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Current induced abnormal electroresistance effect observed in epitaxial $La_{0.9}Hf_{0.1}MnO_3$ thin films

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$La_{0.9}Hf_{0.1}MnO_3$ thin films with thickness 100 nm were prepared by using a pulsed laser deposition technique. Transport behaviors were investigated under various applied currents without an applied magnetic field. When the applied current is not too large, the peak value of the resistance gradually decreases with increasing current, demonstrating a normal electroresistance (ER) effect. However, when the current reaches a critical value, a high-resistance state appears at a lower temperature below the Curie temperature. And the appeared resistance peak at low temperature turns out to be extremely sensitive to a weak current. Even a very small current could greatly depress the height of the peak, an abnormal ER effect appears. Maximum resistance ratio ER, defined as $[R(1\,\mu A)-R(100\,\mu A)]/R(100\,\mu A)$, is about 1257% at 50 K. Physics related to the appearance of the novel state and the abnormal ER effect is discussed. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4879318]

I. INTRODUCTION

Doped rare-earth manganite oxides have been extensively studied since the discovery of colossal magnetoresistance (CMR).[1] Due to the strong cross-coupling among charge, spin, orbital, and lattice, such compounds are often sensitive to the external stimuli such as magnetic field, electric field, light, etc.[2–4] For example, Jin *et al.* report that the resistivity of $La_{0.67}Ca_{0.33}MnO_3$ film has a thousandfold change under an external magnetic field.[2] Kiryukhin *et al.* observed an X-ray induced transition in $Pr_{0.7}Ca_{0.3}MnO_3$ from the insulating antiferromagnetic state to the metallic ferromagnetic (FM) state.[3] And Mathews *et al.* fabricated a field effect device with $La_{0.7}Ca_{0.3}MnO_3$ film as the semiconductor channel layer and $PbZr_{0.2}Ti_{0.8}O_3$ as the ferroelectric gate electrode. They found the channel conductance has a 300% modulation at different poling voltages.[4] Recent studies suggest that spatial inhomogeneity with multiphase coexistence in these systems plays a key role.[5] Various coexistent phases compete with each other and come to a new equilibrium state. Such a subtle balance is always unstable and behaves extremely sensitively to external perturbations, which increases the technological potentials for these kinds of materials. In fact, in addition to magnetic field, electric field, and light illumination, electric current has also produced dramatic effects on transport properties of manganites. It has been observed that an electric current could trigger the transformation of the electrically insulating charge-ordered state to a ferromagnetic metallic state.[6] Current-induced switching of resistive states in the $La_{0.8}Ca_{0.2}MnO_3$ films has also been reported.[7] Furthermore, some groups reported on the influence of electric current on the transport properties of thin films of mixed-valence manganites.[8–14] Their studies revealed that a current with a high density can significantly affect the balance of multiphase coexistence and cause a series of changes in transport properties. For example, Gao and Hu have ever reported an abnormal state and an anisotropic conduction in $La_{0.8}Ca_{0.2}MnO_3$, $La_{0.7}Ca_{0.3}MnO_3$, and $La_{0.9}Ba_{0.1}MnO_3$.[8–11] A typical colossal electroresistance (ER) for $La_{0.8}Ca_{0.2}MnO_3$ reaches 1175% at 50 K for a current changing from 0.7 to 11 μA.[10] Xie examined several systems including $La_{1-x}Ca_xMnO_3$ (x = 0.2, x = 0.33), $La_{0.67}Sr_{0.33}MnO_3$, $Pr_{0.7}Ca_{0.3}MnO_3$, and $La_{0.35}Pr_{0.32}Ca_{0.33}MnO_3$ and found the anisotropic conduction is a universal phenomenon for manganites.[11] Although these manganites exhibit similar abnormal states under the excitation of a current with high current-density, they still present some distinct inconsistency. And the generation mechanism of the abnormal state and physical picture of the large current effect on such complicated systems are still open questions. Therefore, further work is essential to understand the mechanism.

