Unusual current-induced electroresistance in epitaxial thin films of $La_{0.8}Ca_{0.2}MnO_3$

F. X. Hu and J. Gao*

Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China

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The transport behavior of $La_{0.8}Ca_{0.2}MnO_3$ thin films with Curie temperature T_C at ~286 K has been investigated under various applied currents in the absence of magnetic field. An unusual current-induced electroresistance (ER) was observed. When the applied current density reaches a critical value, the films could not revert to the initial state. A novel state can be induced by a suitable large current, in which the insulation-metal transition temperature remains almost unchanged comparing with the initial state, whereas the value of the peak resistance is very sensitive to the applied current. Even a rather low current density can depress it significantly. ER reaches ~43% under a small current of 0.5 mA (density $\sim 1\times 10^4$ A cm^{-2}). The observed ER effect seems to favor a percolative phase separation picture.

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Manganese oxides of the general formula $R_{1-x}A_xMnO_3$ (where R and A are rare- and alkaline-earth ions, respectively) have attracted much attention because of their distinctive properties, especially the colossal magnetoresistance (CMR) effect. Lots of experiments on polycrystals, single crystals, and thin films have been carried out to investigate the CMR behavior and its intrinsic physics. Phase separation together with concomitant percolation behavior has been supposed to be the core of CMR effect.[1–3] It has been suggested that the largest MR is associated with spatial inhomogeneity related to multiphase coexistence, which generically causes a sensitivity of physical properties to external perturbations, such as application of magnetic fields, pressure, current bias, or light illumination.[1–10] Several reports[6–10] proved that the balance of multiphase coexistence can be influenced not only by a magnetic field but also by an electric field or current bias. It has been observed[6,7] that an applied current bias could lead to a transition from the electrically insulating charge-ordered (CO) state to a ferromagnetic (FM) metallic state, even for $Y_{0.5}Ca_{0.5}MnO_3$ in which a large magnetic field (~40 T) has no effect on the charge-ordered state. Furthermore, a correlation between electroresistance (ER) and MR has been established in $La_{0.82}Ca_{0.18}MnO_3$ single crystal, and the action of an electric current of 0.3 mA was found to be equivalent to 1.5 T at a temperature below Curie temperature (T_C) and to 0.4 T at room temperature.[8] A rough estimation shows that a 1 nm wide filamentary path biased with 1 mA could cause a magnetic field of 1 T.[8] Considering the strong effect of external perturbations, especially magnetic field and current bias, on the balance of multiphase coexistence, it can be expected that an enough high magnetic field or current bias could thoroughly disturb the subtle balance of multiphase coexistence and then may induce a new equilibrium state of coexistence, in which different novel CMR characteristics might appear. However, the investigation of an extremely high field on the multiphase coexistence is not easy to be carried out due to the technological limitation of generating a very high magnetic field. Fortunately, a current with very high density could be easily applied to a microbridge of CMR thin film and thus the influence of high current density on the multiphase coexistence state can be investigated. Previous investigations on ER of mixed-valent manganites were performed mainly on bulk single-crystal materials or bulk films. Experiments employing a current with very high density have rarely been reported.

In this paper, we choose $La_{0.8}Ca_{0.2}MnO_3$ (LCMO) thin film with Curie temperature T_C of ~286 K to study the effect of high current density on the balance of multiphase coexistence in view of the strong interest for exploring novel devices working at room temperature. We observed an interesting resistive behavior in a new state induced by a high current density, in which the peak resistance was found to be very sensitive to a small current. The strong dependence of resistance on a small current near room temperature would be of great interest not only for fundamental physics but also for potential technological applications of CMR thin films.

The present LCMO thin films were grown on single-crystal substrates of $SrTiO_3$ with (100) orientation using pulsed laser deposition technique. A disk of stoichiometric $La_{0.8}Ca_{0.2}MnO_3$ was used as the target. The deposition took place in a pure oxygen of 1 mbar. The energy of the laser beam was ~200 mJ, wavelength was 308 nm, and the pulse frequency was 6 Hz. The substrate temperature was 750 °C as measured by a k-type thermocouple inserted into the heater block. The thickness of the film was about 100 nm, controlled by deposition time. A postannealing at 800 °C for 1 h was made in air in order to avoid oxygen deficiency. The composition of the film determined by energy dispersive x-ray analysis was very close to the stated composition.

