Unusual resistive switching induced by voltage in La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films

Zhong-tang Xu · Kui-juan Jin · Can Wang · Hui-bin Lu · Cong Wang · Le Wang · Guo-zhen Yang

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Abstract The hysteretic and reversible resistive-switching effect was observed in La$_{0.7}$Sr$_{0.3}$MnO$_3$ films at room temperature. The resistive switching was found to be most obvious in films fabricated at 30 Pa oxygen pressure, and more distinct in films fabricated on SrTiO$_3$ substrates than those fabricated on LaAlO$_3$ substrates. Moreover, La$_{0.7}$Sr$_{0.3}$MnO$_3$ films fabricated at a certain oxygen pressure with indium electrodes showed double ‘8’ type current-voltage loops. Some of the results are explained by considering the influence of the interface effect, electrodes and oxygen vacancies, but the mechanism of the double ‘8’ type current-voltage loops remains an open question.

1 Introduction

The resistive-switching (RS) effect has been investigated in many transition metal oxide materials, such as TiO$_2$ [1], ZrO$_2$ [2], NiO [3], Cu$_x$O [4, 5] and perovskite-type oxides including SrTiO$_3$(STO) [6], and Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) [7–9], due to its potential applications in high-performance nonvolatile resistance random access memory devices. Those materials exhibit a bistable switching of resistivity between a high resistive state and a low resistive state, through the application of an appropriate voltage. Compared with charge based storage concepts, memory devices based on resistive switching are more promising for future high-density nonvolatile memory for scalability reasons [10]. However, the possible underlying mechanism is still under discussion. Many of the previous works have been focused on manganites under charge ordered state, like PCMO [7–9], which can be switched to a ferromagnetic metal by applying large magnetic or electric fields. Different from PCMO, La$_{0.7}$Sr$_{0.3}$MnO$_3$(LSMO) [11] is generally considered as a double-exchange perovskite compound and exhibits a significant magnetoresistance (MR) effect near the room temperature for its high Curie temperature ($\sim$370 K). This suggests a possibility to combine the resistive-switching and MR properties into one system. Sun et al. have investigated the current effect in LSMO films, which show large MR and RS at varied thicknesses and temperatures [12]. They related this observed RS to lattice distortion. However, the role of metal contacts in these samples goes beyond the lattice distortion. In this paper, we report the systematic investigation of the RS behavior of LSMO thin films with varied fabricating oxygen pressures on various substrates and electrodes.

2 Experiment procedure

LSMO thin films were grown on STO (001) and LaAlO$_3$ (LAO) (001) substrates by a computer-controlled laser molecular-beam epitaxy system with a pulsed XeCl excimer laser beam (\textsim 20 ns, 2 Hz, \textsim 1.5 J/cm$^2$) focused on a sintered ceramic LSMO target [13]. The STO and LAO substrates were carefully cleaned with alcohol, acetone, and deionized water before being moved into the growth chamber. Subsequently, LSMO films with a thickness of 100 nm were deposited at a temperature of 750°C under oxygen pressures of 10, 20, 30, and 40 Pa, respectively, and then in situ annealed under the same conditions for 20 min, before cooling down to room temperature in O$_2$ atmosphere. X-ray diffraction (XRD) with Cu K$_{\alpha}$ radiation was used to determine the
Fig. 1 X-ray diffraction patterns for LSMO thin films with different fabricating oxygen pressures on the substrates of STO and LAO. The inset shows a rocking curve of the LSMO (001) reflection with fabricating oxygen pressure of 30 Pa on STO substrate.

structure properties. Except for (00l) diffraction peaks of LSMO films and substrates, there are no diffraction peaks from impurity or randomly oriented grains. Figure 1(a)–(d) show the X-ray diffraction patterns of the LSMO thin films fabricated in the different oxygen pressure on the substrate of STO and LAO, respectively. The full width at half maximum of the LSMO (001) peak fabricated in the oxygen pressure of 30 Pa on the STO substrate is 0.4°, as shown in the inset of Fig. 1(b), indicating a very high degree of crystalline and c-axis orientation of the films. The resistance-temperature (R–T) relation was measured by Physical Property Measurement System (PPMS). The current–voltage (I–V) curves were measured by a Keithley 2400 source meter and a two-point measurement at 300 K.

3 Results and Discussions

Figure 2 displays the I–V characteristics of LSMO films grown on STO substrates under different oxygen pressure with indium electrodes, and the inset shows the R–T relation of the films measured in four-point mode. Quite noticeably, with a typical loop of the bias sweeping (0 → +V_{max} → 0 → −V_{max} → 0) applied on LSMO films, I–V curves show hysteresis loops, indicating the RS effect in the system. In our experiment, no obvious change can be distinguished in the performance of resistive switching of our samples during several weeks. When the applied voltage goes from rising to falling, for all samples with the fabricating oxygen pressure of 10 Pa, 20 Pa, and 30 Pa, a transition from high resistive state to low resistive state occurs.

