A study on correlation between strain effect and conduction mechanism of La$_{0.9}$Ca$_{0.1}$MnO$_3$ films

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ABSTRACT

Thin films of La$_{0.9}$Ca$_{0.1}$MnO$_3$ with thicknesses in the range of 40-200 nm grown on (100) SrTiO$_3$ employing pulsed laser deposition (PLD) technique have been investigated by measuring structure and transport properties. The structural properties of the films were studied by X-ray diffraction (XRD) technique employing 2θ-ω scan and the results show a high quality crystalline nature with '*b*' axis orientation. The Jahn-Teller strain (ε_{J-T}) was found to decrease with thickness. Transport measurements were performed using standard four probe technique, which shows an insulating behavior for all the thickness at low temperatures. The high temperature resistivity obeys the small polaron hopping. Further more, the obtained results from the transport measurement shows lowering of polaron binding energy for the films grown under tensile strain as compared to our previous work on La$_{0.9}$Sr$_{0.1}$MnO$_3$ films.

Keywords: Perovskite manganites; polycrystalline ceramics; magnetoresistance effect; transport mechanism.

Introduction

Since the discovery of colossal magnetoresistance in hole doped perovskite type A$_{1-x}$B$_x$MnO$_3$ (where A= La^{3+}, Pr^{3+}, Nd^{3+} & B = Sr^{2+}, Ca^{2+}, Ba^{2+}), substantial progress in understanding the electronic and magnetic properties has been made [1]. It has been demonstrated that the oxides of perovskite manganites show a significant difference in the transport properties based on the type of the samples such as thin films, single crystals and polycrystalline ceramics. In the case of polycrystalline material, the presence of grain boundaries leads to a large magnetoresistance effect over a wide range of temperature below the curie temperature (T$_c$). However, in the case of single crystalline or thin films, the large magnetoresistance effect is found to exist in a relatively narrow temperature around T$_c$. Since commercial applications require these materials as thin films rather than bulk or single crystals, a detailed knowledge of electronic and magnetic properties is mandatory to exploit the potential use of the manganites.

The substitution of trivalent rare earth ions by divalent rare earth alkaline ions creates mixed Mn(III)/Mn(IV) state resulting in mobile charge carriers and this in turn influences the physical properties. Double exchange mechanism and Jahn-Teller effect successfully explains the physical properties of these manganese oxides [2]. The basic feature of double exchange mechanism entangles

with the transfer of 'e$_g$' electrons between Mn^{3+} and Mn^{4+} ions. During the transfer, the carrier avoids strong on site Hund exchange energy and facilitates hopping process. Along with the transfer of 'e$_g$' electrons it accompanies lattice distortions which have been explained well by Jahn-Teller effect. Such Jahn-Teller distortion around Mn^{3+} localizes the charge carriers and gives rise to polaron formation [3]. The existence of polarons has been confirmed from many experimental results and reported elsewhere [4-6].

In general, the polaronic state emerges due to the consequence of strong electron-phonon coupling of the Jahn-Teller active Mn^{3+} ions. To get deep insight into the polaronic behavior and to exploit the mechanism causing the semiconductor like transport properties at higher temperature, a large number of models have been proposed. The models include thermal activation, variable-range hopping and adiabatic small polaron conduction [7]. In most cases for the observed transport properties, the hopping conduction of small polarons in the adiabatic approximation is accounted [8]. Hence, using this adiabatic approximation, investigation was made on the conduction mechanism of La$_{0.9}$Ca$_{0.1}$MnO$_3$ thin films in the light of our previous study on La$_{0.9}$Sr$_{0.1}$MnO$_3$ films, where the strain dependence of the electronic transport properties and the thickness dependence of the polaron formation energy was

studied [9]. The present study emphasis how the transport mechanism behaves in a different strain states as a consequence of strain effect. At lower substitution level, the competition between electronic and magnetic properties drives the phase separated state to be a stable ground state. In this study, we used low level doped high quality epitaxial $La_{0.9}Ca_{0.1}MnO_3$ films grown by Pulsed laser deposition technique deposited on (100)-oriented $SrTiO_3$ substrate.

