Current-induced resistive switching effect in oxygen-deficient $La_{0.8}Ca_{0.2}MnO_{3-\delta}$ films

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A colossal current-induced resistive switching effect caused by low bias current has been found in oxygen-deficient $La_{0.8}Ca_{0.2}MnO_{3-\delta}$ film at temperatures below the Curie temperature. The switching effect takes place as the bias current or voltage exceeds a threshold value I_{th} or V_{th}. An electroresistance (ER) ratio as large as 98.1% was found with a low bias current $I=2$ mA at temperature of 125 K. Such a current-induced ER suggests the sensitivity of ferromagnetic insulator state to the external electric field or current in the manganite films which have oxygen deficiency. These effects can be understood within the mixed-phase scenario.

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I. INTRODUCTION

Doped manganese oxides with a perovskite structure have been a focus of intensive studies due to their rich physical properties and potential applications in spintronic devices.[1] One of the interesting properties of manganese oxides is that they are sensitive to the external stimuli such as magnetic field,[1] light,[2,3] and electric field or current.[4,5] These phenomena open up new approaches for applications of manganites. Compared to others, the transition switched by applying an electric voltage or electric current may be more convenient for potential applications. Recently, there have been many investigations into manganites with charge-ordered (CO) antiferromagnetic (AFM) insulator ground state. For example, Asamitsu *et al.*[4] found current switching of resistive states in $Pr_{1-x}Ca_xMnO_3$ single crystal. Liu *et al.*[6] showed that electric pulse–induced resistance changes in $Pr_{1-x}Ca_xMnO_3$ thin films are nonvolatile, accumulative, polarity dependent, and reversible. However, even though the AFM insulator state can be manipulated by an external electrical field or current, the required energy exceeds a practical value. More recently, it has been found that the subtle competition between CO and ferromagnetic (FM) states may result in the formation of a new metastable state,[7] which is the so-called intermedium state and is often associated with a lower activation potential.[8,9] This naturally leads us to explore electric field–induced effects in manganites which have a ferromagnetic insulator (FMI) ground state. To date, a few experiments have investigated electroresistances (ERs) in ferromagnetic insulating single-crystal or polycrystalline manganites and they reported a decoupling between ER and magnetoresistance.[9,10]

Among the various doped manganese oxides, $La_{1-x}Ca_xMnO_3$ series compounds are very interesting due to their rich phase diagram over the whole composition (x).[11] There is a critical region near $x\sim0.2$ in the $La_{1-x}Ca_xMnO_3$ system. For $x<0.18$, the ground state is a FMI, while for $x>0.2$, it is a ferromagnetic metal (FMM).[11] Instead of changing doping level, varying the oxygen deficiency is another popular approach to control the properties of manganese.[3,12] Meanwhile, studies on oxygen-deficient manganites could substantially broaden experimental possibilities for fine tailoring of the material characteristics to a specific basic research or application. Recent investigations showed that the changes in the physical characteristics of the $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ series ($0<\delta<0.34$) are qualitatively similar to those obtained by varying the cation composition x.[12] In this paper, we investigate the electric field–induced switching effect in oxygen-deficient manganite thin films. The system studied in this work is low-doped $La_{1-x}Ca_xMnO_{3-\delta}$ thin film with FMI ground state. The finding presented herein is the colossal switching effect between higher resistive state and lower one induced by an external low current, which is associated with the existence of a weak FMI state caused by oxygen deficiency.

