

Oxygen electromigration induced nonvolatile resistance switching at Ag/La₂CuO_{4+x} interface

J. P. Shi, Y. G. Zhao,^{a)} H. J. Zhang, H. F. Tian, and X. P. Zhang

Department of Physics and State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

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The authors report on the temperature dependence of electronic transport property of Ag/La₂CuO_{4+x} (LCO) heterostructures with different oxygen contents. Bipolar resistance switching was observed in the sample with larger oxygen content and disappears below 200 K, consistent with the characteristic temperature of oxygen migration in LCO. The resistance relaxation of the low resistance state shows similar behavior as that of oxygen diffusion in LCO and vanishes below 200 K. Analysis of the results strongly indicates that the resistance switching results from the modulation of Schottky barrier by oxygen electromigration at the interface. © 2009 American Institute of Physics. [DOI: 10.1063/1.3133353]

The resistance switching effect in metal/oxide heterostructures has been extensively studied due to its potential applications in resistance random access memory, which has been proposed as a next-generation nonvolatile memory.¹ Although great progress has been made, the mechanism of the resistance switching effect is still an open question.^{1,2} One of the interesting scenarios is the migration of oxygen at the interface of metal/oxide,^{3,4} which has been regarded as one of the key issues in understanding the switching effect.¹ Nian *et al.*³ studied the electrical pulse induced resistance change in Ag/Pr_{0.7}Ca_{0.3}MnO₃/Pt heterostructure. By comparing the resistance relaxation behavior of their samples (assuming that the resistance is proportional to the concentration of oxygen vacancy) with the oxygen diffusion behaviors in Bi₂Sr₂CaCu₂O_{8+δ},³ they concluded that the switching effect is related to the pileup of oxygen ions (vacancies) near the metal electrodes due to current injection during a switching pulse. Quintero *et al.*⁴ studied the electrical pulse induced resistance change in silver paste/Pr_yLa_{0.375-y}Ca_{0.325}MnO₃/silver paste. They found that the switching effect shows a maximum at a certain low temperature. The temperature dependence of the resistivity for the samples with different oxygen contents was calculated based on the double exchange interaction and the result shows strong oxygen content dependence at low temperatures. They proposed that the resistance switching effect originates from the switching pulse induced oxygen content change at the interface. However, no evidence of oxygen migration was present in their work. It is also puzzling why the switching effect is absent at room temperature (RT) considering that oxygen migration is expected to be more remarkable at RT than that at low temperatures. Moreover, the oxygen migration in both Pr_{0.7}Ca_{0.3}MnO₃ and Pr_yLa_{0.375-y}Ca_{0.325}MnO₃ used in Refs. 3 and 4, has not been well established so far, which hinders a straightforward correlation between the resistance switching effect and the oxygen migration. Therefore, it is essential to choose a material with well characterized oxygen migration to explore its role in the switching effect. In this regard, La₂CuO_{4+x} (LCO) is a suitable candidate because it contains extra oxygen which is

mobile above 200 K and the oxygen diffusion in this system has been well established.^{5,6} Sawa *et al.*⁷ studied the resistance switching in metal/LCO only at RT, and attributed the resistance switching effect to the charging effect of traps at the interface without considering the role of oxygen migration. In this letter, we investigate the temperature dependence of electronic transport property of metal/La₂CuO_{4+x} and resistance relaxation. Strong correlations between the resistance switching and oxygen migration in the temperature dependence and relaxation behavior are presented, demonstrating that oxygen electromigration at the interface results in the resistance switching effect.

La_{1.85}Sr_{0.15}CuO₄ (LSCO) layer with a thickness of about 200 nm was first deposited on SrTiO₃ (001) (STO) single crystal substrates by pulsed laser deposition (deposition details were reported in Ref. 8), followed by the deposition of La₂CuO_{4+x} film on LSCO with a substrate temperature of 770 °C. After that, the chamber was filled with O₂ to get 1 atm pressure, and then cooled down to RT. These samples were denoted as LCO-M. The thickness of the LCO film is about 150 nm. In order to get the samples with smaller oxygen content, some samples were annealed *in situ* in vacuum at 350 °C for 10 min and denoted as LCO-L. Here, the metallic LSCO layer is used as the bottom electrode to provide an Ohmic contact to LCO because it has almost the same work function as that of LCO.⁹ The films are (001) oriented as shown by the x-ray diffraction patterns. LCO films were also grown on SrTiO₃ in order to check their resistances. Four probe measurements showed that the resistance of LCO-M is much smaller than that of LCO-L, indicating that the oxygen content of LCO-L is smaller compared to that of LCO-M because the resistivity of La₂CuO_{4+x} increases dramatically with decreasing *x*.¹⁰ Ag and Au electrodes were deposited as the electrodes using a shadow mask. The schematic illustration of the samples is shown in the inset of Fig. 1(a). Current-voltage (*I-V*) curves of the samples were measured using a two-probe method with a Keithley 2400 source meter with a compliance current of 10 mA. A pulsed dc voltage with a width of 2 ms and an interval of 2 s was applied in the *I-V* measurements. The positive bias is defined for current flowing from the LSCO bottom electrode to Ag electrode.