Perovskite $La_{0.9}Hf_{0.1}MnO_3$ (LHMO) is a tetravalent cation doped manganite in which the La^{3+} ions of the parent compound $LaMnO_3$ are substituted by tetra-valence Hf. The transport and magnetic properties of low doped LHMO have been studied in detail.[15,16] The results from X-ray photoelectron spectroscopy (XPS) indicate that the LHMO film is in a mixed valence state of Mn^{2+} and Mn^{3+}, implying an electron-doped conduction mechanism. It makes LHMO to be a potential candidate for fabricating pn junctions based on manganite oxides. However, studies on the electron-doped manganites have seldom been reported so far. Like other mixed-valence manganites, the LHMO compound shows a similar CMR effect and a current-induced ER effect. Triggered by recent reports on abnormal ER in other hole-doped manganites,[8–14] in this paper, we report an abnormal ER effect in LHMO thin films. It was found that the resistance gradually decreases when the applied current is not too large. However, when the current reaches a critical value, a high-resistance state appears at a lower temperature

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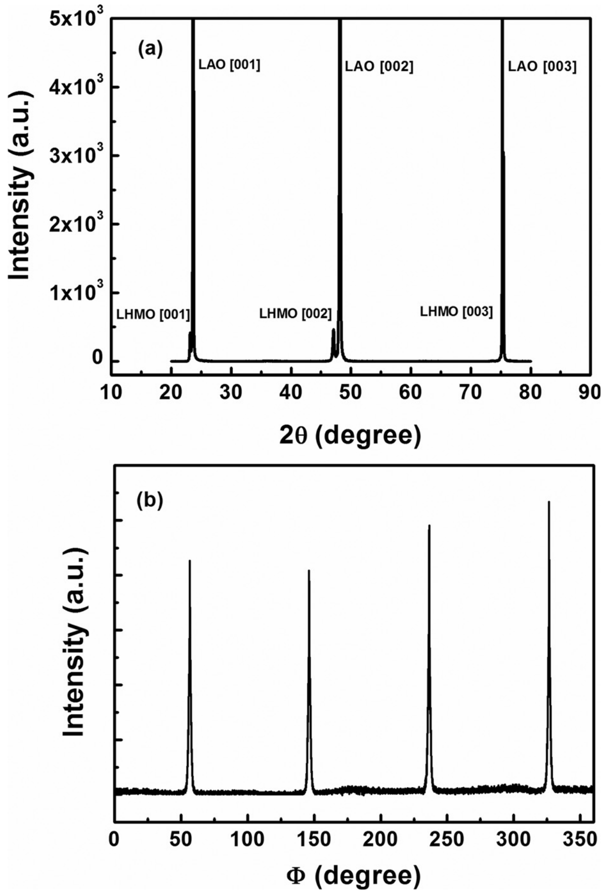

FIG. 1. Typical X-ray diffraction spectra for $La_{0.9}Hf_{0.1}MnO_3$ thin film: (a) θ-2θ scan and (b) Φ scan.

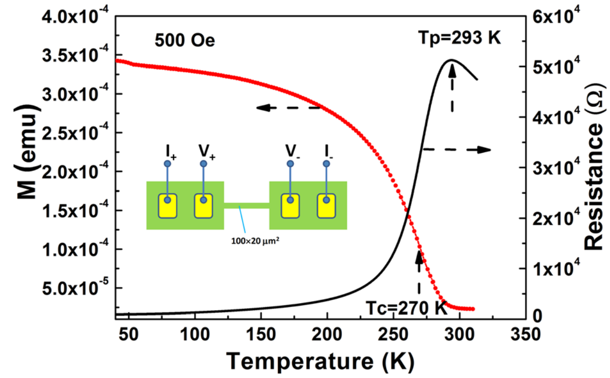

FIG. 2. Temperature dependence of dc magnetization measured under 500 Oe and resistance at zero field for a $La_{0.9}Hf_{0.1}MnO_3$ thin film. Inset is a schematic diagram for resistance measurements.

below the Curie temperature. And the appeared resistance peak at low temperature turns out to be extremely sensitive to a weak current. Even a very small current (100 μA) could greatly depress the peak resistivity. Measured maximum resistance ratio ER = [R(1 μA) − R(100 μA)]/R(100 μA) is about 1257% at 50 K.