II. EXPERIMENT

The $La_{0.8}Ca_{0.2}MnO_{3-\delta}$ (LCMO) films were grown on single-crystal substrates of $SrTiO_3$ using pulsed laser deposition. The deposition temperature was 730 °C. The deposition took place in a pure oxygen atmosphere of the pressure of 0.1 mbar. The energy of the laser beam was ~400 mJ, the wavelength was 248 nm, and the pulse frequency was 3 Hz. The thickness of the film was about 200 nm, controlled by deposition time. The experiments of x-ray diffraction demonstrated that the grown films were highly epitaxial and of single phase. In order to avoid oxygen deficiency, one sample was postannealed at 800 °C for 1 h in air. The annealed $La_{0.8}Ca_{0.2}MnO_3$ sample is called LCMO-A. To confirm the existence of oxygen deficiency in LCMO films, the x-ray photoelectron spectroscopy (XPS) measurements were done. The electrical transport properties were measured in the temperature range of 20–300 K using a closed-cycle refrigerator. To avoid the effect of metal-oxide interfacial layers, both temperature dependence of resistivity (ρ-T) and voltage-current characteristics (V-I) were measured using four-probe method. The voltage probe separations ranged around 1 mm, about 1/3 of the total lengths of the samples. The dimensions of the film sample were 3×2.5 mm^2. To provide Ohmic contact, Ag electrodes were evaporated on film surface by lithography mask. The magnetization of the sample was measured on a Quantum Design superconducting quantum interference device (SQUID) magnetic property

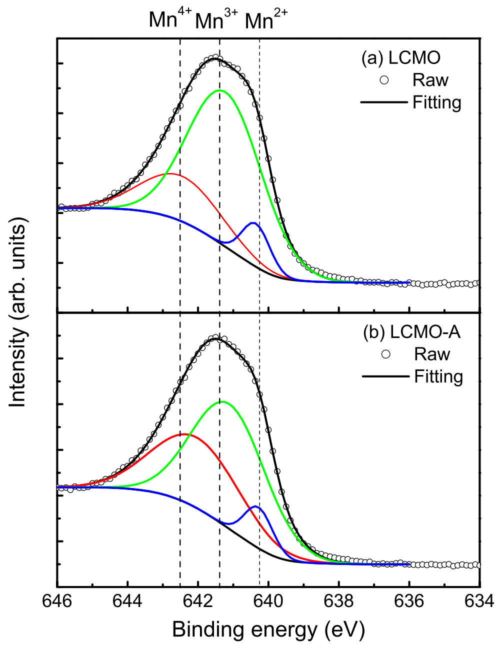

FIG. 1. (Color online) XPS spectra of Mn 2*p* on (a) LCMO and (b) LCMO-A films.

measurement system (MPMS) system (1.9 K$\leq T \leq$400 K, 0 T$\leq H \leq$5 T).

III. RESULTS AND DISCUSSION

In Fig. 1 there are shown parts of Mn $2p_{3/2}$ spectra of (a) LCMO film and (b) LCMO-A film. It can be seen that the Mn $2p_{3/2}$ spectra are wide and consist of a number of superimposed peaks. This spectrum contains three peaks of manganese with different valence states. The peak of high binding energy corresponding to Mn^{4+} in LCMO films is low compared with that in LCMO-A films. It is evident that the ratio of Mn^{4+}/Mn^{3+} in as-grown LCMO films is smaller than that in annealed LCMO-A samples. This characteristic implies that the existence of oxygen deficiency affects the ratio of mixed-valence manganese ions, and thus the transport properties.[1] The oxygen deficiency δ is about 0.05, calculating from the XPS results. As for the small and lower peak around 640 eV in XPS spectrum of Mn 2*p*, it can be attributed to the existence of Mn^{2+} ions formed by oxygen vacancies at the surface of these films which is normal for the manganite films.[13,14]

The field-cooled (FC) temperature dependence of magnetization $M(T)$ is shown in Fig. 2(a) for the LCMO and LCMO-A films. Measurements were performed within 5–300 K with a field of 100 Oe applied parallel to the film surface. The Curie temperature (T_C) of the LCMO films (defined as the one corresponding to the peak of dM/dT in the M vs T curves) is about 173 K, which is smaller than that of annealed film (T_C=178 K). Moreover, the temperature range of a FM-paramagnetic (PM) phase transition of LCMO film is broader than that of LCMO-A film, implying a wider distribution of the magnetic exchange interactions in the Mn-O-Mn network, i.e., the increase in magnetic inhomogeneity.