And the LSMO film fabricated at 30 Pa oxygen pressure exhibits the most significant hysteresis among all these samples. For the film grown under the highest oxygen pressure of 40 Pa the shape of the hysteresis loop looks like ‘8’ for both positive and negative voltage, which is an interesting phenomenon and has not been reported in manganites so far as we know. From the R–T curves, we can see that LSMO films with the fabricating oxygen pressure of 10 Pa and 20 Pa are semiconductor while LSMO films with the fabricating oxygen pressure of 30 Pa and 40 Pa are metallic at room temperature. The dependence of RS behavior in LSMO thin films on the fabricated oxygen pressure indicates that the oxygen vacancies in the films play an important role in the RS property in LSMO films.

Figure 3 shows the I–V characteristics of LSMO films grown on the substrates of LAO with indium electrodes and the inset shows the R–T relation of the films measured in four-point mode. For LSMO films with different fabricating oxygen pressure, the hysteresis loops still exist. However, it is obvious that the RSs are much smaller than those grown on the substrates of STO. A possible reason is the different lattice mismatches of LSMO with STO and LAO, which are 0.7% and −2.3%, respectively, and inducing tensile and compressive strains in LSMO films [14], respectively. The quite large ‘8’ shape loops is found in the films with the fabricating oxygen pressure of 30 Pa, while very tiny ‘8’ shape loops can also be observed in the films with the fabricating oxygen pressure of 40 Pa. Manganite is known to behave a metal-insulator transition passing through the Curie temperature which can be greatly influenced by stress or doping [15, 16]. As shown in the insets of Figs. 2 and 3, for LSMO films fabricated at lower pressures (10 Pa and 20 Pa), the Curie temperature is much lower than that of LSMO films.
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Fig. 3 I–V characteristics of LSMO films on LAO substrates with different fabricating oxygen pressure and Indium electrodes under the excitation of voltage. The inset shows the resistance-temperature relation of the films at different fabricating oxygen pressure fabricated at higher pressures (30 Pa and 40 Pa), as more oxygen vacancies are introduced into the films. The reason of the resistivity of 40-Pa film is higher than 30-Pa film could be that the crystallization of the film fabricated in too low vacuum (40 Pa) is worse and with higher resistivity.

To investigate the effect of electrodes, platinum electrodes were used as an alternative. Figures 4 and 5 show the I–V characteristics of LSMO films on the substrates of STO and LAO, respectively, with platinum electrodes. Compared with those with indium electrodes, the RS effects still exist, but are smaller. In addition, the ‘8’ shape loops cannot be found any more. Compared the I–V characteristics of LSMO films with different substrates and electrodes, the properties of LSMO films influenced by oxygen vacancies and substrates determine the magnitude of RS effect, while the interface of electrode and LSMO film determines the appearance of the ‘8’-type I–V loop. Considering that the platinum electrode is electrochemically inert, while the indium electrode is electrochemically active, we speculate that the indium oxide interface layer between indium and LSMO may contribute to the ‘8’ shape loops of I–V curve in LSMO films measured with indium electrode. And the Schottky barriers built at the interfaces of the films and the electrodes should also play some roles in the different RS behavior of the system. Combining the above four figures, it might be concluded that the electrodes with different chemical activities, work functions, and lattice mismatches between films and substrates should be crucial in the transport of LSMO films, and the most obvious RS effect was found in films fabricated at 30 Pa oxygen pressure for all the samples, indicating the oxygen vacancies in the films play an important role in the RS property in LSMO films.

The mechanism of the RS effect remains elusive despite significant progress in experiment in the past several years.

From the present results, the lattice mismatch, electrodes and oxygen vacancies should play important roles in the RS property of LSMO films. It has been proposed the electric field can alter the spatial distribution of charges in MnO$_6$ octahedra [17], thus enhance the double-exchange transfer of carriers. To understand the transport property of LSMO films fabricated in the condition mentioned above, we have measured the R–T relations of our samples with indium electrodes from 5 K to 390 K in four-point mode, and plotted them in the inset of Fig. 2 and Fig. 3. According to our experimental result, films on different substrates fabricated at the same deposition condition have different loops in I–V curve, thus we speculate that the interface effect between LSMO films and the substrates may also play some
role in transport property, as well as the resistance switching for the LSMO films. Indium electrode reacts easily with oxygen, which makes oxygen vacancies increased in LSMO film, while platinum is not easy to react with oxygen, so that the hysteresis loops on LSMO films with indium electrodes are larger than those on LSMO with platinum electrodes.

4 Summary

In summary, we have investigated the transport property of LSMO films on STO and LAO substrates with different fabricating oxygen pressures and electrodes. The sensitivity of the $I-V$ loops of LSMO films with oxygen pressure, substrates and electrodes indicates that the RS of LSMO films can be strongly affected by oxygen vacancies, interface effect, and Schottky barriers and oxidation of the interface in metal-manganite contact. For LSMO films with indium electrodes, ‘8’ shape $I-V$ loops were observed in particular fabricating oxygen pressures, the mechanism for such an interesting phenomenon is still an open question. The largest RS was found for LSMO films fabricated in the oxygen pressure of 30 Pa on both substrates of STO and LAO with both electrodes of indium and platinum.

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References

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