Controllable colossal electroresistance in $La_{0.8}Ca_{0.2}MnO_3$ epitaxial thin films

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We observed a significant enhancement of electric resistivity excited by a dc current in $La_{0.8}Ca_{0.2}MnO_3$ epitaxial thin films. Such an enhanced resistance can be achieved when the applied dc current exceeds a threshold value. It also strongly depends on the duration of the dc current excitation. The induced enhancement in resistance can be well controlled by varying the duration of the current excitation. More attractive is that the enhanced resistance is extremely sensitive to weak currents. Even a very small dc current can remarkably depress the induced resistance, showing a colossal electroresistance (ER) in a very wide temperature range, even to room temperature. The maximum of ER can reach ~1350% for temperatures lower than ~50 K and ~580% even at 300 K when the current changes from 0.7 to 10 μA. Structure measurements on a microarea by the micrometer x-ray diffraction technique were carried out. No change of the structure and lattice parameter was found upon current treatments. Phase separation is taken into account in the interpretation of the observed phenomena.

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Mixed-valence-doped manganese perovskites with the general formula $R_{1-x}A_xMnO_3$ (where R and A are rare- and alkaline-earth ions, respectively) have triggered intense interest due to the interesting interplay between spin, charge and orbital degrees of freedom in these materials. Their colossal magnetoresistance (CMR) has also attracted much attention for various applications. It has been proven that phase separation together with concomitant percolation conductivity is an intrinsic feature of these materials and it may even lie at the very core of the CMR effect.[1–3] Recent studies suggest the largest MR in the mixed-valence doped manganites is associated with spatial inhomogeneity related to multiphase coexistence, which generically causes a sensitivity of physical properties to external perturbations, such as magnetic or electric fields, pressure, current bias, or illumination with light or x rays. A significant electroresistance (ER) effect induced by a static electric field has been demonstrated in thin films using field-effect configurations. The ER and CMR effects are found to be remarkably complementary and strongly favor a percolative phase separation picture.[4] Furthermore, it has been observed[5] that an applied current can lead to a transition from the electrically insulating charge-ordered 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. Current-induced switching of resistive states in a $La_{0.8}Ca_{0.2}MnO_3$ single crystal has also been reported.[6,7]

Recently, we observed a remarkable ER effect induced by a current in epitaxial thin films of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.85}Ba_{0.15}MnO_3$.[8] Further studies revealed that a current with a high density could significantly affect the balance of multiphase coexistence and cause a series of changes in transport properties.[9]

Manganite perovskites $La_{1-x}ca_xMnO_3$ are characterized by a complex phase diagram containing a rich variety of magnetic and electronic phases. Because of the subtle competition between charge-carrier motion and magnetic spin as well as orbital moments, the phase-separated state becomes the stable ground state, especially for the less doped samples. The possibly appearing charge ordering in the sample would suppress ferromagnetism and electron itineracy. However, it has been observed that the charge-ordered phase is less stable in thin films due to the strain effect, compared with single crystals. Therefore it is expected that the less stable charge or orbital order in thin films may be easier to disturb and the response to an electric current or field can be more significant compared than in the bulk. Furthermore, an extremely large current or a high electric field can be easily applied to a patterned microbridge in thin-film samples, providing a system to investigate the response of the strain-modified electric properties to extreme conditions. In this paper, we report a controllable colossal electroresistance effect introduced by a large current in $La_{0.8}Ca_{0.2}MnO_3$ epitaxial thin films.

The $La_{0.8}Ca_{0.2}MnO_3$ thin films were grown on single crystal substrates of $SrTiO_3$ with (001) orientation using the pulsed laser deposition technique.[9] The films were grown with the (00l) orientation and with a thickness of about 90 nm. The temperature dependences of electric resistance were measured by using the standard four-probe technique. In order to apply a current with high current density (J), every film was patterned into microbridges with a width of 50 μm and length of 200 μm using the lithography technique. Silver

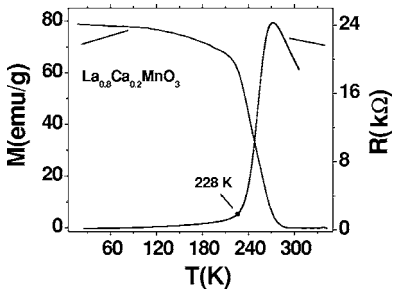

FIG. 1. The temperature dependence of resistivity at zero field and magnetization measured under 100 Oe for a thin film of $La_{0.8}Ca_{0.2}MO_3$.

