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Effect of bias current on the resisitivity and photoconductivity of oxygen-deficient $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films

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The influence of bias current on resistivity and photoconductivity in oxygen-deficient $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films has been investigated. There exists a giant resistance drop induced by dc electrical currents alone especially near the temperature of resistance peak (T_P). Moreover, the photoconductivity emerges only when the current exceeds a threshold and this effect is quite different from magnetoresistance induced by magnetic fields. It is found that the magnitude of photoconductivity increases with increasing of bias current and the threshold current increases with decreasing temperatures and increasing magnetic fields. The magnitude of photoconductivity achieves 10.2% at temperature of 100 K with light density of 4.3 mW/cm^2 and current of 1 mA. The current-assisted electroresistance and photoconductivity are discussed based on the delocalization of localized state by light illumination and bias current. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2803741]

I. INTRODUCTION

Many complex transition metal oxides, including cuprates and manganites, are strongly correlated electron systems close to a metal-insulator transition. Consequently, small changes in the carrier density may produce large changes in the resistivity. The salient feature of these systems, however, is the strong coupling between charge, spin, and orbital degrees of freedom, which is at the foundation of a rich set of coexisting phases with similar ground state energies. Small external perturbations may shift this delicate balance between different phases and may induce dramatic changes in the physical properties. Recent interests of research have been attracted to the influence of electric field or the electric current on the colossal magnetoresistance materials for their potential applications.[1,2] Studies on the effect of the electric field in perovskite manganites included colossal electroresistance (ER) and strong current-induced abrupt resistivity jumps. Many experiments performed on charge-ordered $Pr_{1-x}Ca_xMnO_3$ samples involve current injection into highly conducting filamentary paths. Very recently, Gao *et al.* found that electric current can suppress resistance and shift the temperature of the resistance peaks (T_P) of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.85}Ba_{0.15}MnO_3$ thin films dramatically[3] and Zhao *et al.* found a large ER in $La_{0.67}Ca_{0.33}MnO_3$ film without T_P shift.[4]

As another kind of perturbation, light illumination of manganite oxides provides a convenient way to induce new properties through modifications of the carrier density and changes in this interplay between different phases. Recently, Takubo *et al.* have observed a persistent phase transformation of $Pr_{0.55}(Ca_{1-y}Sr_y)_{0.45}MnO_3$ thin films into a low temperature phase induced by pulsed laser without any assisting electric field.[5] Moreover, Dai *et al.* have also observed that the resistivity of $(La_{0.3}Nd_{0.7})_{2/3}Ca_{1/3}MnO_3$ films still kept decreasing by about 4% after shutting off the laser and stopping the electrical transport measurement for 3 h.[6] Otherwise, metal-insulator transition triggered by the photocarrier injection is not permanent in a single crystal $Pr_{0.7}Ca_{0.3}MnO_3$, in the sense that the sample reverts to an insulator after removal of the applied electric field.[7,8] However, the relationship between the photoconductivity and applied electric current (field) in the manganese oxides, which is very important in realizing the useful application of ER and photoconductivity in these compounds in the future, is not very clear until now. In this paper, we perform studies on the effect of the electric current on the resistivity and photoconductivity in an oxygen-deficient $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ (LSMO) thin film. The results show that there exists a giant resistance drop induced by dc electrical currents alone especially near the T_P and the photoconductivity emerges only when the applied current exceeds a threshold current (I_{th}).

II. EXPERIMENTS

LSMO films used in this experiment were grown on heated Si (001) wafers without prechemical treatment by the off-axis dc-magnetron sputtering technique with the substrate temperature of 750 °C. The films were ~300 nm in thickness measured by field emission scanning electron microscope. The structure and phase purity of the film were checked by means of x-ray diffraction using Cu $K\alpha$ radiation at room temperature. The electrical transport properties were measured in the temperature range of 10–300 K using a closed-cycle He refrigerator with optical windows. For the photoconductivity effect measurement, the sample was mounted in a vacuum room which was sealed by a double quartz glass window, a He–Ne laser of the wavelength λ =632.8 nm with variable power density was used to illuminate on LSMO film surface perpendicularly through the window. Simultaneously, the magnetic fields in the range of