The experiments of x-ray diffraction reveal sharp peaks of the formed ABO_3 phase with the c axis perpendicular to the substrate surface. Besides the reflection from substrate and the $(00l)$ peaks of the LCMO, no other peaks are visible, demonstrating that the grown films are of single phase. The electric measurements were done by using the standard four-probe technique in a closed cycle cryostat. In order to apply a current with high density, the films were patterned into a microbridge with the width of 50 μm and length of 200 μm using lithography technique. Four silver contacting pads were then evaporated on the sample and the current leads

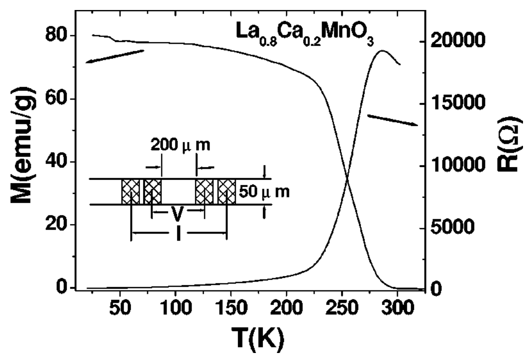

FIG. 1. The temperature dependence of resistivity at zero field and magnetization measured under 100 Oe for a LCMO thin film. Inset is the schematic microbridge with size of $50\times 200\ \mu m^2$ for resistance measurements. The dark parts are the evaporated silver pads.

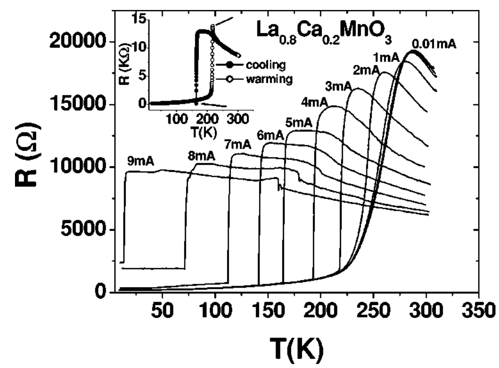

FIG. 2. The *R-T* dependences for an as-grown LCMO thin film with different currents measured in a cooling process. The current was applied in a sequence of 0.01, 0.05, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, and 9 mA. Inset is the *R-T* curve measured using 5 mA on cooling and warming processes.

were connected to the silver pad using an MEI-907 supersonic wire bonder to obtain low Ohmic contacts. A constant current source with a high voltage limit (Sorensen DCS 300 V-3.5 A) was employed when a large current flow needs to be applied. Magnetic measurements were performed using a superconducting quatum interference device magnetometer.

Figure 1 presents the temperature-dependent resistivity without magnetic field and magnetization measured under 100 Oe. It is found that the Curie temperature T_C of $La_{0.8}Ca_{0.2}MnO_3$ film is much higher ($\sim$286 K) than that of its bulk material, and also higher than that of $La_{0.7}Ca_{0.3}MnO_3$ film we just studied in a previous report.[10] The expected T_C of bulk $La_{0.8}Ca_{0.2}MnO_3$ is only ~190 K according to the relative phase diagram.[11] Such a phenomenon, we observed, is fully consistent with a previous report[12], in which one found that the unit-cell volume of $La_{0.8}Ca_{0.2}MnO_3$ film is much smaller than that of its bulk material, and also smaller than that of $La_{0.7}Ca_{0.3}MnO_3$ film. It was suggested that the reduction in the unit-cell volume due to strain effect would enhance the transfer integral of electron hopping between Mn^{3+} and Mn^{4+} and thus T_C. Additionally, another possible scenario should be also taken into account. It is generally believed that the localized lattice distortions, arising from the Jahn-Teller effect, play a key role in determining the observed resistivity behavior and the magnetic transition temperature in CMR mixed-valent manganites.[13] The strain effect due to substrate might release the Jahn-Teller lattice effect in $La_{0.8}Ca_{0.2}MnO_3$ film and, consequently, suppress the competing effects with double-exchange interaction, resulting in the enhancement of T_C. Inset of Fig. 1 is the schematic microbridge of the film for resistance measurements.