II. EXPERIMENTS

The $La_{0.9}Hf_{0.1}MnO_3$ thin films were grown on $LaAlO_3$ (001) substrates by pulsed laser deposition technique using a KrF excimer laser. The oxygen atmosphere and the substrate temperature were kept at 60 Pa and 750 °C, respectively. The energy of the laser beam is 360 mJ and the repetition frequency is 3 Hz. The thickness of films was about 250 nm by controlling the deposition time. To avoid oxygen vacancy, the as-grown films were post annealed in air at 900 °C for 1 h. In order to apply a current with a high density, the films were then patterned into a micro-bridge by conventional photolithography technique. The dimension of the micro-bridges is 20 μm × 100 μm (see inset of Fig. 2). Four silver pads were evaporated thermally on the film as electrodes and the current leads were connected to the silver pad using a MEI-907 supersonic wire bonder to obtain good ohmic contacts. Standard four probe method was used to measure temperature dependence of resistance and current-voltage characteristics.

III. RESULTS AND DISCUSSIONS

To characterize the structure of the films, we performed XRD measurement. XRD was performed on the Siemens D5000 X-ray diffractometer with Cu Kα radiation (λ = 1.5405 Å) Fig. 1(a) shows a typical X-ray diffraction spectrum of the LHMO films. Only peaks from (00l) reflection of the $LaAlO_3$ (LAO) substrates and LHMO films are observed in the normal θ-2θ scans. No other peaks from impurity phases such as HfO_2 could be resolved, indicating that the LHMO films are of single phase. The out of plane lattice constant of LHMO was calculated to be 3.857 Å according to the (002) peak. Φ scan of LHMO (111) diffraction peak is shown in Fig. 1(b). Four sharp and discrete peaks, 90° apart, are observed for the film, which reveals the LHMO film is in-plane aligned with the substrate and grown epitaxially.

The temperature dependence of the dc magnetization of LHMO films was investigated as shown in Fig. 2. The magnetization measurement was under a magnetic field of 500 Oe in field-cooling (FC) mode. The sample exhibits a paramagnetic (PM) to FM transition behavior. The Curie temperature Tc, defined as the peak temperature in the curve of dM/dT versus temperature, is 270 K. Fig. 2 also displays a typical resistance-temperature relation of LHMO film without magnetic field measured by the standard four-probe method. Inset is a schematic for electric-transport measurement of samples. LHMO presents a metal-insulator-transition (MIT) behavior at 293 K.

As reported earlier, a giant ER can be induced in various divalent cation-doped $La_{1-x}A_x$ MnO_3 (A = Ca, Ba, etc.) systems by electric currents with a high current density.[8–14,17] The impact of an electric current on the transport of LHMO thin films has been studied as well. Fig. 3 presents a typical temperature dependence of resistance of LHMO film under different currents from 10 μA to 2 mA. With the increase of the applied currents, a striking observation is the significant decrease of the peak resistance (R_p). The observed reduction ratio, i.e., the electroresistance ER = [R_p(10 μA) − R_p(2000 μA)]/R_p(2000 μA), is ~20%.

It is noted that the transition peak shifted to lower temperatures and became wider as currents increased. This is due to the self-heating of the thin film under application of a high current.[18] Due to the Joule heating, the temperature

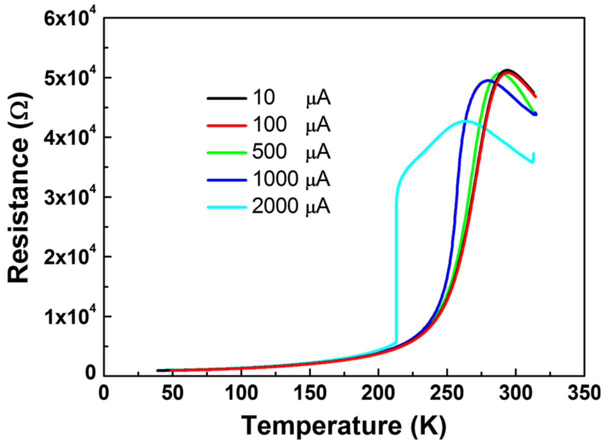

FIG. 3. R-T dependences for $La_{0.9}Hf_{0.1}MnO_3$ thin film upon applying different currents.

