The Response of Transport Properties to Static Electric Field in $La_{0.7}Ce_{0.3}MnO_3$ Epitaxial Thin Films

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We investigated the influence of static electric field on the transport properties in $La_{0.7}Ce_{0.3}MnO_3$ epitaxial thin films by using a simple field effect configuration (FEC), which was formed on a single layer film. Substrates act as gates and films as channels. Such an easily manipulative technique avoids many possible problems appeared in multilayer structures, such as poor interface and severe inter-diffusion, which may influence the intrinsic characteristics of investigated targets. One knows that tetravalence-doped $La_{0.7}Ce_{0.3}MnO_3$ (LEMO) systems exhibit metal-insulator transition and ferromagnetic behavior, similar to the ditravalence-doped $La_{0.7}Ca_{0.3}MnO_3$. However, for the conductive mechanism of LEMO, strong controversies have existed for a long time with whether it is intrinsically electron-type or hole-type. Our experiments give evidence of the hole-type nature in LEMO. In the device with LEMO as channel and $LaAlO_3$ (LAO) as gate, applied positive bias poles gate and induces charge at the area between gate and channel. The polarized charge in the gate is compensated by inducing electrons in the channel. If LEMO is of electron-type, the increased carrier density would cause a decease of channel resistance. However, we experimentally found the channel resistance remarkably increases upon a positive bias. Such a fact is completely the same as the behavior observed in hole-doped $La_{0.7}Ca_{0.3}MnO_3$ channel, and thus strongly supports the hole-type nature in LEMO channel. Furthermore, we found that the large field effect in LEMO is nonlinear and polarity dependent on the applied bias. A percolative phase separation picture is taking into account to interpret the observed field effect.

***Index Terms*—Field effect configuration (FEC), $La_{0.7}Ce_{0.3}MnO_3$ (LEMO) films.**

I. Introduction

LOTS of research interests have been attracted to the so-called "colossal electroresistance" (CER) effect in colossal magnetoresistive (CMR) manganites [1]–[10]. Namely, their electronic conductance may be controlled by an electric current or a static electric field. It has been observed that an electric current could trigger the transformation of the electrically insulating charge-ordered state to a ferromagnetic metallic state [3]. Current-induced switching of resistive states in $La_{0.8}Ca_{0.2}MnO_3$ single crystal has been reported [4]. Recently, we focused on the influence of electric field/current on the transport properties in thin films of mixed-valent manganites [6]–[10]. Our studies revealed that a current with a high density significantly affects the balance of multiphase coexistence and causes a series of changes of transport properties. However, in the case that a large current is applied, local heating due to highly filamentary conduction inevitably occurs and makes the schemes complicated. If using the field effect configuration (FEC) to investigate the electroresistance (ER) effect, there will be no concerns for local heating effect. Previously, multilayer technique was employed to form field effect configuration [1], [2], [5]. A rigorous process is usually needed to fabricate multilayer structures with clear interfaces. Films with lower quality often lead to various problems, such as a poor interface and severe inter-diffusion, which may influence the intrinsic characteristics of the investigated targets. Using lithography art, we successfully fabricated a very simple FEC on a single-layer film [10] and investigated the electroresistance effect of various manganite films. Surprising results have been achieved. Field effect was found to be significant for $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Ba) channels [10]. In this paper, we report the response of transport properties to static electric field in $La_{0.7}Ce_{0.3}MnO_3$ epitaxial thin films by employing the simple FEC formed on monolayer films.

CMR manganites with formula $La_{1-x}A_xMnO_3$ exhibit a hole-type nature when the doping ion A is a divalent cation such as Ba, Ca, Sr, etc. In the parent compound $LaMnO_3$, a proportionate amount of Mn^{3+} with electric configuration of $t_{2g}^3e_g^1$ is substituted with Mn^{4+} with $t_{2g}^3e_g^0$, resulting in holes on the e_g band and hope-type conductive mechanism. However, if the doping ion A is a tetravalent cation such as Ce, Sn, etc., a mixed-valence state of Mn^{3+} and Mn^{2+} and electron-type conductivity can be expected. For Ce-doped $LaMnO_3$ systems, Mandal and Das [11] first reported the metal-insulator transition and ferromagnetic behavior in the bulk materials and suggested an existence of mixed-valence of Mn^{3+} and Mn^{2+} and electron-like conductivity. However, thermopower measurements performed by Philips and Kutty [12] demonstrated that the Ce-doped $LaMnO_3$ bulk showed hole-like behavior. As for thin film systems, Mitra *et al.* [13] presented the experimental evidence of the existences of Ce^{4+} and the mixed-valence of Mn^{3+} and Mn^{2+} by performing X-ray absorption spectroscopy. However, Zhao *et al.* [14] argued the difficulty of doping Ce ions into $LaMnO_3$, and a significant peak of CeO_2 impurity was identified in the X-ray diffraction in their films. Furthermore, Yanagida *et al.* [15] presented the evidence of hole nature in $La_{0.7}Ce_{0.3}MnO_3$ films, and demonstrated that the cation deficiencies due to the formation of nanoclustering cerium oxides in the annealed films are responsible for the emergence of the metal-insulator transition and ferromagnetism phenomena. Obviously, strong controversies have existed for a long time with whether it is intrinsically electron-type or hole-type for the conductive mechanism in Ce-doped $LaMnO_3$ systems. In this paper, we present a simple method to prove hole conductive nature in $La_{0.7}Ce_{0.3}MnO_3$ (LEMO) films.