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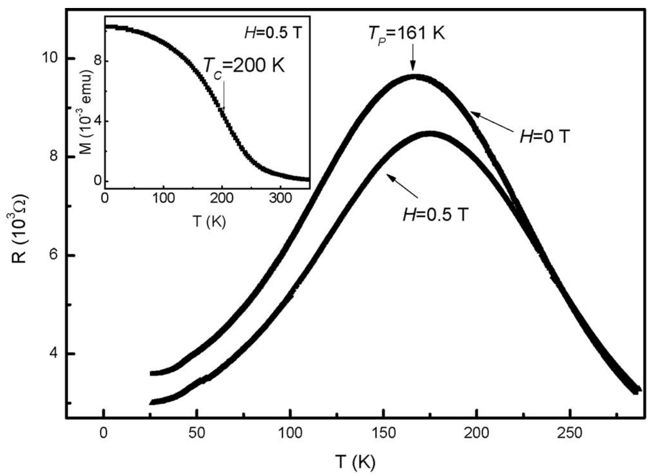

FIG. 1. Typical temperature dependence of electrical resistance $R(T)$ at various magnetic fields H (H//film plane) of LSMO film. The inset shows the temperature dependence of magnetization $M(T)$ of the LSMO film taken at $H=0.5$ T (H//film plane) under ZFC mode.

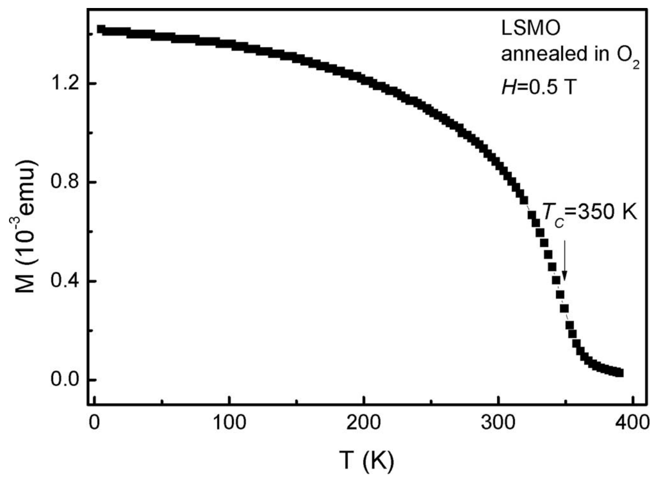

FIG. 2. The temperature dependence of magnetization $M(T)$ of the annealed $La_{2/3}Sr_{1/3}MnO_3$ film taken at $H=0.5$ T (H//film plane) under ZFC mode.

0–1 T are supplied by a water-cooled magnet. A schematic illustration for the current and voltage contact configuration with respect to the illuminated region is shown in Fig. 4. The magnetization of the sample was measured on a Quantum Design superconducting quantum interference device magnetic property measurement system ($1.9\ \text{K} \leqslant T \leqslant 400$ K, $0\ \text{T} \leqslant H \leqslant 5$ T) and the Curie temperature (T_C) of LSMO films is located at 200 K (not shown here).

III. RESULTS AND DISCUSSION

The temperature dependence of resistivities at zero field and fields of 0.5 T with dc of 0.1 mA are shown in Fig. 1. The static field was applied parallel to the film plane. The metal-insulator transition at $T_P=161$ K is observed. In the inset of Fig. 1, the zero-field cooled (ZFC) temperature dependence of magnetization $M(T)$ is shown for the LSMO film. Measurements were performed with a field of 0.5 T applied within the plane of the films. The Curie temperature T_C of the LSMO films (defined as the one corresponding to the peak of dM/dT in the M vs T curves) is about 200 K, which is much smaller than that of oxygen stoichiometric film ($T_C \sim 350$ K). In order to find the reason for the decreasing of T_C of LSMO films, the LSMO film has been annealed for 40 min in flowing oxygen at $T=850$ °C. The magnetization of annealed sample was measured in the same way and the results are shown in Fig. 2. It is found that the T_C of the annealed $La_{2/3}Sr_{1/3}MnO_3$ films is about 350 K, which implies that decreasing of T_C in oxygen-deficient LSMO films is associated with oxygen deficiency, which is in agreement with the literature.[8,9] Moreover, the oxygen deficiency δ is about 0.13, gaining from previous literature.[9]

