Current-induced asymmetric *I-V* behavior of $La_{0.82}Ca_{0.18}MnO_3$ thin films and its tunability

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Asymmetric *I-V* behaviors induced by large currents in $La_{0.82}Ca_{0.18}MnO_3$ (LCMO) films are studied. The contribution of LCMO to the asymmetric *I-V* behaviors is demonstrated by eliminating the contribution of the LCMO/electrode interface. The asymmetric *I-V* behaviors of LCMO can be tuned by the negative voltage pulse and positive current excitations between two resistive states. A band bending model based on the local oxygen electromigration at the grain boundaries of LCMO is proposed to account for the results. This work is helpful for understanding the mechanism of the current effect on manganites and also its applications. © *2007 American Institute of Physics*.
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The hole-doped manganites $R_{1-x}A_xMnO_3$ show a variety of electronic phases, which are competing and energetically close to each other, and have attracted wide attention due to their rich physics and potential applications.[1] It has been shown that external electric current/field disturbance can cause remarkable resistance change in manganites,[2–5] namely, the colossal electroresistance, which is important for both the understanding of manganite physics and applications. Recently, there were also some reports on the distinct asymmetric transport properties of $La_{1-x}Ca_xMnO_3$ (LCMO) thin films induced by large electric currents.[6–8] Hu *et al.* studied the remarkable asymmetric *I-V* behavior in $La_{0.8}Ca_{0.2}MnO_3$ thin films,[6] and they believed that the electric field associated with the large current may strongly impact the orbital order of the phases in LCMO, leading to the asymmetric *I-V* behavior. Sun *et al.* reported similar results in $La_{0.7}Ca_{0.3}MnO_3$ thin film,[7] and they suggested that the asymmetry of the two-lead *I-V* curves cannot be attributed to $La_{0.7}Ca_{0.3}MnO_3$ film alone, and the different Schottky barriers at the two Ag–$La_{0.7}Ca_{0.3}MnO_3$ interfaces should also be considered.[7]

In order to understand the mechanism of the current-induced asymmetric *I-V* behavior, it is essential to know where it comes from, i.e., from the film, or the film/electrode interface, or both. A careful design for the measurement is needed. The two-lead method used by Sun *et al.* cannot eliminate the effect of electrode contact.[7] Hu *et al.* adopted the four-probe method with the four electrodes in line. For this configuration, as recently pointed out by Xie *et al.*,[8] processing current may pass through the conductive inner electrodes via the underlying manganite film, which is expected to introduce some contribution to the current effect. Xie *et al.* claimed that they clarified the origin of the asymmetric transports of $La_{0.8}Ca_{0.2}MnO_3$ by rearranging the electrodes after current processing.[8] Two-lead method was used in their work, which cannot eliminate the contribution from the interface of Ag electrode/$La_{0.8}Ca_{0.2}MnO_3$. There are some evidences that Schottky barrier or degraded interface can be formed at the interface of Ag/LCMO.[9] Large current processing is also expected to lead to some changes at the interface of Ag/manganite and the surface of LCMO film. Rearrangement of electrodes cannot eliminate the contribution of Ag electrodes/LCMO surface because of their adopted two-lead method.[8] Therefore, further work is needed to clarify the origin of the current-induced asymmetric *I-V* behavior in $La_{1-x}Ca_xMnO_3$ thin films, which is essential for understanding its mechanism.

In this letter, we report a special design of the electrode configuration with H shaped patterning of LCMO epitaxial thin films in the electrical measurement. Using this configuration combined with the four-probe method, we demonstrated the contribution of LCMO to the current-induced asymmetric *I-V* behavior. We also found that the current-induced state of the films can be tuned by a dc disturbance. A band bending model was proposed to account for the results.

LCMO thin films were grown on (100) $SrTiO_3$ by the pulsed laser deposition technique. The thickness of the films is about 100 nm. The oxygen pressure was 100 Pa and the substrate temperature was 750 °C during deposition. A post-annealing at 770 °C for 90 min was made in flowing oxygen to avoid oxygen deficiency. The x-ray diffraction analysis shows good epitaxy of the films (right-bottom inset of Fig. 1). For the electrical measurements, LCMO films were patterned into H shaped samples with 50 μm width. Four separate Ag electrodes were deposited by the magnetron sputtering and the layout of the sample is shown in Fig. 1.