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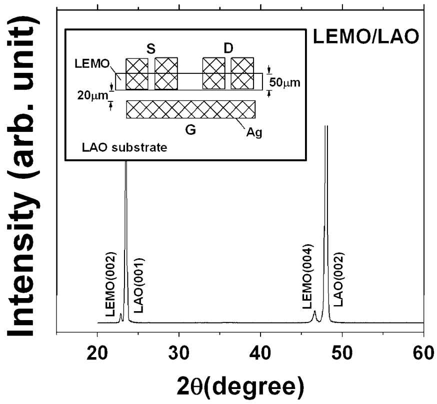

Fig. 1. X-ray diffraction spectra of $La_{0.7}Ce_{0.3}MnO_3$ epitaxial thin films grown on $LaAlO_3$ substrates. Inset shows a top view of the device geometry.

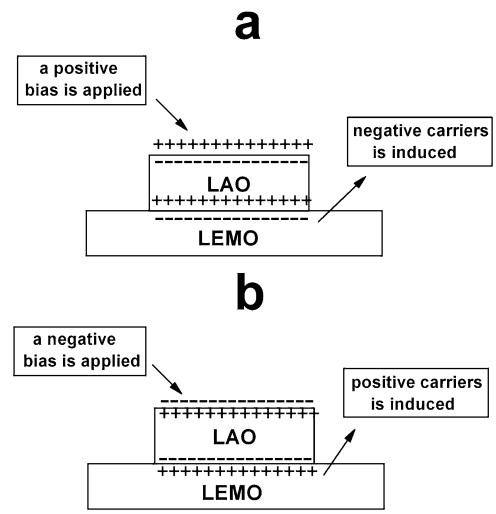

Fig. 2. Schematic diagram of a simplified model for the FEC device with $La_{0.7}Ce_{0.3}MnO_3$ as channel and LAO as gate under a) positive bias, and b) negative bias.

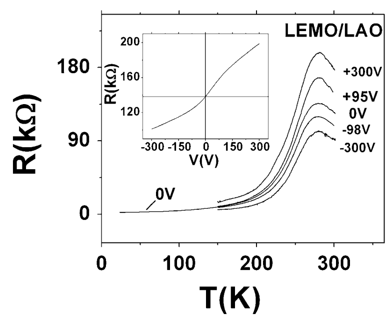

Fig. 3. Temperature dependent resistance of $La_{0.7}Ce_{0.3}MnO_3$ channel for field bias ranging from +300 to −300 V. Inset shows the channel resistance as a function of gate voltage at 281 K.

II. Experimental

LEMO thin films were grown on single crystal substrates of $LaAlO_3$ (LAO) with (100) orientation using the pulsed laser deposition technique. Disks of stoichiometric $La_{0.7}Ce_{0.3}MnO_3$ were used as the targets. The deposition took place in a pure oxygen of 1 mbar. The energy of the laser beam was $\sim$ 500 mJ with a wavelength of 248 nm, and the pulse frequency was 5 Hz, respectively. The substrate temperature was 750 ° C as measured by a k-type thermocouple inserted into the heater block. The thickness of the films was about 100 nm controlled by the deposition time. A post-annealing at 800 °C for 1 h was made in air in order to avoid oxygen deficiency.