Figure 3(a) shows the temperature dependence of resistance of LSMO under different dc's. There exists a giant drop of resistance of LSMO film with increasing of applied electric current. Moreover, the temperature T_P where metal-insulator transition occurs does not move within the whole measurement current range. Figure 3(b) describes the temperature dependence of ER under different currents. The ER, defined as $[R(I)-R(0.01\ \text{mA})]/R(0.01\ \text{mA})$, is negative because the current reduces the resistance. It is also noted that ER is maximum at T_P and reaches −39.3% with $T=160$ K and $I=0.25$ mA. ER becomes very small at low temperatures. The inset of Fig. 3(a) is the variation of the peak resistance R_P with dc density. It shows a nonlinear behavior and can be fitted exponentially by $R_P=8736.4 \times \exp(-J/4.28)+10\,239.8$; the unit of J is $10^3 A/\text{cm}^2$. Such an exponential decreasing of R_P with current is consistent with the results in Ref. 4. It should also be pointed out that the value of the resistance comes back up sharply again when the current is reduced, indicating that the effect is reversible.

A difficult problem which one unavoidably faces in the process of investigating the effect of electric current/field on

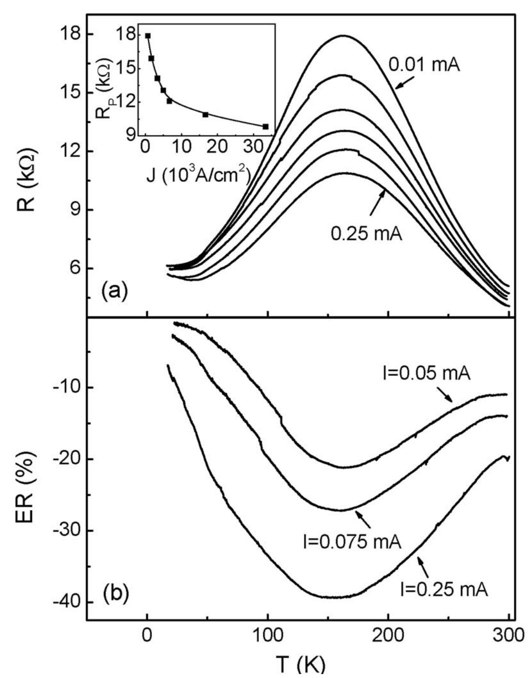

FIG. 3. (a) Temperature dependence of resistance for LSMO film under different dc's. From top to bottom, $I=0.01$, 0.025, 0.05, 0.075, 0.1, and 0.25 mA, respectively. The inset is the variation of the peak resistance as a function of dc density. (b) Temperature dependence of ER $[R(I) - R(0.01\ \text{mA})]/R(0.01\ \text{mA})$ for LSMO film under different dc's.