Experimental

Thin films of $La_{0.9}Ca_{0.1}MnO_3$ with different thicknesses were deposited on (100) oriented (a = 3.905 Å) $SrTiO_3$ substrate using pulsed laser deposition technique. The deposition process was performed in a pure oxygen gas of pressure 0.405 mbar. The substrate temperature was kept at 800°C during the growth. An excimer laser (Lambda Physik) with the laser fluency of 1.6 J cm^{-2}, wavelength of 248 nm with pulse frequency of 5 Hz was employed. To maintain the oxygen stoichiometry after deposition, the as grown films were subjected to annealing in air at 900°C for 30 min. The thickness of the films was controlled by calculating the ablation period during the growth process.

The as grown thin films were subjected to various characterization techniques. The structural properties of the as grown films were studied by Bruker D8 X-ray diffractometer in the mode of 2θ-ω scan with Cu Kα radiation (λ = 1.54056 Å). Transport properties were measured using standard four-probe method. To establish electrical contacts, evaporated chromium-gold pads and silver epoxy were used to attach the gold wires to the film and DC current was kept at 10^{-7}A during the measurement. The obtained results are compared for the various thickness to validate the adiabatic small polaron hopping model.
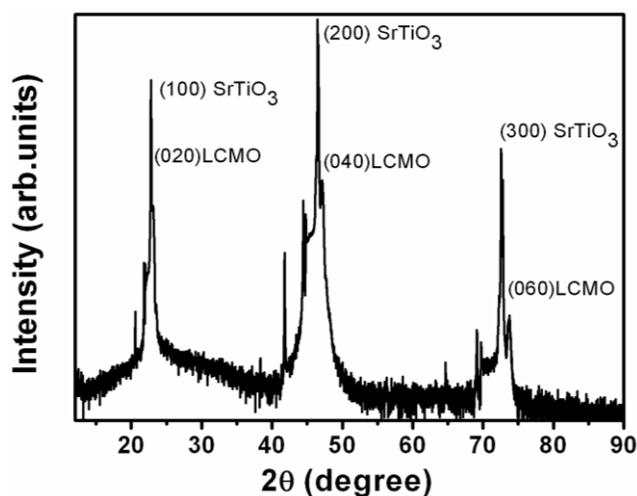

Fig. 1. 2θ-ω scan of 40 nm thick $La_{0.9}Ca_{0.1}MnO_3$ films.

Results and discussion

The XRD diffractogram (2θ-ω scans) for the $La_{0.9}Ca_{0.1}MnO_3$ film (40 nm) is shown in **Fig. 1**. No other parasitic peaks are observed besides the reflections from the substrate and (010) reflections of the film. The evaluated cell parameters demonstrate that $La_{0.9}Ca_{0.1}MnO_3$

possess orthorhombic crystal structure with P_{nma} space group with a tensile in-plane epitaxial strain and a detailed lattice parameter values for series of $La_{0.9}Ca_{0.1}MnO_3$ evaluated by Nelson-Riley function [10]. For the 40 nm film, the cell volume is calculated to be 234.41 Å, which is smaller by 0.83 % compared to the bulk cell volume (236.37 Å). However, in the case of 200 nm, an increase in cell volume of about 0.07 % is observed. It is presumed that the variation of cell volume might be due to the differences in the oxygen content for various thicknesses. The mixed valence state of Mn^{3+}/Mn^{4+} caused by the substitution of Ca^{2+} by La^{3+} develops orthorhombic distortion which is measured by the asymmetry parameter δ = $(\sqrt{2}c/(a^2+b^2)^{1/2})_{-1}$, **Fig. 2**.
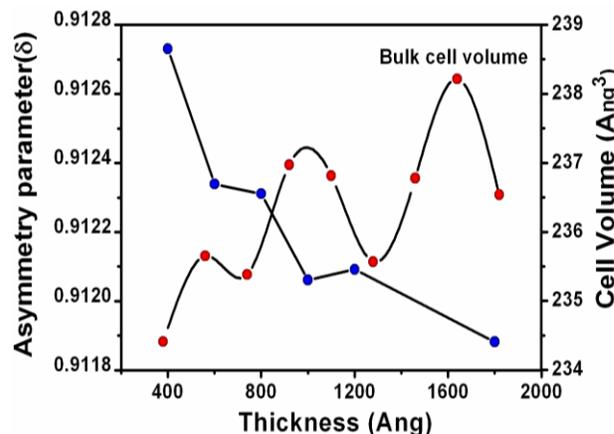

Fig. 2. Variation of the asymmetry parameter and cell volume of $La_{0.9}Ca_{0.1}MnO_3$ films with thickness.

