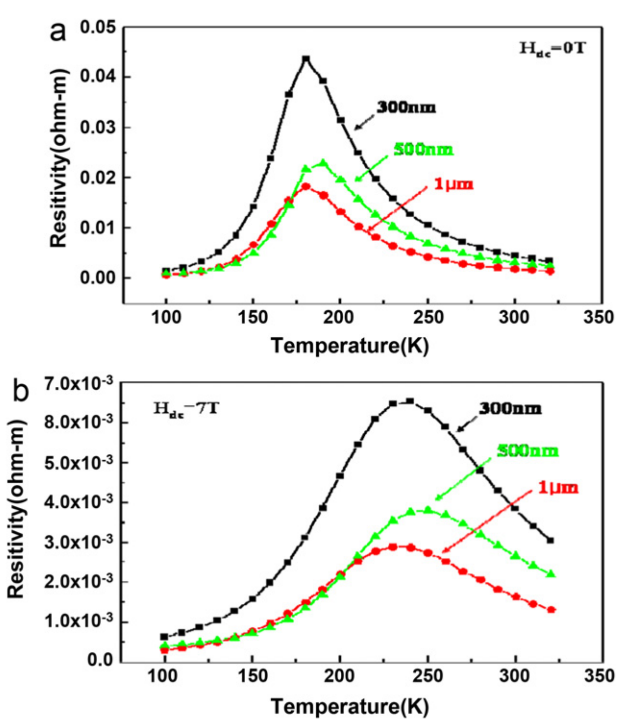

Fig. 3. Temperature dependent of resistivity of LCMCO thin films with different thickness. (a) Zero field and (b) magnetic field ($H_{dc} = 7$ T).

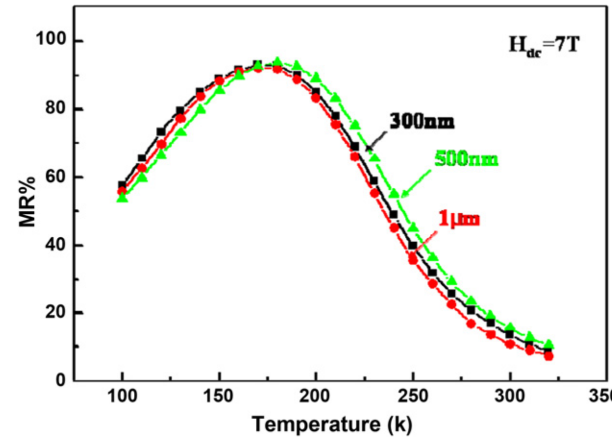

Fig. 4. Temperature dependent of MR (%) of LCMCO thin films with different thickness.

structure, which is strongly coupled with electronic system, must be account for the such type of observed behavior [10].

The value of the TCR makes manganites, especially in thin film form, is very useful for uncooled or moderately cooled infrared imaging (bolometric) applications, which is calculated as:

$$\mathrm{TCR}\ \ (\%) = \frac{1}{R}\left(\frac{dR}{dT}\right) \times 100 \tag{2}$$

In Fig. 4, we show the data of the TCR (Temperature coefficient of resistance) as a function of temperature of LCMCO thin films with different thicknesses. We found that 300 nm thick film shows 2% TCR near the T_{MI} at 160 K where as TCR increases with increase in film thickness (Fig. 5).

The TCR values are 5.8% at 139 K for 500 nm film where as 15.8% at 149 K for 1 μm film. For good uncooled or moderately cooled infrared imaging (bolometric) applications the value of the TCR should be negative. In the present study, it is observed that all the films show a negative TCR value at room temperature which increases with increase in the film thickness. But the operating temperature still low (149 K). To improve the operating temperatures further investigations are in progress.

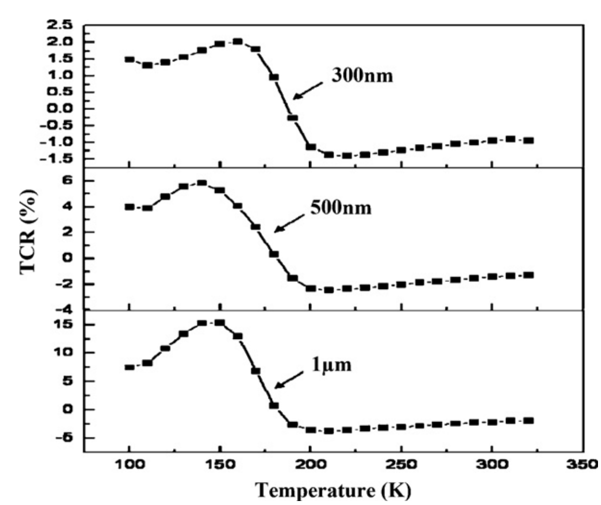

Fig. 5. Temperature dependent of TCR (%) of LCMCO thin films with different thickness.

4. Conclusions

We have successfully grown the epitaxial layers of LCMCO on $LaAlO_3$ (0 0 1) substrate with different thickness. An XRD measurement reflects a progressive relaxation of in the plane compressive strain with increase in the film thickness. It is observed that ferromagnetic to paramagnetic transition temperature increases with increase in thickness of film. The value of the magneto resistance has been found to increase with the thickness and have a maximum value for 1 μm thick film. TCR value is negative at room temperature and with increase in film thickness.

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