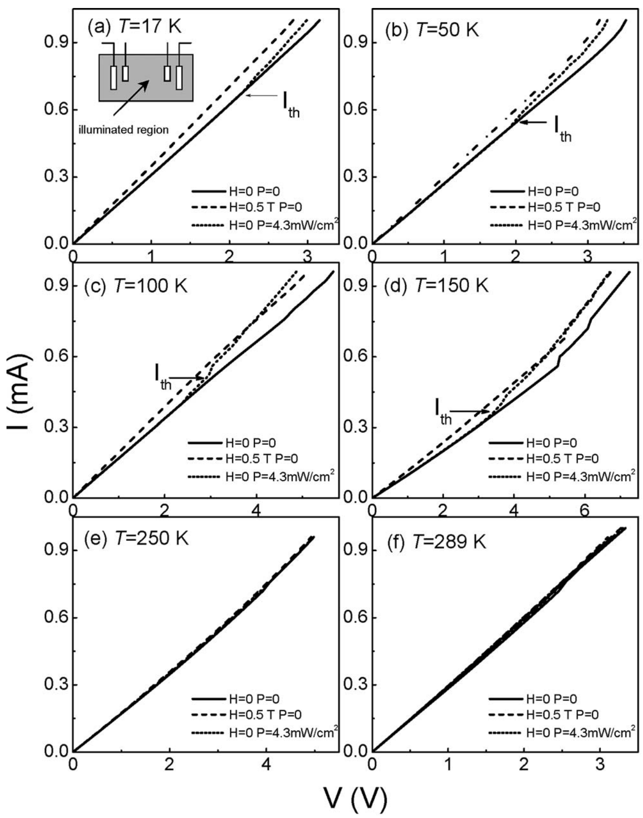

FIG. 4. *I-V* characteristics at different temperatures of oxygen-deficient LSMO films by tuning bias currents. The inset shows experimental current and voltage contact configuration with respect to the illuminated region.

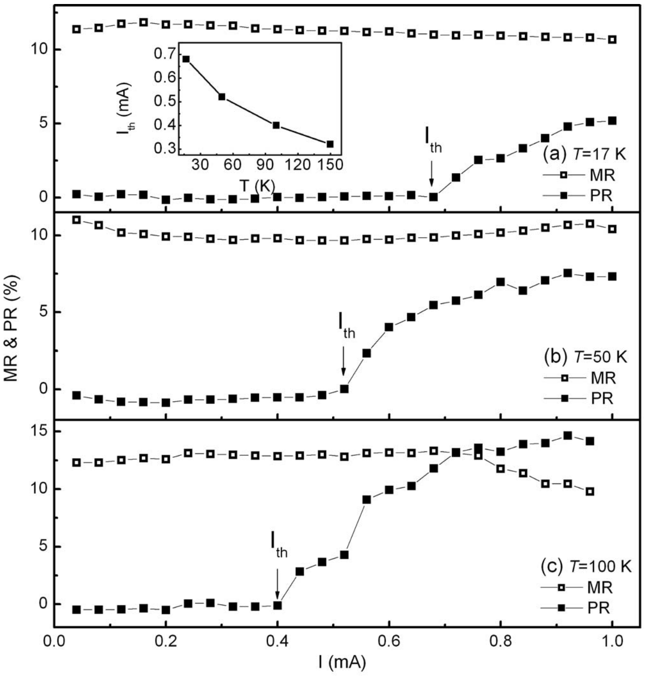

FIG. 5. MR (defined as $[R(0)-R(H)]/R(0)$) for $P=0$, $H=0.5$ T, and photo-induced resistance (PR) (defined as $[R(0)-R(L)]/R(0)$) for $P=4.3$ mW/cm^2, $H=0$ as functions of applied current at temperatures of (a) 17, (b) 50, and (c) 100 K. The inset shows the temperature dependence of I_{th}.

resistance is Joule heating. If the heating effect is severe because of poor heat diffusion, T_P of LSMO film would shift to lower temperatures as mentioned in Ref. 3, in which the heating problem hinders the visibility of the intrinsic current effect. As for our results, Fig. 3(a) clearly shows that T_P remains unchanged with increasing the electric current and the peak resistance drops remarkably. The insensitivity of T_P to current differs from the dependence of T_P on magnetic field as the magnetic field shifts T_P to higher temperatures.[10] The value of ER is comparable to magnetoresistance (MR) induced by a strong magnetic field of several Tesla.[11]