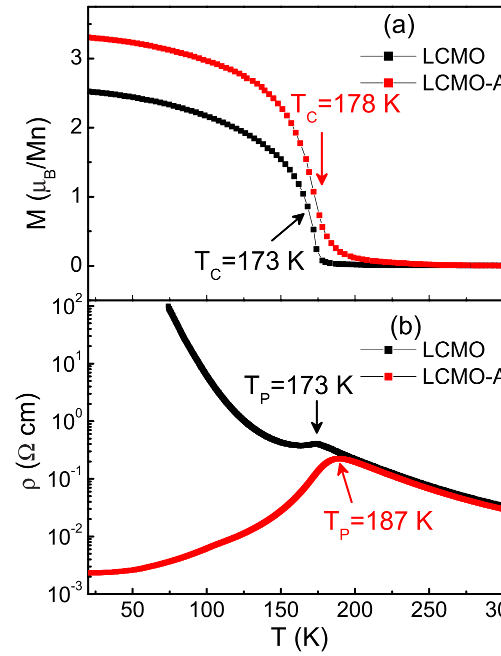

FIG. 2. (Color online) (a) The temperature dependence of magnetization $M(T)$ of the LCMO and LCMO-A films taken at H =100 Oe ($H\|$film plane) under FC mode. (b) Temperature-dependent resistivities of $La_{0.8}Ca_{0.2}MnO_{3-\delta}$ with two different oxygen contents. The resistivities are presented on a logarithmic scale and the current was chosen as I=0.05 mA during the resistance measurement. The arrows in the figure indicate the (a) Curie temperature T_C and (b) metal-insulator transition temperature T_P.

From the magnetic field dependence of magnetization of these films (not shown here), the coercive field (H_C) of LCMO-A film is about 50 Oe, while the H_C of as-grown LCMO film is a little bit larger as 74 Oe because of the existence of mixed phases at low temperature which will be discussed later. In Fig. 2(b), the temperature dependences of resistivity (ρ-T) of LCMO and LCMO-A films are shown. The resistivities are presented on a logarithmic scale and the current I=0.05 mA was chosen in measurements for both LCMO and LCMO-A samples. It is found that a typical metal-insulator transition (MIT) takes place at T_P=187 K for the LCMO-A film. As for the oxygen-deficient LCMO sample, the ρ-T behavior shows a significant lower transition temperature with T_P=173 K. Then, it has another a transition to a low-temperature insulating state with decrease in temperature, which is similar to previous results.[10,15] Such dramatic changes and oxygen-content sensitivity have been noted in other thin-film manganite systems.[16] The oxygen vacancy concentration is clearly responsible for this behavior. As shown in XPS data described above, the hole density of the LCMO film is just near the phase-transition critical region at which the transition of ground state from FMI to FMM takes place. The ground state near the critical region is quite sensitive to the external disturbance. Another point that should be noted in Fig. 2(b) is that the ρ-T behaviors of sample with and without oxygen deficiency are similar to each other at higher temperature $T > T_p$. This feature is accordant with the results of magnetization measurements shown in Fig. 2(a).

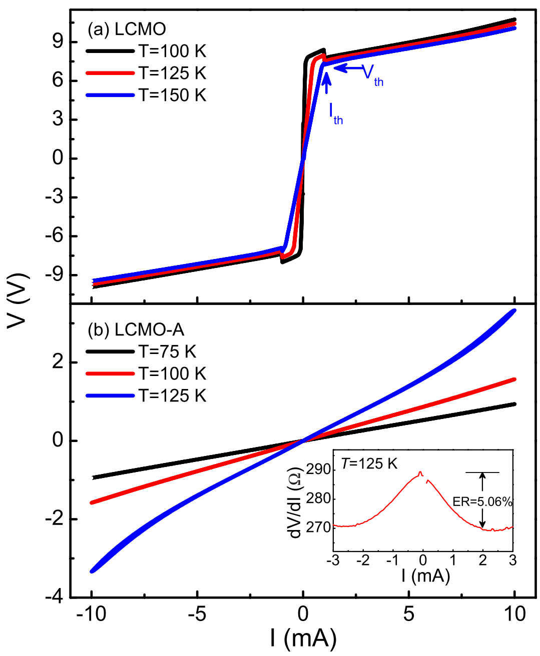

FIG. 3. (Color online) (a) V-I characteristics of LCMO film measured at temperatures of 100, 125, and 150 K. Arrows indicate the threshold bias current I_{th} and corresponding bias voltage V_{th}. (b) V-I characteristics of LCMO-A film measured at temperatures of 75, 100, and 125 K. The inset shows the differential resistance (dV/dI) as a function of current I at temperature of 125 K.