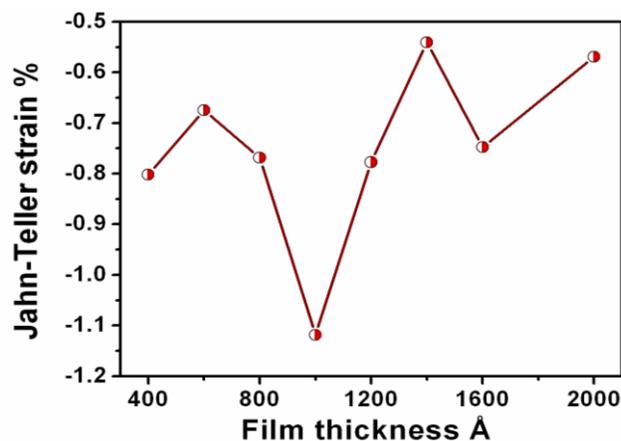**Fig. 3.** Jahn-Teller strain versus thicknesses of the $La_{0.9}Ca_{0.1}MnO_3$ films.

It is evident that a reduction of 'δ' is observed for orthorhombic distortion, which in turn facilitates the enhancement of Mn-O-Mn bond angle close to the ideal value 180°. The cell size reduction will lead to the reduction of Mn-O bond lengths. As a consequence of bond length modifications, the system inhibits the formation of charge ordered phase. These two factors stabilize the insulating phase for all the thicknesses as observed in electrical transport measurements.

It is well known that the increase of Jahn-Teller strain facilitates the formation of polarons by providing strong

electron-phonon coupling and as a consequence, the polaron binding energy increases. Jahn-Teller strain (ε_{J-T}) is evaluated by $\sqrt{1/6}\ (2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})$, where ε_{zz} is out-of-plane and ε_{xx} and ε_{yy} are in-plane strain components [**11**] and is shown in **Fig. 3**.

Despite there is not a distinct trend observed on ε_{J-T}, one can observe a decrease of Jahn-Teller strain with increase of film thickness. This feature reflects a reduced contribution of ε_{J-T} especially for the higher order thickness, which demonstrates the weak strain approach as a result of strain relaxation upon increasing film thickness. This characteristic nature correlates well with the decreasing values of polaron binding energy as shown in **Table 1**.

Table 1. Influence of thickness on polaronic formation energy.

Thickness (Å)	Binding energy (eV)
400	0.1291
800	0.1421
1000	0.1405
1600	0.1281
2000	0.1182

The appearance of charge-ordered phase (CO) for 200 nm is presumably due to reduced Jahn-Teller strain. However, such a charge ordered phase was not observed for thinner films due to pronounced ε_{J-T}.

Temperature dependent electrical transport measurement was performed with the four-probe method, **Fig. 4**. The measured resistivity data shows distinct differences for various thicknesses and the data clearly evidences an insulating feature. It is generally regarded that the insulator like behavior below T_c is associated with the existence of polaronic regime [**12**].
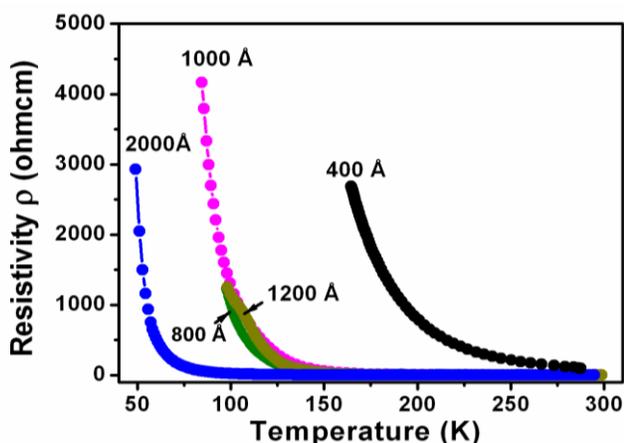
Fig. 4. Resistivity versus temperature graphs for 100 nm and 200 nm thicknesses of the $La_{0.9}Ca_{0.1}MnO_3$ films.