Recently, Cauro *et al.* have reported the photoconductivity in oxygen-deficient LSMO thin films and they found that the photoconductivity increases with oxygen deficiency. They discussed the photoinduced effect based on the collective light-induced magnetism.[12] In our previous work, the photoconductivity was also observed in this LSMO film at low temperatures.[13] It is well known that physical properties of manganites can be tuned by external disturbance due to the breaking balance of various interactions in the material. As mentioned above, the external electric-current-induced ER was also found in the LSMO film. So, it should be of significance to test whether the observed photoconductivity can be influenced by the electric current. To test whether the photoconductivity of LSMO film can be influenced by applied electric current, the current versus voltage (*I-V*) with and without light illumination and magnetic field, respectively, of the oxygen-deficient LSMO films are measured by tuning the applied current, and the typical results are presented in Fig. 4. At high temperature (above T_C), as seen in Figs. 4(e) and 4(f), all *I-V* curves in different conditions are close to each other, which indicates that the applied magnetic field and the light illumination hardly affect electrical transport behavior of LSMO films above T_C. As $T<T_C$, the transport of LSMO film behaves in a different way. As seen from Figs. 4(a)–4(d), the *I-V* curves under $H=0$ and 0.5 T are nearly linear. However, the voltage for $H=0.5$ T is smaller than that for $H=0$ T at the same current bias, i.e., behaving as a negative MR which is consistent with results in Fig. 1. An intriguing phenomenon occurs when the laser illumination is applied. It is found that the *I-V* curves for $H=0$ and $P=4.3$ mW/cm^2 are the same as the curves for $H=0$ and $P=0$ under low bias currents. However, as the current bias exceeds a threshold I_{th}, the *I-V* curves for $H=0$ and $P=4.3$ mW/cm^2 deviate from the original orientation and approach the curves for $H=0.5$ T and $P=0$ gradually. That is to say, the photoconductivity effect only appears as $I>I_{\text{th}}$ and $T<T_C$. These results imply that the photoconductivity effect in oxygen-deficient LSMO films has an intimate relation not only with the magnetic state of the sample itself but also with the magnitude of the applied bias current. Further calculation indicates that the MR (defined as $[R(0)-R(H)]/R(0)$ for $P=0$, $H=0.5$ T) ratio almost keeps constant within the whole current range at a fixed temperature. However, the photoinduced resistance (PR) ratio (defined as $[R(0)-R(L)]/R(0)$ for $P=4.3$ mW/cm^2, $H=0$) increases sharply from zero as $I>I_{\text{th}}$. This point can be clearly reflected as in Figs. 5(a)–5(c), in which both the MR (defined as $[R(0)-R(H)]/R(0)$ for $P=0$, $H=0.5$ T) and the PR (defined as $[R(0)-R(L)]/R(0)$ for $P=1$ mW, $H=0$) as functions of applied current are presented at $T=17$, 50, and 100 K, respec-

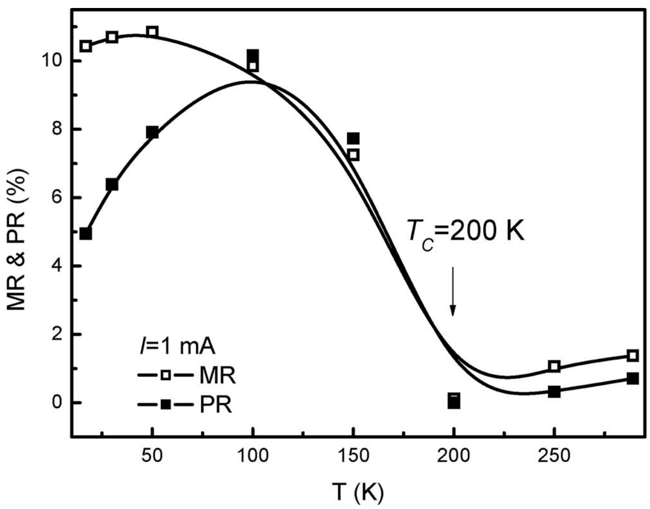

FIG. 6. MR under a field of 0.5 T and PR at a light density of 4.3 mW/cm^2 at $I=1$ mA as functions of temperature.