Figure 3 presents a series of voltage-current (V-I) curves for the LCMO sample at various temperatures $T<T_C$. For each measurement, the sample was initially cooled to the desired temperature and then the current was swept at a constant rate (0.39 mA/s) from zero to a maximum value of 10 mA, then to the negative maximum, then again to zero. From the data, it is evident that there is abrupt change in V-I curve with increase in bias current. Such an abrupt change occurs symmetrically for both current directions. In addition, the onset of the change takes place at a critical current I_{th}. The V-I curves behave almost linearly in both regions below and above the I_{th}. The main difference between these two regions is the slope of the V-I lines. It implies that the electrical transport of LCMO film switches from a high-resistivity state to a low-resistivity state as the bias current exceeds I_{th}. This feature is the typical evidence of the FMI-FMM transition in LCMO films. The data displayed in Fig. 3 are fully repeatable and do not show any significant hysteretic behavior. It is also found that the current-induced effect observed here is independent of the current rate. Similar experiments were performed at temperatures higher than T_C and no switching effect was observed, which implies that the current-induced switch effect in oxygen-deficient LCMO films is associated with FMI state at low temperatures.

Although there are many reports about the effect of Joule heating of manganites,[17,18] the electrical power I^2R measurement herein is far less than that used in Ref. 18. In earlier reports the internal thermal gradient caused by Joule heating was realized as the origin of the V-I nonlinearity.[17] Actually, the V-I curves of LCMO film in our experiments are almost linear within whole measurement range as shown in Fig. 3. Another point that should be noted is that the change in V-I behavior in Fig. 3 is abrupt, which is quite different from the typical behavior caused by Joule heating. Moreover, there is no hysteretic transition in our results, which is common effect caused by Joule heating. It is reasonable, therefore, to conclude that the Joule heating does not cause the observed current-induced switching effect in LCMO films.

For comparison, similar measurements of V-I characteristics were performed on the oxygen-stoichiometric LCMO-A films. The typical results are shown in Fig. 3(b). No current-induced switching effect is observed in the whole studied temperature range, implying that the current-induced switching effect in oxygen-deficient LCMO films is associated with oxygen vacancies. In whole range of bias current (-10 mA $\leq I \leq +10$ mA), the V-I relation is almost linear at $T<100$ K. As temperature increases above 125 K, the nonlinear and hysteretic behavior emerges at high bias current as shown in Fig. 3(b). Moreover, there also exists small ER at low bias current in stoichiometric LCMO-A film if we studied the V-I relation carefully. The inset of Fig. 3(b) shows the differential resistance (dV/dI) as a function of current I at temperature of 125 K. It can be found that the differential resistance decreases with increase in bias current and the ER ratio is only 5.06% at bias current of 2 mA if the ER ratio is defined as $[dV/dI(I=0.02\text{ mA})-dV/dI(I=2\text{ mA})]/[dV/dI(I=0.02\text{ mA})]$, which is much smaller than that in oxygen-deficient LCMO film as shown below. The differential resistance decreases with increasing current, which is opposite to the Joule heating effect. Therefore, it is reasonable to assume that Joule heating is irrelevant to our transport results, qualitatively at least.

As shown above, the V-I curves of LCMO film show discontinuous behavior and the resistance of LCMO film switches from higher value to lower ones driven by bias current at low temperatures. To further explore this ER effect, the differential resistance (dV/dI) as a function of current I was studied carefully. The typical results are shown in Fig. 4. There are two points worthy of special attention in Fig. 4. The first one is the colossal ER. It shows clearly that the differential resistance decreases sharply as bias current exceeds I_{th}. It could be found that the ER achieves 98.1% with $I=2$ mA at $T=125$ K. With increase in temperature the ER ratio decreases at a constant bias current. At $T=150$ K, the ER ratio is also as large as 95.7% with $I=2$ mA. This switch effect observed here may be of worth in the potential applications of new generation of data storage and sensing devices. The second point that should be noted in Fig. 4 is that both the threshold bias current I_{th} and voltage V_{th} (corresponding to the electric field where the current is I_{th}) are temperature dependent. The inset of Fig. 4(a) shows the temperature dependence of I_{th} and corresponding bias voltage V_{th} as $T<T_C$. It is found that the V_{th} of current-induced ER effect increases with decrease in temperature. It can be understood by considering that the insulator phase in LCMO film becomes more stable at low temperatures as reflected in ρ-T relationship.