The as-annealed LCMO film has a T_p of about 267 K, as shown in the upper inset of Fig. 1, much higher than that of the bulk material (~190 K), which is consistent with that reported in the literature.[10] The isothermal *I-V* curve of the pristine state reveals linear behavior. In order to clarify the contribution of the current effect, we first applied a large processing current between electrodes 1 and 3, and then measured the *I-V* curves using the four-probe method. The *I-V* curve starts to show asymmetric behavior when the processing current exceeded 13 mA. The optimized condition was 14.5 mA (current density $\sim 2.8 \times 10^5$ A cm^{-2}) for 8 min. The *I-V* asymmetric behavior measured by the four-probe method was shown in Fig. 1. No hysteresis in the *I-V* curves was found. With the H shaped configuration of the sample and the four-probe method, the contribution of Ag/LCMO interfaces can be eliminated, and thus the measured *I-V* behaviors only come from the film itself. Therefore, the current-

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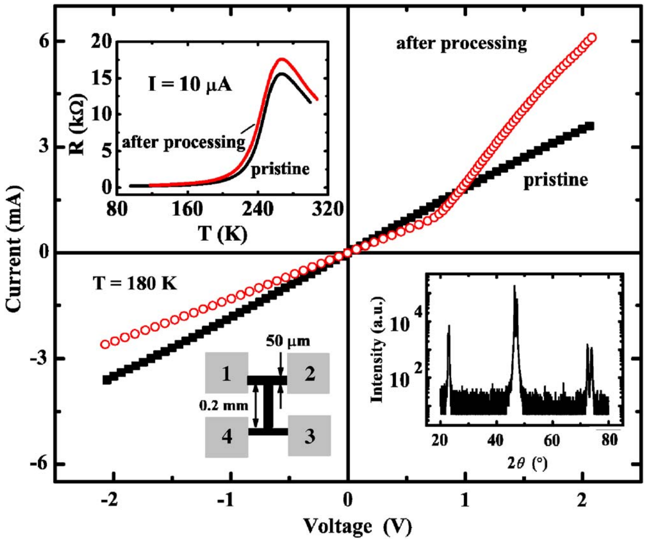

FIG. 1. (Color online) Comparison of *I-V* curves of LCMO before and after 14.5 mA current processing. The insets show the temperature dependent resistance before and after the processing (left-top), the schematic layout of our samples (left-bottom), and the phase examination of XRD pattern of LCMO/STO (right-bottom).

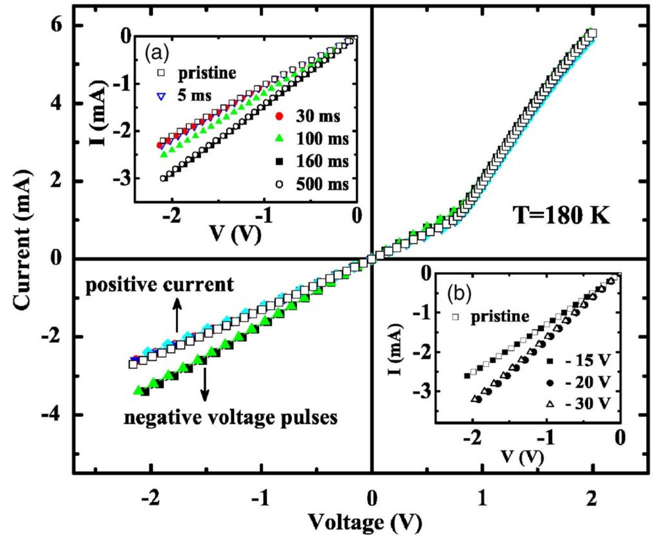

FIG. 3. (Color online) Alternant tuning of *I-V* curves under negative voltage pulse and positive constant current excitations in three different cycles. The open symbol stands for the *I-V* curve of the as-induced state at 180 K. Inset: (a) the effect of duration of the negative voltage pulse on the tuning; (b) the tuning result of the different voltage pulses.

induced asymmetric *I-V* behavior in our sample reflects the intrinsic current effect of the films.