difference between the top of the sample and the bottom of the substrate can be estimated according to the formula $\Delta T = Pl/\kappa s$ in the reference, where P is the dissipated power, l is the "height" of the sample through which heat is transferred, κ is the thermal conductivity, and s is the section of the electrical contact. κ is assumed as 0.15 W/mK near 250 K for a crude estimation.[19] Upon an application of a current of 2 mA, ΔT is ~100 K. The serious self-heating caused by the large current could keep the sample continuously at a higher temperature, while the thermometer shows a lower sample-holder temperature. In fact, the thermometer did not follow the rapid temperature change of the film. So the transition peak shifts to the lower temperature with the increased currents.

Fig. 4 presents the $R-T$ curves under a small dc current of $I = 1\,\mu$A after different current excitations. The current excitation was carried out at 200 K. All the $R-T$ curves are measured in a slow cooling process. The cooling rate is ~3 K/min. The state developing with the increase of applied current and excitation time is clearly manifested. When the applied current exceeds a critical value 6 mA, a new high-resistive broad peak appears at low temperature. With increasing current from 6 to 6.2 mA and excitation time from

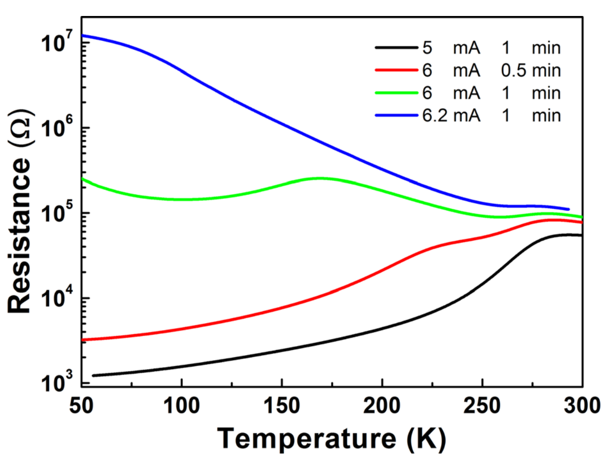

FIG. 4. Temperature dependent resistance of $La_{0.9}Hf_{0.1}MnO_3$ films under a small dc current of 1 μA after excited by different large currents for a period of time.

30 s to 2 min, the peak resistance increases significantly and shifts continuously to the lower temperature. This phenomenon may be attributed to the percolative conduction in the phase-separated state in LHMO. In the CMR manganite family, it is widely believed that the double-exchange ferromagnetic metal phase and the charge–orbital ordered antiferromagnetic phase with similar energy scale compete with each other. The quenched disorder or strain effects arising from the inherent chemical randomness or the impurity doping may cause the phase separation phenomenon on static to dynamic time-scales and on glass-like nano to grain-like micron length-scales. Upon stimulation by external stimuli, not only by magnetic field but also by irradiation with light, x-rays, and electron-beams as well as current injection, the manganites could show versatile unconventional electronic-lattice structural changes or insulator–metal transitions.[20] One possible role of applied current is to locally heat the percolative paths rather than the entire sample. Under the large current excitation, the strong joule heat generated by current might drive the metallic phase into insulating phase. As the current is turned off, the sample is cooled down quickly. The insulating phases have been frozen and been kept at low temperature. Since there exists very strong and unconventional electron–lattice coupling mainly due to the Jahn–Teller (JT) effect in manganite system, the large current stimulation might also have some profound effect to drive the present film into insulating state.[21] When the applied current is high and the excitation time is long enough, the insulating areas become wider and wider and eventually are linked with each other. And at the same time the metallic phases are isolated. The sample becomes a highly resistive state. Actually, the developing of R-T curve shown in Fig. 4 reflects the modulation process of the large current on the coexistence. Shoulder of resistance appeared at lower temperature after excitation of 6 mA may indicate a start of the perturbation of the coexistent multiphase. Continuously increasing the excitation current and processing time to a critical value may substantially increase the relative volume of insulating phases. An abundance of insulating domains would lead to poor connection of minority FM domains and enhance the residual resistivity remarkably. As ultimately all the percolative conduction paths are closed, the sample becomes a high resistive state.[17]