Shown in Fig. 2 is the dependence of resistance of a LCMO film on temperature (*R-T* curve) measured under different currents from $I=10\ \mu A$ to 9 mA. All measurements were carried out in a slow cooling process. Starting temperature is about 300 K, and arriving temperature is about 10 K. The cooling rate is $\sim$3 K/min. The measurements are instantly performed when the applied current is tuned to a desired value. A striking observation is the significant decrease of the peak resistance R_p with increasing current. The relative reduction of R_p reaches ~43% for current increase from $I=10\ \mu A$ to 6 mA. Our previous report on $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.85}Ba_{0.15}MnO_3$ thin films also revealed a similar behavior.[10] The self-heating effect is serious when a large current is applied. However, it does not affect the measured value of the peak resistance, although it may shift the location of the ferro-paramagnetic transition.[10] The temperature within the measured microbridge of the film should be uniform due to its small size ($50\times 200\ \mu m^2$). The widening of the resistance peak with the increase of current recorded in cooling process is associated with self-heating effect. This can be understandable considering the asymmetry of the resistance peak. The slope of *R-T* curve (dR/dT) near but below T_{max} is much larger than that near but above T_{max} due to the sharp ferro-paramagnetic transition. A change of resistance would cause a change of Joule heat. However, the thermometer in the heater block could not rapidly follow the change of the temperature of the film and always displays a lingering temperature. Therefore, the *R-T* curve recorded on cooling shows a tablelike peak and the ferro-paramagnetic transition looks sharper and sharper with increasing current. Inset of Fig. 2 presents a typical *R-T* curve ($I=5$ mA) in both cooling and warming processes for present sample. The cooling and heating rates are the same, 3 K/min. The large temperature hysteresis of the resistive transition in a temperature cycle is due to the existing distance between the thermocouple and thin film. The sharp peaks marked by arrows are not intrinsic but caused by technological reasons. Our constant current source employed cannot follow the rapid change of resistance during a resistance transition and cause a false phenomenon—appearance of the sharp peaks at transition point. Obviously, the *R-T* curves recorded on cooling is more reliable. On cooling, the false peak appears in reverse direction and does not influence the value of peak resistance.

When I exceeds 6 mA, the *R-T* curves remeasured under 0.05 mA show quite a different behavior comparing with the initial case before applying such high currents. However, with the initially applied current equal to or lower than 6 mA, the *R-T* curves remeasured under 0.05 mA remain almost unchanged, same as the one measured directly by

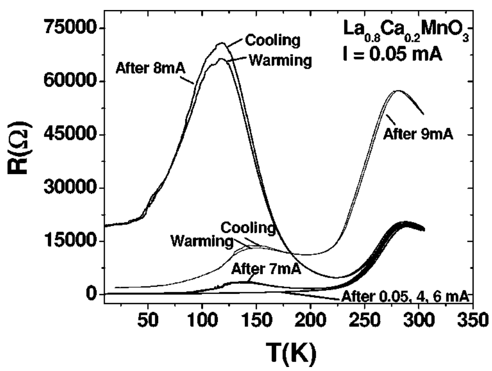

FIG. 3. The temperature dependence of resistance measured using the same current $I=0.05$ mA in cooling and warming processes after each measurement of *R-T* curve for an LCMO thin film. The applied current is in a sequence of 0.05, 4, 6, 7, 8, and 9 mA.

0.05 mA. This meaningful result indicates that the intrinsic state of our LCMO films can be strongly disturbed by a current higher than a critical value I'.