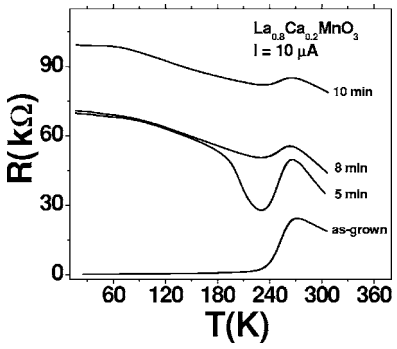

FIG. 2. The $R(T)$ relations measured using the same current of 10 μA for the states induced by applying a dc current of ~9.8 mA at 228 K with different durations δt=5, 8, and 10 min, respectively. For comparison, the R-T curve of the as-prepared state is also plotted.

contacting pads were evaporated on the sample to obtain low-Ohmic contacts. The micrometer x-ray diffraction (XRD) technique (Bede Scientific Instruments, Bede D1 System) was used to check the microarea structure upon current treatments. The cross section of the x-ray spot can reach 50 μm in diameter.

Figure 1 presents the temperature dependence of the resistivity without magnetic field and magnetization measured under 100 Oe. It is found that the Curie temperature T_C of the $La_{0.8}Ca_{0.2}MnO_3$ film is at ~272 K, much higher than that of its bulk material (~190 K).[9] Magnetic and transport properties in CMR manganites were usually explained by dynamic Jahn-Teller and double-exchange effects.[10] The strong electron-phonon coupling due to the Jahn-Teller effect localizes the conduction-band electrons as polarons, leading to a large resistivity. As temperature is decreased through T_C, the polaron effect is reduced due to the competition between electron itineracy and self-trapping, and a sharp drop in resistivity is exhibited. When a large current is applied, the associated electric field in the phase space may be sufficiently high to contribute to the crystal fields. Since the Jahn-Teller distortion arises from crystal fields, it is expected this distortion can be strongly impacted and contribute to a remarkable change in transport properties. We applied a dc current with high density at a specific temperature (~228 K), where the resistance starts to increase in the R-T curve (see Fig. 1) for a short duration δt and investigated the induced effect. The specific temperature of ~228 K was chosen based on the following two considerations. First, the resistance at ~228 K is still small and the direct impact caused by the self-heating effect should be weak. Second, the strong competition between electron itineracy and self-trapping at ~228 K, where the metal-like phase begins to transfer to an insulatinglike phase, would enhance the influence of bias current on the magnetic, structural distortion, and transport properties. We found that applying a dc current of ~9.8 mA ($J=2.2\times10^5$ A cm^{-2}) in such a manner resulted in a strong increase of electric resistance in the whole temperature range from 10 to 300 K. Such an enhancement in resistance is fully controllable by changing the duration of the applied current.

The influence of the duration of the current excitation has been studied. Figure 2 displays the $R(T)$ curves measured for the states induced by the same excitation current of 9.8 mA ($J=2.2\times10^5$ A cm^{-2}) but with different durations (δ=5, 8, and 10 min, respectively). The measuring current for all $R(T)$ curves was kept the same (10 μA). For comparison the $R(T)$ curve of the initial state is also plotted. The state evolution with increasing δt is manifested. When δt reaches 5 min, the electric resistance significantly increases in the whole temperature range. Continuously increasing δt results in an increase of resistance subsequently. For δt increasing from 5 to 8 min, the resistance in the low-temperature range remains nearly unchanged but the resistance around T_C is remarkably enhanced, especially for the resistance around 228 K. Thereby the waveness in the $R(T)$ curve seems becoming weaker. However, the resistance anomaly around T_C always remains, and the position of the resistance peak T_P stays nearly unchanged for all cases. It is worth pointing out that an applied current lower than 9 mA can hardly cause a notable increase of resistance for the present film. It seems that a threshold value of current exists for inducing such transport behavior.

A more attractive feature is that the increased high resistance is sensitive to a weak current. Even a very small dc current can depress the high resistance remarkably, resulting in a colossal ER effect. Figure 3 shows the temperature dependences of the resistance measured using different weak currents. Figures 3(a), 3(b), and 3(c) are for the states induced by a current of 9.8 mA with different durations δt=5, 8, and 10 min, respectively. We found that the three cases with different durations of current excitation exhibit different sensitivity to weak currents. At low temperatures, the enhanced resistance, for all three cases, is highly sensitive to weak currents. The maximum of ER can reach ~1350% at temperatures lower than ~50 K when the current changes from 0.7 to 10 μA. However, at temperatures around T_C, the three cases display different behaviors. For δt=5 min, a weak current lower than 10 μA caused no change in the resistance. With a longer duration of current excitation, the resistance around T_C turned out to be sensitive to weak currents. As can be seen in Fig. 3(b), a current higher than 5 μA can cause a visible decrease of resistance near T_C, for δt =8 min, though currents lower than 1.8 μA still cannot influence the resistance. When the δt further increases to 10 min, the resistance around T_C becomes highly sensitive to a small current. At 300 K, the ER could reach ~580% upon