A most intriguing feature is that such an induced high resistive state is exceedingly sensitive to the weak current. Fig. 5(a) displays the R–T curves measured on cooling utilizing small dc currents, which are replotted in semi-log scale in the inset of Figure 5(a). One can find that a rather weak current can strongly depress the magnitude of the resistance peak. And it is noteworthy that a current of 50 μA could cause an insulator-metal (I-M) transition and the transition becomes clearer when the current is 100 μA. The similar results have been reported in charge-ordered $Nd_{0.5}Ca_{0.5}MnO_3$ films by Rao *et al*. They ascribed the I-M transition induced by small currents to the depinning of the randomly pinned charge solid.[6] From Fig. 5(b), the relative reduction of the ER reaches ~1257% upon current changing from 1 to 100 μA. The ER effect of the novel state is extremely large compared to the normal ER mentioned above. We call it an

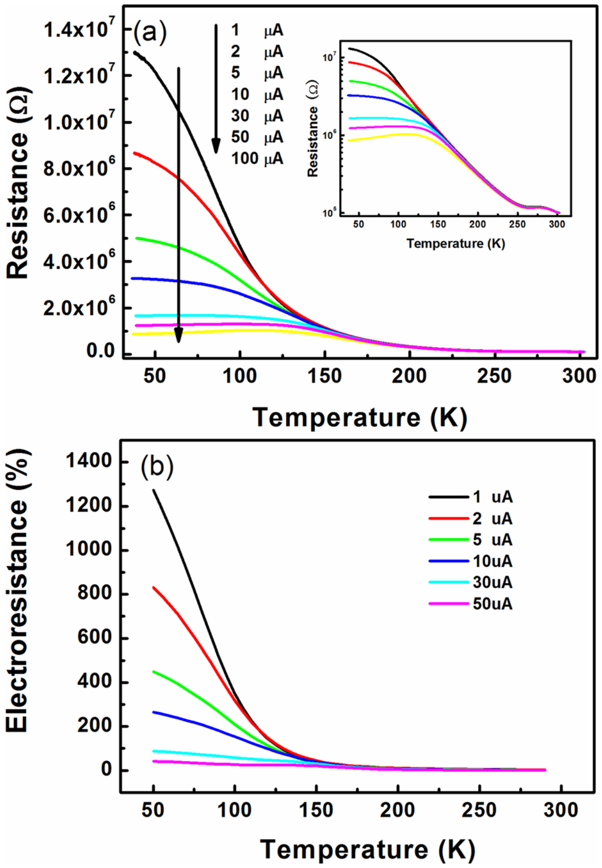

FIG. 5. R-T dependences for $La_{0.9}Hf_{0.1}MnO_3$ film with different small currents after processed by a large current of 6.2 mA with duration of 1 min. Inset is a figure replotted in semi-log scale.

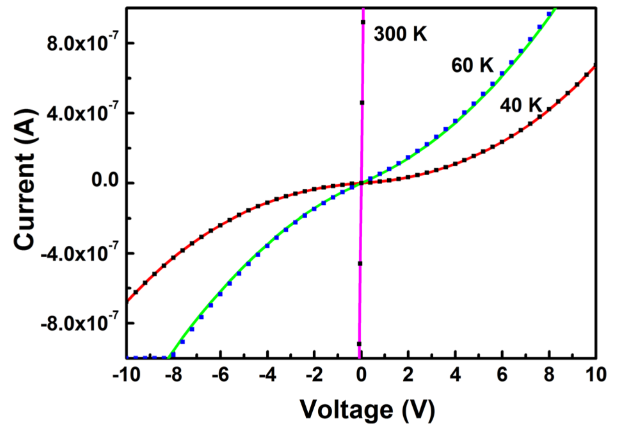

FIG. 6. I–V characteristics measured at 40 K, 60 K, and 300 K for current-processed $La_{0.9}Hf_{0.1}MnO_3$ film.