^{a)}Electronic mail: ygzhao@tsinghua.edu.cn.

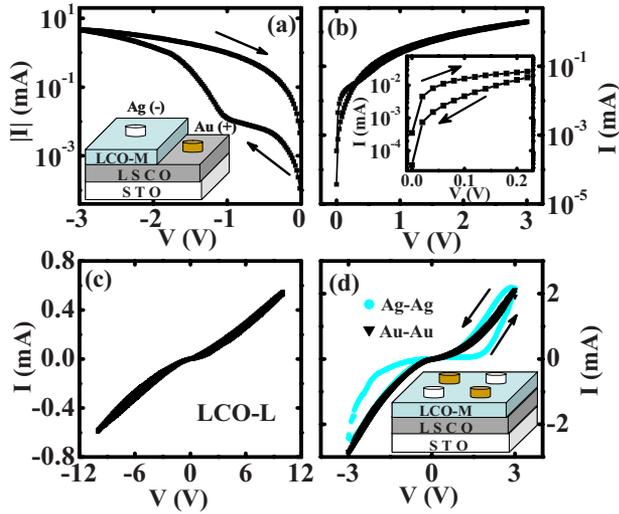


FIG. 1. (Color online) (a) $\log|I|$ - V curves for Ag/LCO-M under negative voltage. The inset is the layout of the device for measurement. (b) $\log I$ - V curves for Ag/LCO-M under positive voltage. The inset is the enlarged curve at low bias. (c) I - V curves for Ag/LCO-L. (d) I - V curves for Ag/LCO-M/LSCO/LCO-M/Ag and Au/LCO-M/LSCO/LCO-M/Au. The inset is the layout of the sample.

Figures 1(a) and 1(b) show the I - V curves for LCO-M, which exhibit large hysteresis. In contrast, almost no hysteresis is present in the I - V curves of LCO-L, as shown in Fig. 1(c). This difference indicates that larger oxygen content favors the resistance switching effect. Moreover, the I - V curves for LCO-M shows remarkable hysteresis for the negative voltage and minor hysteresis for the low positive voltage, as shown in Fig. 1(a) and the inset of Fig. 1(b), respectively. Since LCO-M shows obvious hysteresis in the I - V curves, our investigation will focus on it.

First, it is important to know where the switching effect occurs, at interface or in bulk. In order to achieve this goal, two Au and two Ag electrodes were sputtered on a sample as the top electrodes, as shown in the inset of Fig. 1(d). The four electrodes, each with an area of 0.25 mm^2 , were arranged in a square. I - V curves were measured between Ag and Ag, Au and Au, respectively, and the results are shown in Fig. 1(d). It can be seen that hysteresis appears in the I - V curve measured between the two Ag electrodes, while almost no hysteresis in the I - V curve measured between the two Au electrodes. In metal/LCO-M/LSCO samples, the resistance of metal, and the out-of-plane resistance of film are both very small, so metal/LCO-M interface dominates the electronic transport of metal/LCO-M/LSCO. The work functions of Ag, Au and LCO are 4.2, 5.1, and 5.5 eV, respectively,¹¹ so the Schottky barrier of Ag/LCO-M is much larger than that of Au/LCO-M. This difference in Schottky barrier can account for the remarkable difference between the I - V curve of Ag/LCO-M and that of Au/LCO-M. So it can be concluded that the hysteresis in the I - V curve originates from the interface of Ag/LCO-M and larger Schottky barrier favors the resistance switching effect.

Figure 2(a) shows the temperature dependence of I - V curves of Ag/LCO-M/LSCO with negative voltage. It can be seen that the I - V curve shows large hysteresis at 300 K, becomes smaller at 240 K and disappears at 190 K. The electric pulse induced resistance changes exhibit the similar temperature dependence, as shown in Fig. 2(b), which also shows the resistance relaxation after switching to the low