Further, the manganites act upon the preconditions of polaron formation namely large electron-lattice coupling and low hopping rates [**13**]. It is well established that in the PM regime the localized electronic charge carrier concentration remains constant follows linearity in the Arrhenius plot due to adiabatic hopping motion of small polarons. Such a behavior was observed for the $\ln(\rho/T)$ versus inverse temperature, which is evidenced from **Fig. 5**.
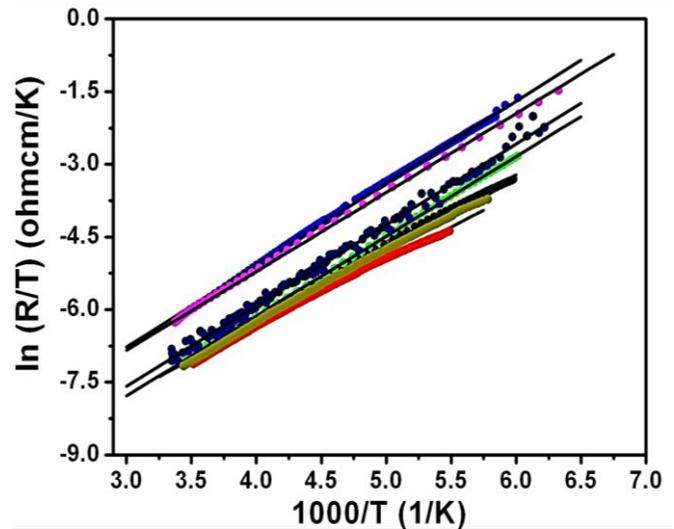
Fig. 5. Plot of ln (ρ/T) versus inverse temperature 100 nm and 200 nm thicknesses of the $La_{0.9}Ca_{0.1}MnO_3$ films.

This linear behavior gives evidence for the adiabatic small polaron conduction mechanism which has been already well ascribed in $La_{1-x}Ca_xMnO_3$ films. The electrical resistivity as a result of hopping of adiabatic small polarons is given by;

$$\rho = AT \exp (E_A/k_BT)$$

where the activation energy, $E_A = E_p/2 + \varepsilon_o - J$, ε_o is the energy required to generate intrinsic carriers and J is the transfer integral, k_B is the Boltzmann constant and the prefactor 'A' depends on the polaronic concentration, hopping distance and the frequency of the longitudinal optical phonon. Values of A and E_A are obtained from the linear fit to the above equation. In the adiabatic limit, the role of ε_o and J may be neglected, therefore the polaronic formation energy is given by $E_p = 2 E_A$.

Table 1 shows the thickness dependence on polaronic formation energy. From the table it is clear that the polaronic formation energy (E_p) decreases with increasing thickness. On comparing with our previous results on $La_{0.9}Sr_{0.1}MnO_3$ [**9**], an opposite trend in polaronic formation energy (E_p) with 10% increase of E_p values was observed. The observed difference in E_p is due to the different strain states exhibited by $La_{0.9}Ca_{0.1}MnO_3$ (tensile) and $La_{0.9}Sr_{0.1}MnO_3$ (compressive). Hence it should be emphasized that the electron-phonon coupling dominates the strain effect through the modifications of Mn-O-Mn bond angle and Mn-O bond lengths.

Conclusion

The structural and transport properties of $La_{0.9}Ca_{0.1}MnO_3$ films grown on $SrTiO_3$ substrate employing pulsed laser deposition technique have been investigated. Structural study by X-ray diffraction technique confirms the single phase nature with (0b0) orientation. The observed

reduction of orthorhombic distortion and unit cell volume leads to the enhancement of Mn-O-Mn bong angle closer to the ideal value. The reduced trend observed for the Jahn-teller strain correlates well with the observed polaronic binding values. In the limit of adiabatic approximation at higher temperature, the transport properties of various thicknesses obey the small polaron hopping conductivity. The polaronic formation energy decreases with increasing film thickness as contrary to $La_{0.9}Sr_{0.1}MnO_3$ films due to different strain states.

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