In order to illustrate the evolution process of the state with the increase of applied current, Fig. 3 presents the remeasured *R-T* curves in cooling and warming processes using the same small current of $I=0.05$ mA after each measurement of *R-T* curve. The cooling rate is the same as the warming rate, ~ 3 K/min. The applied current is increased in a sequence of 0.05, 4, 6, 7, 8, and 9 mA. The state developing with the increase of applied current is clearly manifested. When the applied current exceeds 6 mA, an additional peak at relatively low temperature T_O develops with the resistance peak at T_C remaining. Intriguingly, when the applied current increases from 7 mA to 8 mA, both magnitude and position of the resistance peak at T_C do not change while the peak resistance at T_O increases significantly. However, when I continues increase to 9 mA, the low-temperature peak resistance notably decreases, but the magnitude of the high-temperature peak increases remarkably with its position almost unchanged. Also, all the remeasured *R-T* curves are found almost reversible in a temperature cycle (Fig. 3). The temperature hysteresis for both the peaks at T_O and T_C is small. It is worthy to point out that all the remeasured *R-T* curves using 0.05 mA after different large current applications can be fully reproducible. We made the measurements using the same current of 0.05 mA many times. All results coincide very well.

It is known that the self-heating effect is serious when a high current is applied. The escape of oxygen from a thin film may occur when the film is heated in a vacuum. All the measurements of *R-T* curves are performed in a vacuum of 10^{-2} mbar. To clarify the origin of such an interesting behavior, we studied vacuum annealing effects for an as-grown thin film of present composition with same thickness. The results are very similar to a previous report.[14] Different conditions, such as annealing temperature, time, and vacuum, were tried to compare the effect caused by vacuum annealing with the one caused by applying a current with high density. However, no similar phenomena as described in Fig. 3 were observed at all. Simply annealing in a vacuum could only cause a shift of the position of peak resistance to lower temperature and make the resistance increase. Generally, the reduction of Mn^{4+} ion concentration, caused by escape of oxygen, weakens the ferromagnetic double-exchange interaction and leads to a decrease of ferromagnetic transition temperature T_C and an increase of resistance in manganese oxides. It is clear that the observed behavior in Fig. 3 could not be explained simply by the escape of oxygen caused by self-heating effect.

Nowadays, lots of evidences support the idea that multiphase coexistence acts as a key role in manganites.[1–3] It has been demonstrated[3] that metallic FM and insulating CO states coexist in a broad range of phase space even for $La_{1-x}Ca_xMnO_3$ (Refs. 2, 9, 15, and 16) and the insulating phase in phase separation is the $x=1/2$-type CO state. The subtle balance between these two states with distinctly different electronic properties can be readily influenced by varying physical parameters. Applied electric field (or current) may perturb the coexistence and set up filamentary currents across insulating region, and intense local magnetic fields might be induced by current flow, which may in turn further influence the phase coexistence. Therefore, it is possible that a quite large current flow thoroughly breaks down the balance of multiphase coexistence in the initial state and induces a new state with new coexistence of the phases. Actually, the developing of *R-T* curve shown in Fig. 3 indicates the modulation process of the applied large current on the coexistence and reflects the evolvement of the film state with the increase of large current. Although the escape of oxygen caused by self-heating effect could not be wholly excluded, the modulation of large current on the state of multiphase coexistence should be the main factor that brings about the interesting behavior shown in Fig. 3. An applied current larger than a critical value may significantly change the relative volume of FM and CO phases. For the case that a current higher than 6 mA was applied, the reduction of the electron conduction with decreasing temperature from ~ 200 K (Fig. 3) can be a result of the volume increase of the CO phase and the metalliclike behavior below T_O might suggest percolative conduction through metallic regions embedded in insulating regions. In this picture, the appeared different residual resitivity may be an indication of the different relative volume of FM and CO phases in the states induced by different large currents. An abundance of CO domains would lead to poor connection of minority FM domains and make residual resitivity increase.