Figure 5 shows the temperature dependence of differential resistance of LCMO film with selected currents $I=0.078$, 0.117, 1, and 2 mA. The resistances are also presented on a logarithmic scale. When the bias current is lower than I_{th}, for

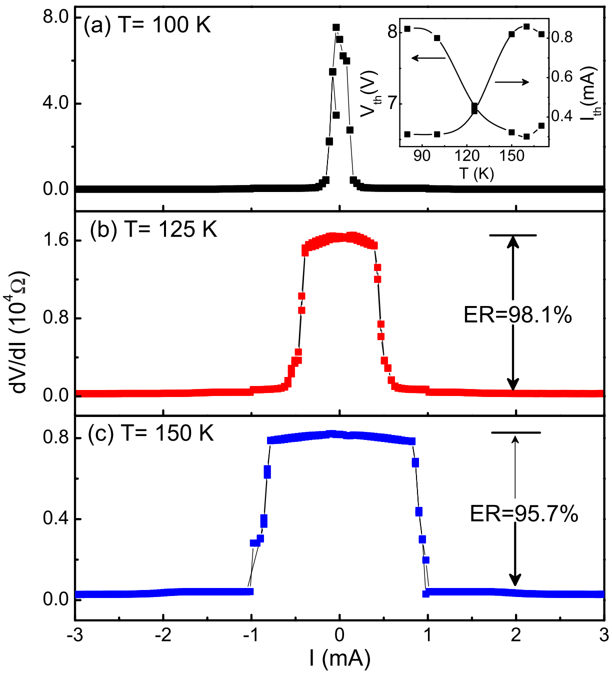

FIG. 4. (Color online) Differential resistance dV/dI characteristics as a function of the superimposed dc bias current (which is cycled from zero to its maximum positive value, then to its maximum negative value, then again to zero) measured at temperatures of (a) 100, (b) 125, and (c) 150 K. The inset of (a) shows the temperature dependence of I_{th} and corresponding bias voltage V_{th} as $T<T_C$.

example, I=0.078 and 0.117 mA, the dV/dI-T behavior is similar to that shown in Fig. 2(b) where the electrical properties were measured with continuous bias current of 0.05 mA. There is an insulator-metal transition at $T_{P1}\sim 170$ K and then another transition to a low-temperature insulating state. As the bias current exceeds the I_{th}, the low-temperature insulating state changes to metallic one and the insulator-metal transition temperature is enhanced to $T_{P2}\sim 212$ K for I=1 mA and $T_{P3}\sim 250$ K for I=2 mA. The observed current-induced insulator-metal transition at low temperatures is similar to the hydrostatic pressure effect in $La_{0.82}Ca_{0.18}MnO_3$ single crystal.[19]

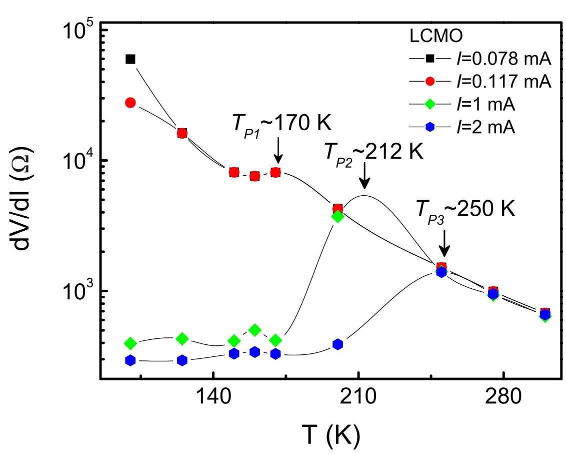

FIG. 5. (Color online) Differential resistance dV/dI characteristics as a function of temperatures with selected bias currents I=0.078, 0.117, 1, and 2 mA.