The as-induced asymmetric *I-V* behavior is stable at 180 K. After 4 h holding at 180 K, the results showed no changes. After the current processing, T_p of LCMO is nearly unchanged compared with that of the pristine state, but its resistivity becomes larger as shown in the left-top inset of Fig. 1. Figure 2 displays the *I-V* curves measured at different temperatures after the current processing. The current corresponding to the same voltage increases and the resistance reduces with decreasing temperature, which is contrary to the results in Ref. 6. The values of diffusion voltage of the samples are between 0.5 and 0.9 V, and increase with decreasing temperature. *I-V* curve at 180 K is shown in the right-bottom inset of Fig. 2, which consists of two nearly linear segments, below and above the critical voltage (V_C). Similar behavior was reported in Ref. 7. Accordingly, the

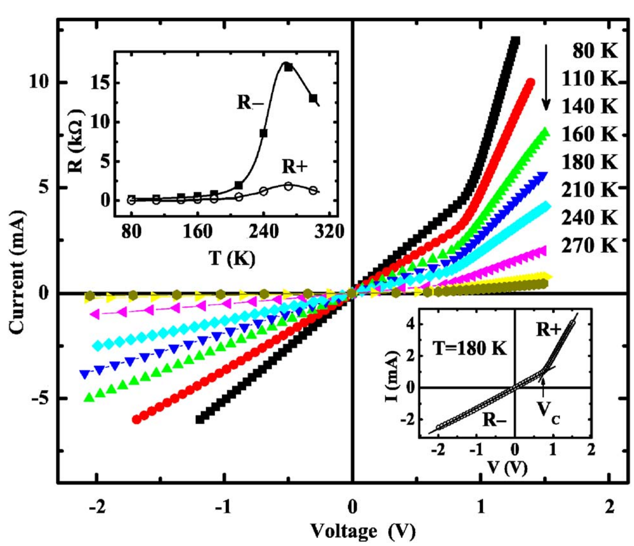

FIG. 2. (Color online) *I-V* curves of LCMO at different temperatures after the current processing. The insets show the detailed characters of the transport behaviors.

film resistance comprises two resistive states and we can get the resistance $R-$ and $R+$ of the two states, respectively. Their temperature dependence is shown in the left-top inset of Fig. 2 and a maximum difference can be seen near T_p.

For the current-induced asymmetric *I-V* behavior, it is interesting to see whether it can be tuned by the electric voltage and current. We applied dc voltage pulses to electrodes 1 and 3 to see the changes of *I-V* curves. At 180 K, positive voltages smaller than 30 V did not affect the asymmetry of the *I-V* curves, which can be understood by considering the high voltage (typically >50 V) at which the asymmetric *I-V* behavior was obtained. In contrast, the effect of the negative voltage excitation is quite different. When the excitation voltage was increased to −20 V, *I-V* curves for $V < V_C$ changed considerably, and the asymmetry was weakened. As shown in Fig. 3, the current corresponding to the same negative voltage is obviously larger than that in the freshly induced state. Further increase of the excitation voltage did not make an obvious difference [see inset (b) of Fig. 3]. These results indicate that negative voltages larger than a threshold value have a comparable tuning effect on the *I-V* curves. We can also change the *I-V* curves back to the original current-induced state by applying a positive constant current of 14.5 mA for 2 min. After this treatment, the *I-V* curves of LCMO in the reverse direction change back and overlap that of the original current-induced state. So an alternant process of negative voltage pulse and positive constant current excitations can modulate the negative *I-V* curves between the two resistive states, and this phenomenon could be repeated very well. In contrast, the *I-V* curves in the forward direction remain nearly unchanged, and the diffusion voltage decreases a little bit with the excitations. The above results have been repeated on several samples. We also studied the effect of duration of the negative voltage pulse by applying a negative voltage pulse to the sample which was in the current-induced state. Negative voltage pulses with 5, 30, 100, 160, and 500 ms durations were applied to the sample, respectively. We found that the negative *I-V* curves were nearly unchanged after the application of a pulse with

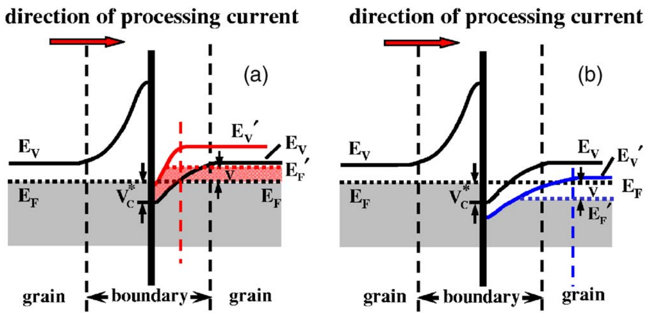

FIG. 4. (Color online) Sketch of the valence band bending at a grain boundary after large current processing. Part of the valence band is shown. Band shift under a positive bias voltage (a) and a negative bias voltage (b).

duration $\leqslant$ 30 ms, while pulses with longer durations can tune the *I*-*V* character more distinctly [see inset (a) of Fig. 3].