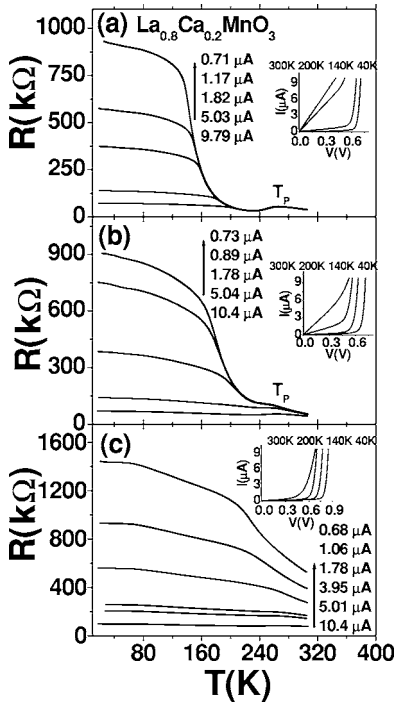

FIG. 3. The *R-T* dependences of $La_{0.8}Ca_{0.2}MO_3$ thin films with different weak currents for the states induced by applying a dc current of ~9.8 mA at 228 K for δt=(a) 5, (b) 8, and (c) 10 min. Insets show the *I-V* curves at different temperatures for the corresponding states.

current changing from 0.7 to 10 μA. The insets of Fig. 3 show the isothermal *I-V* curves at different temperatures for the corresponding states. The direction of the applied currents is the same as that of the excitation dc current. For the case of δt=10 min the non-Ohmic behavior persists even to room temperature, but for the other two cases, the non-Ohmic behavior rapidly becomes weak and even disappears with increasing temperature. For the case δt=5 min, a complete Ohmic behavior appears at room temperature.

The observed phenomena are rather stable. Exposing samples in air at room temperature for quite a long time, such as one month, does not cause any change of the transport properties for all the three cases. However, we found that the application of a small ac current can suppress the resistance enhancement and eliminate the sensitivity to small currents; meanwhile, the non-Ohmic behaviors disappear. Figure 4 shows the *R-T* curves measured using different currents of 0.64 and 10.4 μA, for the case of δt=8 min, after sweeping by a small ac current 10 μA, 0.025 Hz for about 500 cycles. For comparison, the *R-T* curve of the as-prepared state is also plotted. We found that the enhanced resistance has been remarkably reduced in the whole temperature range compared to that of the freshly created state [compare Figs. 2, 3(b), and 4], noting the different scales of the *R* axis in Figs. 2, 3(b), and 4. The magnitude of resistance around T_P at this moment is just slightly higher than that of the as-prepared state. Changing the measuring current from 0.64 to 10.4 μA does not cause a significant change of the electric conductivity. Only a slight change of resistance is found. Repeated measurements indicate that the upturn and the noise of the resistance appearing at low temperatures in the *R-T* curve of 0.64 μA are intrinsic, which might reflect the characteristics of the metastable states developed by the sweeping of an ac current. The inset of Fig. 4 exhibits the isothermal *I-V* curves measured at different temperatures. They are just slightly curved, showing a nearly Ohmic behavior.

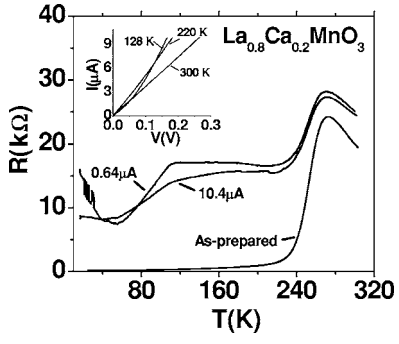

FIG. 4. The *R-T* curves of a $La_{0.8}Ca_{0.2}MO_3$ thin film (excited with δt=8 min) after sweeping by a small ac current of 10 μA for 500 cycles. The measuring currents are 0.64 and 10.4 μA, respectively. For comparison, the *R-T* curve of the as-prepared state is also plotted.