A more attractive feature, for the new state induced by a large current of 9 mA (density $\sim 1.8\times10^5$ A cm^{-2}), is that the magnitude of the resistance peak at T_C is found to be very sensitive to an applied current. Even a small current can depress the peak resistance significantly. Figure 4 displays the temperature-dependent resistance under different currents from $I=0.8$ μA to 1.0 mA measured in cooling process. It is found that the relative reduction of R_p reaches ~43% for a small current of 0.5 mA. When the applied current is lower than or equal to 0.5 mA, the residual resistance is found unchanged (see Fig. 4) and all the *R-T* curves remeasured under 0.01 mA after any current applications lower than 0.5 mA remain unchanged, same as the one measured directly by 0.01 mA. One should note that the self-heating effect produced by a current less than 0.5 mA is small. Inset of

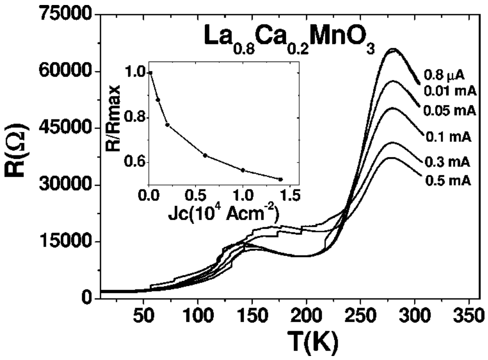

FIG. 4. The *R-T* dependences for a LCMO thin film with different bias currents of 0.0008, 0.01, 0.05, 0.1, 0.3, and 0.5 mA for a new state induced by a large current flow of 9 mA. The inset shows the normalized resistance R_p as a function of current density J_c.

Fig. 4 plots the normalized resistance as a function of current density. It does not show linear behavior. Another important feature, which is indeed noteworthy, is that the position of the insulation-metal transition at T_C remains nearly unchanged upon the application of different currents. A similar behavior that an electric field causes no change in the peak position of resistivity has been also observed in LCMO using a field effect configuration.[9] Such a characteristic is very different from the case of general MR, implying that different mechanism might exist between ER and MR.

Generally, an application of magnetic field can improve the spin alignment in an ABO_3 compound and affect its conduction. As a result, the resistive point shifts to higher temperatures, yielding CMR. Our recent study[10] showed that the ER induced by a current might ascribe to two aspects: one is the strong interaction between carrier spins and localized spins in Mn ions, and the other is the percolative mechanism of phase separation. The former means that the interaction between carrier spins and localized spins in Mn ions would force the localized spins to be parallel. A direct consequence is the high-temperature shift of T_p. However, we have not observed any shift of T_p upon the application of current. For the initial as-grown state, a relatively large current is needed to produce a significant ER. In this case the self-heating effect is strong and the T_p could not be detected exactly. It seems that the ER observation favors the percolative mechanism of phase separation at least for the present new state induced by a large current. The new state is metastable compared to the initial as-grown state. A small local electric field or current is enough to perturb the new equilibrium of phases with different electronic densities and set up filamentary currents across insulating region. It induces further polarization of FM regions and the reduction of resistance, causing an ER effect. The many-step changes of resistance appearing near the low-temperature peak (Fig. 4) are not caused by measurement technique. They are an intrinsic feature. When remeasured the steps can be fully recovered in all *R-T* curves when the applied current is lower than 0.5 mA. Such a phenomenon reflects the significant difference between the new metastable state and the initial as-grown state. The step change of resistance might indicate the abrupt transformation between FM and CO states induced by temperature variation. Such a transformation should be of first order in nature. However, further studies are needed to fully understand the observed effect.

In summary, unusual current-induced ER has been observed in $La_{0.8}Ca_{0.2}MnO_3$ epitaxial thin films with T_C at $\sim$286 K. It is found that a current with high density could significantly influence the coexistence of FM and CO states in the picture of percolative phase separation. After a suitable large current is applied, a novel state can be induced, in which the peak position remains unchanged but the peak resistance is very sensitive to the applied current. Even a small current can make the peak resistance reduce remarkably. ER $\sim$43% was found with a small current of 0.5 mA. The appearance of the novel state is not caused by the escape of oxygen due to self-heating effect. The modulation of large current on the coexistence of multiphases might play an important role. Such a large ER near room temperature achieved using a small current would be of great significance for both basic research and technological applications.

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*Author to whom correspondence should be addressed. Email address: jugao@hku.hk

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