The experiments of X-ray diffraction reveal sharp peaks of the formed ABO_3 phase with c-axis perpendicular to the substrate surface (see Fig. 1). Besides the reflection from LAO substrate and the (00l) peaks of the LEMO films, no other peaks are visible, demonstrating that the grown films are of single phase. The resistance measurements were done by using the standard four-probe technique in a closed cycle cryostat. Curie temperature T_C of the LEMO films was determined $\sim$279 K based on thermal magnetization measured under a low field of 100 Oe. In order to apply a static electric field to the film, an FEC was fabricated on monolayer films using the lithography technique, in which the LEMO film was used as channel, and LAO substrate as gate. The inset of Fig. 1 shows a top view of the device geometry. The LEMO films grown on LAO substrate were first patterned into long bridges with width of 50 μm, silver pads were then evaporated onto the bridge and the exposed LAO substrate, forming an FEC. The gate thickness is controlled by the positions of the evaporated silver pads. In this paper, the gate thickness is 20 μm (see the inset of Fig. 1). Electrical leads were connected to the silver pads using a MEI-907 supersonic wire bonder to obtain low Ohmic contacts. A voltage source with a high limit of $\pm$300 V (Sorensen DCS 300 V-3.5 A) was employed to supply gate bias. Our repeated measurements indicated that the gate current is very small ($<$1 nA) even under a bias of 300 V

III. Results and Discussion

Fig. 2 is the schematic diagram of a simplified model for the FEC device with LEMO as channel and LAO as gate under bias. An application of a positive bias Fig. 2(a) polarizes the LAO gate and causes a buildup of a positive charge on the other side of LAO. The induced positive charge tends to be compensated by the appearance of negative carriers in the channel. Similarly, if the applied bias is negative Fig. 2(b), positive carriers will be induced in the channel. If we assume LEMO channel is of electron-type, the increased (decreased) carrier density upon positive (negative) bias would cause a decease (an increase) of the channel resistance [2]. However, we observed opposite results. Shown in Fig. 3 is the temperature dependent resistivity of LEMO channel for field bias ranging from −300 to +300 V. One can find the conductive resistance grows up with a positive gate voltage but becomes down with a negative gate voltage, which is completely consistent with the observations in hole-doped $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Ba) channels [10], and thus strongly supports the hole-type nature in LEMO channel [2]. We agree with the suggestion [15] that the appearance of metal-insulator transition and ferromagnetic phenomena, and the hole nature in LEMO films originate from the cation deficiencies caused by the formation of nanoclustering cerium oxides in the post-annealed films.

The results of field effect for LEMO channel obtained by employing the simple FEC formed on monolayer film are similar to the previous observations using multilayer device configuration [5], indicating that we were measuring intrinsic properties. The enhancement (reduction) of the resistance for LEMO channel upon a bias of $+300$ V (-300 V, 1.5×10^5 V/cm) reaches 47% (25%). Another attractive feature is that the position T_P of the insulating-metallic transition keeps nearly unchanged upon applying any electric field in any directions. Such a characteristic is very different from the case of general MR. Generally, an application of magnetic field improves the spin alignment and affects the electric conduction in the sample. As a result, the resistive point T_P shifts to higher temperatures, yielding CMR effect. Inset of Fig. 3 presents the LEMO channel resistance as a function of the gate voltage at temperature $T_P \sim 281$ K. The change of resistance is asymmetric, and nonlinear dependence is shown for sweeping the gate voltage along both positive and negative directions. This fact is similar to that observed in $La_{0.7}Ca_{0.3}MnO_3$ channel by using multilayer configuration [5]. One knows that electric field effects observed in high-Tc superconducting perovskites can be completely explained by field-induced modulation of mobile carrier density [16]. Electric fields modulate the conductive resistivity in superconducting perovskites. The induced field effect is also dependent on the bias polarity. However, the fact that the nonlinear dependence of resistance for sweeping gate voltage in CMR manganites differs from the linear dependence observed in superconducting perovskites. Besides, an electric field can considerably shift the superconducting transition temperature but cannot cause any shift of T_P in CMR manganites. To understand the results of field effect, a percolating phase separation picture is considered in CMR manganites. More and more evidence supports the idea that phase separation is a universal phenomenon in mixed-valence manganites. It was supposed [5] that the electric field in the phase space changes the relative volume fractions of the metallic and insulating phases by pushing the interface to move. The field polarity controls the direction of interface movement. Applying a negative gate voltage pushes the interface moving to insulating phase, leading to an increase of metallic fraction and thus a decrease of resistance. A positive voltage does the opposite, leading to an increase of resistance.

IV. Conclusion

In summary, the response of transport properties to static electric field in $La_{0.7}Ce_{0.3}MnO_3$ films was investigated by using a very simple field effect configuration formed on a single layer film. In the device with LEMO as channel and LAO as gate, the conductive resistance grows up with a positive gate voltage but becomes down with a negative gate voltage, strongly supporting the hole-type nature in LEMO channel. Field effect was found to be significant and nonlinear and polarity dependent on the applied bias. The enhancement (reduction) of the resistance upon a bias of $+300$ V (-300 V, 1.5×10^5 V/cm) reaches 47% (25%). Phase separation picture is considered for understanding the observed results of field effect.

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