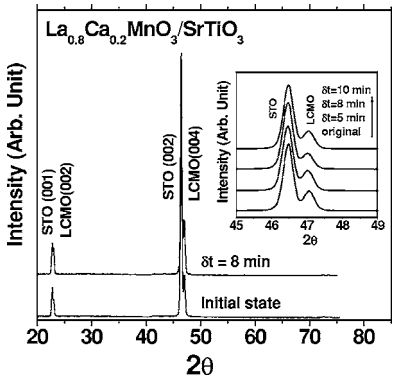

FIG. 5. The micrometer XRD spectrum in the case of δt =8 min in comparison with the original one. Inset exhibits the details of the three cases upon different current treatments in comparison with the original one.

It is known that the escape of oxygen from thin films might occur when the sample is heated in a vacuum. The application of an excitation dc current at 228 K is performed in a vacuum of 10^{-2} mbar since a proper vacuum is needed to obtain thermal isolation. To make sure the interesting observations are not caused by escape of oxygen due to self-heating, various experiments were performed. First, we studied vacuum annealing effects for an as-prepared thin film with identical composition and thickness. The results are very similar to the previous report.[11] Simply annealing in a vacuum only causes a shift of the position of the peak resistance to lower temperature and makes the resistance increase. No similar phenomena as described in Fig. 3 were observed at all. 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 the ferromagnetic transition temperature T_C and an increase

of resistance in manganese oxides. Noting that the microbridges for current treatments are small (50 μm in width and 200 μm in length), magnetization measurements cannot be carried out on such a small area. By using micrometer XRD technique with a probe beam of 50 μm in diameter, we carefully examined the local microstructure. Figure 5 presents the obtained XRD data on the case of $\delta t = 8$ min, which is compared with the original one. No change of the structure and orientation was found upon current treatments. The inset of Fig. 5 exhibits the detailed spectra of the three cases upon different treatments compared with the original one. An obvious escape of oxygen usually is accompanied by an enlargement of the lattice,[11] causing a considerable shift of the diffraction peak to smaller 2θ. However, we did not detect an obvious shift of the characteristic peak, implying that the escape of oxygen should be very little if there is any. In order to ensure that the sample is not destroyed by the current treatments, we also performed measurements of the energy dispersive spectra (EDS) and x-ray photoelectron spectra on the microarea before and after current treatments. No change in the composition and element valence was found. The influence of the deposited silver electrodes on the transport observations has also been investigated. We redeposited silver electrodes on other positions or even replaced them by silver paste after current excitation. The transport properties were unchanged.

It is known that thin films grown on single-crystal substrates may have various defects, e.g., misfit dislocations, misoriented *c* grains, point defects, etc. Although we did not detect a large amount of oxygen loss in the microstructure XRD diffractogram, one might think of a little escape of oxygen from the existent defects or conductive paths under a large current. Insulating areas around the defects or along percolative paths might appear due to the low concentration of Mn^{4+} ions caused by the increase of oxygen vacancies in the areas. As with the effect of grain boundaries in the CMR manganites,[12] a high resistance and nonlinear conductivity across the insulating barrier would appear due to the tunneling mechanism. In this picture, the high resistance and the non-Ohmic behavior for the newly created states can be explained. However, the fact that application of a small ac current can erase the enhanced resistance and eliminate the non-Ohmic behaviors, as discussed earlier (Fig. 4), cannot be explained in this frame. It is not possible that the lost oxygen is restored back to the sample upon treatment by a small ac current.

Much research supports the idea that multiphase coexistence plays a key role in manganites.[1–3] It has been demonstrated that metallic and insulating states coexist in a broad range of phase space even for $La_{1-x}Ca_xMnO_3$ (LCMO).[2,4,13] Recent NMR (Ref. 14) and structural investigations[15] on low-doped LCMO systems have confirmed that the phase-separated ground state is constituted of two ferromagnetic phases with different orbital order (OO). In one phase an antiferrodistorsive-type OO is favored by FM superexchange interactions, giving insulating characteristics, while in the other phase the ferrodistorsive-type OO promotes double-exchange interactions, exhibiting metallic behavior. It was experimentally found that an electric field could directly affect the directional order of orbitals and thus alter the magnetic and conducting states.[16] In an inhomogeneous sample, partly metallic and partly insulating, an applied electric field has a distribution in the phase space depending on the size, shape, and distribution of the phases. When the applied current is high enough, the associated electric field distributed in the phase space may strongly impact the orbital order of the phases and enforce a thorough change in the topology of the phase coexistence. In addition to the direct influence of the electric field, the disorder effect induced by a large current and its intense self-magnetic-field may also destabilize the robust orbital-order phases. Eventually a new state with new coexistence of the phases may appear. The action of the strong current on the topology of the phase coexistence or the rearrangements of the orbital domains may be realized either by means of carrier injection or by direct interaction with elastic forces. Therefore, it is understandable that the process is not instantaneous. A sufficient dose of the excitation current is needed. Suitably prolonging the acting time or increasing the magnitude of the current for excitation can further improve the induced orbital distortion. A remarkable increase of the volume of the insulating phase may occur with longer duration of excitation, resulting in a strong decrease of electric conductivity. The appearance of the new resistive state is a natural effect of the coexising multiphase with different orbital ordering upon application of a large dc current. The possible self-heating effect cannot be the reason because we can hardly image that the oxygen lost by self-heating can return to the sample simply on applying a small ac current. The local elastic forces existing in the microstructure stabilize the orbital distortion and make it robust. It cannot spontaneously return to its initial state without external perturbations.