abnormal ER effect. The modulation process of current on resistance is reversible. The novel state with high resistance induced by an electric current seems a universal phenomenon in manganites with electronic phase separation. Similar behaviors were observed not only in films but also in single crystals of mixed-valent manganites. The appearance of the novel state is a natural effect of the coexistent multiphase upon an application of a large dc current.

The reduction of the peak resistance may be understood qualitatively from phase separation scenario. One might consider a state of equilibrium in which metallic ferromagnetic clusters were embedded in a paramagnetic insulating matrix. An applied electric field or current perturbs the coexistence of different phases and sets up filamentary currents across the insulating region. Current flowing through a space-limited path might induce an intense local magnetic field. According to Markovich's analysis,[22] a 0.3 mA current has an equivalent effect on resistance as 1.5–2 T magnetic fields at low temperature. In this scenario, we can understand the decrease of peak resistance and the high-temperature shift of Tp with the currents. This explanation could be corroborated by the work of Gao and Xie.[12,23] In their work, the resistivity of the abnormal state was reduced upon an application of a magnetic field. Another possible origin of local field is coming from the spin polarization effect. In manganites, the electron (spin, charge, and orbital) and lattice degrees of freedoms are all activated. The applied current could induce the spin polarons to align with each other. This effect enhances the local field. The local magnetic field at the lattice sites will improve the spin alignment on Mn sites and enhance the current effect in the vicinity of the region. It is intriguing that the freshly formed metastable states are still robust. All their transport properties persist even exposing the sample in air at room temperature for a few weeks.

Fig. 6 shows I–V relations of the samples measured at 40 K, 60 K, and 300 K. To diminish the influence of current, the current sweep was limited to $\pm 1\ \mu$A. The solid lines are for the first measurement. After several days, the experiment was repeated, with dotted data shown in the figure. It is easy to see the data has an excellent reversibility. As shown in Fig. 6, the current-voltage exhibits a non-ohmic behavior and this feature is stronger at lower temperature and becomes gradually weak with high temperature. Nonlinear I–V curve appears only at lower temperature, which is different from the previous results reported in $La_{1-x}Ca_xMnO_3$ (x = 0.2, 0.33) films.[8] Sawa suggested that there was a Schottky barrier at the interface of the metallic electrode and insulating sample.[24] However, it is not true for our sample, because the I–V measurement from I+(I−) port to V+(V−) port was linear. Nonlinear I–V curves induced by large current have been reported by several groups.[8,9,12–14] Sun and Zhao proposed that electromigration of oxygen at the grain boundaries determined the nonlinear I–V curve.[12–14] Although the picture is attractive, it is not consistent with our work because the directional migration of oxygen seems to result in an asymmetric I–V curve. In our experiment, the I–V curve is symmetric. In the phase-separated scenario, metallic ferromagnetic clusters were embedded in a paramagnetic insulating matrix. We can imagine a barrier could be introduced at the interface between insulating and metallic domains, like the depletion region in the *p-n* junction or Schottky junction. Metallic and insulating domains are distributed alternatively, forming a multijunction cascaded in series. That is the reason why a nonlinear and symmetrical I–V curve appears at low temperature.

IV. CONCLUSION

We have investigated the impact of applied current on the transport properties in $La_{0.9}Hf_{0.1}MnO_3$ thin films. A novel state with high resistivity can be introduced by a large dc current. The novel state behaves metastable characteristics. A small current could make the resistance reduce remarkably. The observed ER reaches $\sim$1257% at 50 K for a measurement current changing from 1 to 100 μA. The enormous modulation of small current on the coexistent multiphase plays a key role. The extremely high sensitivity of the resistivity to feeble currents would be of great significance for both basic research and technological applications.

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