The colossal ER caused by low currents in oxygen-deficient LCMO film observed here suggests the sensitivity of FMI state to external electric field or current. Recently, more experiments were reported in this field. Some effects observed in different charge-ordered manganite systems are attributed to the formation of conducting ferromagnetic regions within the antiferromagnetic medium.[8,20] The transport in these systems is often interpreted in terms of spin-polarized tunneling conduction across the insulating phase and a percolative conduction mechanism. However, other explanations can be found in the literature, and some of them are listed below. For example, Guha *et al.*[20] attributed their observations of a nonlinear transport in $Nd_{0.5}Ca_{0.5}MnO_3$ thin films to depinning of the charge-/orbital-ordered state. In contrast, Tokura and Nagaosa[21] suggested that the electric field may directly influence the direction of the orbital ordering in the highly insulating state and alter the magnetic state. Moreover, Stankiewicz *et al.*[8] suggested that the formed mixed state is less resistive and highly magnetized than the initial charge-ordered state. Nucleation of ferromagnetic metallic clusters triggered by the electric field has also been proposed as an explanation. A collapse of the charge-ordered phase due to electrical current and formation of ferromagnetic conducting paths might be a cause too.[4] There is evidence that the spatial orientation of the anisotropic d orbitals can be modified by an electric field.[9] Similar phenomena have been found also in non-charge-ordered manganites. In this case, the role of the electric field in altering the spatial distribution of charge in MnO_6 octahedra, thus favoring the double-exchange transfer of charge carriers and enhancing conductivity, has been invoked.[22] For our experiments, the ground state of LCMO film at low temperature is weak FMI state as stated above. As discussed in Ref. 23, the oxygen deficiency in LCMO films introduces disorder and hence localization. Because the oxygen vacancies cause a large electronic imbalance and local lattice distortion, inhomogeneous electronic and magnetic phases emerge around vacancies. Moreover, the broader FM-PM phase transition and magnetic inhomogeneity have been observed in Fig. 2(a). It is reasonable, therefore, to believe that there is coexistence of FMI and FMM in FMI medium in our LCMO films as $T<T_C$. Indeed, recent experimental and theoretical studies implied that the doped manganites are intrinsically inhomogeneous and that phase separation is common in these materials.[1] Moreover, the way that the V-I curves behave (the discontinuity at lower temperatures driven by low current) in our experiments strongly suggests that the conduction is percolative and correlated with the phase separation. Below T_C, there are delocalized regions in localized background in oxygen-deficient LCMO film. The localized states can be "dislodged" under the influence of current excitation. The delocalization of such state should immediately lead to the appearance of a metallic state (FMI-FMM transition) accompanied by a large number of mobile charge carriers (or by a large Fermi surface), and hence is intrinsically different from conventional semiconductors or band insulators.

IV. CONCLUSION

In summary, we report the current-induced switching effect in oxygen-deficient LCMO film. As oxygen content in the $La_{0.8}Ca_{0.2}MnO_{3-\delta}$ film decreases, the ground state of $La_{0.8}Ca_{0.2}MnO_{3-\delta}$ film changes from FMM state to FMI state quickly. More interesting result is the observation of colossal electroresistance caused by low bias current in oxygen-deficient LCMO film. Such a current-induced switch effect takes place dramatically as the bias current or voltage exceeds a threshold value I_{th} or V_{th}. It is found that the ER ratio achieves 98.1% with the bias current $I=2$ mA at $T=125$ K. This colossal ER caused by low currents observed here suggests the sensitivity of FMI state in oxygen-deficient LCMO film to external electric field or current, which benefits the application of these compounds. These effects are understandable within percolation scenario. It is known that the electrical properties are associated to magnetic state tightly in doped manganese oxide system. Hence, further studies on the bias current effect on magnetism in oxygen-deficient LCMO film are encouraged.

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