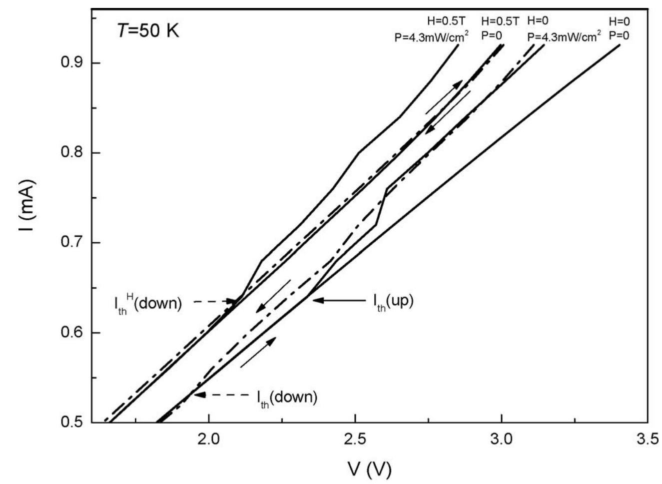

FIG. 7. I-V characteristics of the LSMO films at $T=50$ K.

tively. It shows clearly that the PR ratio increases sharply from zero as $I > I_{th}$ and increases with increasing of bias current. This switch effect may be of worth in the potential applications of new generation of data storage and sensing devices. The inset of Fig. 5 shows the temperature dependence of I_{th}. It is found that the I_{th} of current-assisted photoconductivity effect increases with decreasing of temperature. It can be understood by considering that the insulator phase in LSMO film becomes more stable as the temperature decreas. Therefore, a larger applied current density is needed to change it into a metastable phase which can be affected by light illumination. Another point worthy of noting in Fig. 4 is that there are some kinks in the I-V curves at the temperature of 150 K, as shown in Fig. 4(d). It is considered as a result of emergence of prominent ER near the T_P as electric current increases, which is consistent with the results of resistance measurement under different electric currents, as shown in Fig. 3.

In order to explore the variation of MR and PR at different temperatures further, MR under the magnetic field of 0.5 T and PR under the light density of 4.3 mW/cm^2 at a selected bias current of 1 mA has been studied, and the results are shown in Fig. 6. It is found that the maximum of MR is 10.8% at $T=50$ K and $H=0.5$ T, and that the PR achieves 10.2% at $T=100$ K with the light density of 4.3 mW/cm^2. One point deserving special attention is that both MR and PR rise sharply as T is lower than T_C of LSMO films ($T_C \sim 200$ K). These results reveal that there exists a close relation between electrical transport and magnetization in oxygen-deficient LSMO films, which is similar to previous reports.[5,7]

As stated above, the I-V curves of LSMO film show discontinuous behavior and the resistance of LSMO film changes from higher resistance state to lower resistance state under the coaction of light illumination and bias current at low temperatures. To further explore this current-assisted photoconductivity effect of LSMO film, the I-V measurements at different conditions were carried out. The typical results at temperature of 50 K are shown in Fig. 7. There are two points worthy of special attention in Fig. 7. The first one is that there exists hysteresis in the I-V curves with light illumination. In both the branch curve of sweeping current up and down, there exists threshold current I_{th} where photoconductivity effect emerges. It is found that the I_{th}(down) when current sweeps down is smaller than I_{th}(up). That is to say, the higher threshold current is necessary for LSMO films to change from higher resistance state to lower resistance state with sweeping current up. As for the current sweeping down, the lower resistance state can keep longer until the current is lower than I_{th}(down). Otherwise, the hysteresis behavior of LSMO films is negligible when the magnetic field is applied alone as shown in Fig. 7. The second one is that only MR exists as $I < I_{th}^H$(down), and photoconductivity presents itself as $I > I_{th}^H$(down) with $H=0.5$ T and $P=4.3$ mW/cm^2. The accumulation of MR and photoconductivity proves that a difference between MR and photoconductivity exists. It is obvious that the I_{th}(down) increases from 0.52 to 0.64 mA as a magnetic field 0.5 T is applied and the magnitude of resistance reduction (MPR) (defined as $[R(0) - R(L,H)]/R(0)$) with $H=0.5$ T and $P=4.3$ mW/cm^2 is smaller than the summation of PR ($H=0$ T, $P=4.3$ mW/cm^2) and MR ($H=0.5$ T, $P=0$ mW/cm^2). For example, the MPR is 14.6% at current bias of 1 mA, which is smaller than the summation of PR (~7.31%) and MR (~10.42%). These results reveal that the effects on conductivity by the magnetic field and the light illumination, respectively, are not independent completely but correlative with each other.