The induced states with orbital distortion exhibit high electric resistance. The development of the *R-T* curve shown in Fig. 2 actually reflects the evolvement of the film state. With increasing duration of the current excitation, the continuous increase of resistance in the whole temperature range can be a result of the increased volume of the insulating phase. Similar to the typical systems of single crystals or thin films,[5] an applied current will influence the insulating clusters, establish a percolative conductive path, and thus dramatically affect the resistivity. A key factor is that the newly formed multiphase coexistence with orbital distortion is metastable compared to the as-prepared state, reacting more sensitively to external perturbations. A small current can strongly influence the conductivity, leading to a colossal ER. The non-Ohmic and negative differential resistance behaviors upon applying an electric current are also consistent with that observed in typical systems,[5] in which it was suggested that the electrical-field-induced depinning of the charge in the solid is responsible for the non-Ohmic decrease of resistance. Similar to the spin-valve effect, a large transport current may enforce local ferromagnetic ordering due to strong Hund's coupling. The transport-induced FM order leads to a high conductivity and negative differential resistance. Here, we only present a possible analysis. A clearer picture of this resistive state and the physical nature of its formation and evolution along with the change of microstructure requires more detailed experiments.

Recently, Markovich *et al.* reported electric-field- and current-induced resistive states with memory in a

$La_{0.8}Ca_{0.2}MnO_3$ single crystal.[6,7] It was found that application of current pulses at low temperatures could lead to appearance of states with a high resistance. The established state exhibits metastable characteristics with memory. Sometimes it may even spontaneously return to its pristine state. Similar to the present observations, application of an ac current can also erase the high-resistance states with memory and make the sample return to its pristine state. It seems that a current-induced state with high resistance is a universal phenomenon at least in $La_{0.8}Ca_{0.2}MnO_3$ systems. When a large current is applied to an inhomogeneous system, the associated electric field in the phase space may be sufficiently high to influence the crystal fields, inducing an electroelastic effect.[17] After the exciting current is removed, a residual electroelastic effect may remain in the structure of the sample. At this moment when a small ac current was applied, the associated ac electric field may disturb the residual distortion through influencing the crystal field and make the residual distortion gradually become weak; consequently, the sample changes toward its initial state. For the present films, the high resistivity and the non-Ohmic properties significantly decrease but do not completely disappear under ac current treatments. From Fig. 4, we can see that the resistance, after an ac treatment, is insensitive to a small current but still somewhat higher compared to that of the as-prepared state. We think this might be related to some irreversible distortions, which cannot be erased during ac current treatments. The reason might be associated with the strain effect in films or some irreversible process caused by a possible small escape of oxygen due to self-heating. Further investigations are currently under way.

In summary, we have investigated the influence of an electric current with high current density on the transport properties in $La_{0.8}Ca_{0.2}MnO_3$ epitaxial thin films. It is evident that the influence of a current on a coexistent multiphase with different orbital order can be fully controllable by the duration of the current excitation. The appearance of states with high resistance is a natural effect of the multiphase upon application of a large dc current, and not caused by the self-heating effect. It has been verified that there is no change of the structure and lattice parameter upon current treatments by using the micrometer XRD technique, indicating that the escape of oxygen caused by the self-heating effect is very little if any. The induced states with high resistance exhibit metastable characteristics. A weak current can remarkably influence the conductivity, showing a colossal electroresistance effect in a very wide temperature range, even to room temperature. Application of a small ac current can destabilize the induced orbital distortion and make the sample change toward its initial state.

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