The mechanism of the current-induced asymmetric *I*-*V* behavior of manganites is still an open question. Our present work eliminates the interference of the LCMO/electrode interface, so we will focus on LCMO itself. In $La_{0.8}Ca_{0.2}MnO_3$ films, the impact of electric field on the orbital ordering phases has been assumed to be related to the asymmetric *I*-*V* behavior of the sample.[6] Although this scenario is attractive, it is not consistent with the work of Sun *et al.* on $La_{0.7}Ca_{0.3}MnO_3$ thin films[7] because no orbital ordering is reported in $La_{0.7}Ca_{0.3}MnO_3$ films of thickness >70 nm.[11] Moreover, it has been shown that spin, charge, lattice, and orbital degrees of freedoms are strongly coupled in manganites. So if the electric current has strong influence on the orbital ordering in LCMO, some change in the lattice will be expected, which can be shown in the x-ray diffraction (XRD) pattern of the sample. However, no change was observed in the XRD patterns of the sample before and after the electric current processing.[6] Therefore, it is likely that the grain boundaries of LCMO play an important role in the electric current effect. In our experiment, the electric field accompanied by large currents reaches 10^5 V/m, and the local temperature increase due to Joule heating can be 100 K or larger. The simultaneous driving forces from the large electric field and temperature increase may provide enough energy for the electromigration of oxygen at the grain boundaries. In fact, the electromigration of oxygen has been reported in ceramic $BaTiO_3$ even in the grain core region.[12] Electromigration of oxygen can cause the band bending at the grain boundaries of LCMO. The sketch of band bending of LCMO after large current processing is shown in Fig. 4, which can account for the asymmetric *I*-*V* behavior of LCMO. The oxygen vacancy conglomeration at one side of the boundary results in the bending down of the valence band and the top of it can pass the Fermi energy level. That forms an energy barrier for electron tunneling. When a positive bias voltage is applied, the barrier is attenuated, which increases the tunneling current. If the bias voltage reaches V_C^*, the barrier disappears. In this case, the *I*-*V* curve shows linearity and its slope increases (see Fig. 1) because it is determined by the grains and the grain boundaries without band bending effect. When a negative bias voltage is applied, the enhanced barrier decreases the tunneling current. It should be pointed out that the bias voltage is applied on grain boundaries in series. Thus the partial voltage drop V_C^* of each boundary is not large ($V_C = nV_C^*$, n is the number of grain boundaries), and the tunneling current dominates for $V < V_C^*$. This can account for the linear *I*-*V* curves for $V < V_C^*$. The excitation of negative voltage pulses would drive the migratory oxygen return to its original place, which causes the reduction of the band bending. Thus the decrease of resistance for $V < V_C^*$ (positive and negative voltages) is observed. A positive constant current would drive the oxygen to the contrary direction, leading to the enhanced band bending. For $V > V_C^*$, the resistance of LCMO remains unchanged before and after the tuning because it is determined by the grains and the grain boundaries (without band bending effect). Therefore, the modulation of negative *I*-*V* curves between the two resistive states can be comprehended in terms of this band bending model. The effect of duration of the negative voltage pulse on tuning, as shown in the inset (a) of Fig. 3, indicates that the tuning process is much slower than the response of electronic charge transfer which is on a microsecond time scale set by the RC time constant.[13,14] Therefore, this result favors the oxygen electromigration mechanism.

In conclusion, we demonstrated that large current processing can result in the asymmetric *I*-*V* behavior in LCMO film. The *I*-*V* curves can be modulated by the alternant process of negative voltage pulse and positive constant current excitations between two resistive states. A band bending model based on the electromigration of oxygen at the grain boundaries is proposed to account for the results.

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