The same light-induced experiments are performed on the stoichiometric $La_{2/3}Sr_{1/3}MnO_3$ films on Si substrate. No current-assisted photoconductivity effect is observed in the whole studied temperature range, implying that the current-assisted photoconductivity effect in oxygen-deficient LSMO films is associated with oxygen vacancies. As discussed in Ref. 12, the oxygen deficiency in LSMO films introduces strong disorder and hence localization. Because the oxygen vacancies cause a large electronic imbalance and local lattice distortion, inhomogeneous electronic and magnetic phase emerges around vacancies. Indeed, there is growing experimental and theoretical evidence that the doped manganites are intrinsically inhomogeneous and that phase separation is common in these materials.[14,15] As thoroughly documented,[16–18] this mixture is usually formed by a ferromagnetic conductive and a highly insulating charge/orbital ordered (CO/OO) phase. Moreover, the oxygen-deficiency-activated CO/OO transition has also been observed in *c*-oriented $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films.[19] It is well known that the inhomogeneous electronic and magnetic phases in manganite films are sensitive to the external stimulation such as the light illumination and bias current. Recently, the photoconductivity effect was found in perovskite manganite thin films of $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ (Ref. 12) and $La_{0.7}Ca_{0.3-x}Ba_xMnO_{3-\delta}$,[20] in which the origin of photoconductivity was suggested to be associated with the oxygen vacancies of the samples. Moreover, a large electroresistance of ~76% at 10^5 V/cm was found in $La_{0.7}Ca_{0.3}MnO$ film.[21] Similarly, Asamitsu *et al.* have found that the switching of resistive states in $Pr_{0.7}Ca_{0.3}MnO_3$ crystal can be achieved not only by a magnetic field but also by an electric current.[22] As for our experiments, the way that the *I-V* curves behave (the discontinuity at lower temperatures under light illumination) strongly suggests that the conduction is percolative and correlated to the phase separation of oxygen-deficienct LSMO films at low temperatures. Below T_C, there are localized and delocalized regions. The localized states can be "dislodged" under the influence of light excitation. The delocalization of such state should immediately lead to the appearance of a metallic state 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. The same analysis can be applied to observed current effect as well and the bias current is helpful for the photon-induced delocalization process. Accompanied with coaction of light illumination and bias current, the LSMO film changes from higher resistance state to lower resistance state at a certain bias current I_{th} with P $=4.3$ mW/cm^2, as shown in Fig. 4. As for effect caused by small magnetic field (~0.5 T), it can be attributed to the suppression of the spin disorder and reduction of the spin-dependent scattering, leading to MR. Therefore, MR is independent of bias current and different from the ER and PR observed.

This bias current dependence of photoconductivity is similar to that observed by Miyano *et al.* in $Pr_{0.7}Ca_{0.3}MnO_3$ single crystal.[7] They found that the photoconductivity was very sensitive to the applied voltage and the sample reverts from a metal to an insulator after removing the applied electric field. Moreover, electric field dependent photogenerated carrier separation in organic semiconductor has also been observed.[23] For our work, we only give a possible explanation for the observed current-assisted photoconductivity in LSMO film. A comprehensive understanding of the present observation requires a full knowledge on the band structure of the oxygen-deficient LSMO film.

In summary, we have studied the influence of dc bias on electrical conductivity and photoconductivity in the oxygen-deficient LSMO thin film. There exists a giant resistance drop induced by dc electrical currents alone especially near the T_P in LSMO film. Moreover, it is found that the photoconductivity can emerge only as applied current $I > I_{th}$. The magnitude of photoconductivity achieves 10.2% at $T = 100$ K and $I = 1$ mA with light density of 4.3 mW/cm^2. It is also found that I_{th} increases with decreasing temperatures and increasing magnetic fields. The giant electroresistance and current-assisted photoconductivity are suggested to be related to the delocalization effect of localized states by coaction of light illumination and bias current.

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