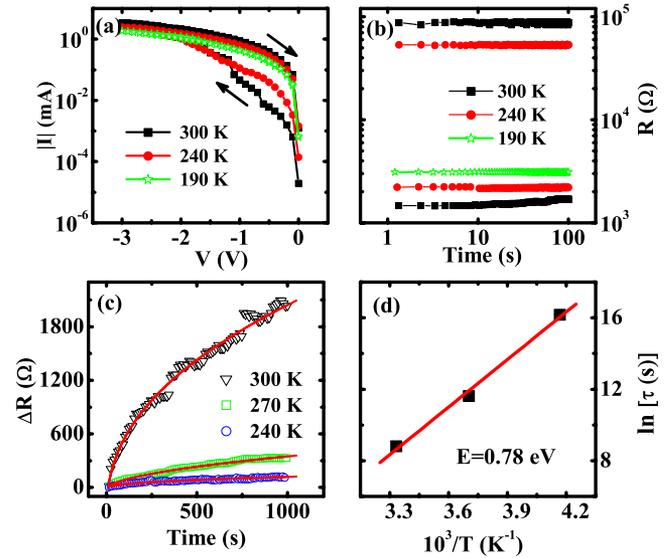


FIG. 2. (Color online) (a) $\log|I|$ - V curves under negative voltage at 300, 240, and 190 K. (b) Relaxation of resistance for HRS and LRS at 300, 240, and 190 K. (c) ΔR vs T curves at 300, 270, and 240 K. The lines are the fitting curves. (d) $\ln \tau$ vs $10^3/T$ curve.

resistance state (LRS) and high resistance state (HRS). The LRS and HRS were realized with a -3 V voltage pulse and $+3 \text{ V}$ voltage pulse, respectively. The pulse width is 100 ms and reading voltage is 0.1 V. The resistance ratio between HRS and LRS decreases with decreasing temperature and becomes 1 below 200 K due to the disappearance of resistance switching. It has been reported that the migration ability of the excess oxygen in LCO is lost below 200 K,⁶ which is consistent with the temperature that resistance switching disappears in Ag/LCO-M/LSCO. The correlation between the resistance switching and oxygen migration in the temperature dependence indicates oxygen ion migration plays a critical role in the resistance switching effect. The resistance relaxation after switching to the LRS and HRS can also provide some information about the role of oxygen migration in the resistance switching effect. As shown in Fig. 2(b), the HRS resistance remains unchanged with time, but the resistance of LRS increases with time showing relaxation behavior. As reported,^{12,13} the oxygen migration induced resistance relaxation with time can be described by the stretched-exponential type function as follows:¹²

$$\Delta R(t) = R(t) - R_0 = (R_\infty - R_0)(1 - \exp[-(t/\tau)^\beta]), \quad (1)$$

where τ and β are the characteristic relaxation time and exponent, respectively; R_0 and R_∞ denote the initial and final values of resistance. As shown in Fig. 2(c), ΔR increases markedly with time at 300 K, and becomes smaller with decreasing temperature. Below 200 K, no obvious resistance change can be seen. The ΔR versus t curves can be well fitted by the stretched-exponential type function, as shown by the fitting lines in Fig. 2(c). The temperature dependence of τ follows $\tau = \tau_0 \exp(E/kT)$,¹³ where E is the activation energy for oxygen ion migration. By plotting $\ln \tau$ versus $1/T$ [Fig. 2(d)], we obtained an activation energy of 0.78 eV, which is close to the value (0.83 eV) in $\text{La}_2\text{CuO}_{4+x}$.¹⁴ In order to explore the relation between the relaxation process and pulse induced resistance switching, a voltage pulse was applied on the sample after relaxation for 1000 s, and the resistance of the sample returns to the initial value. This

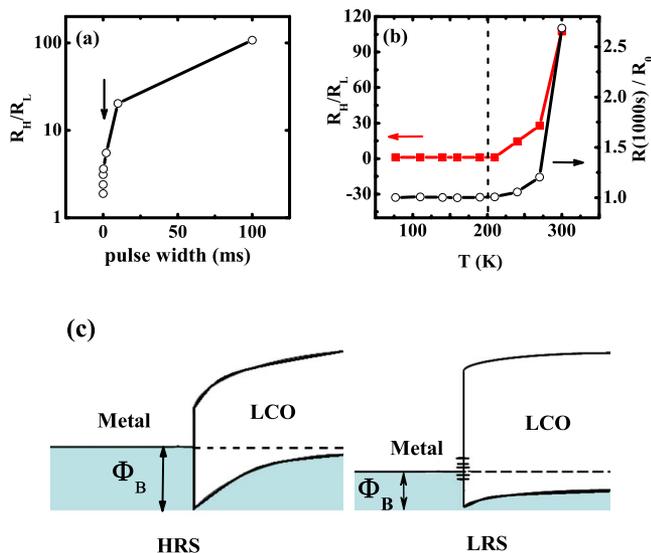


FIG. 3. (Color online) (a) Pulse width dependence of the resistance ratio of R_H/R_L . R_H and R_L stand for the resistances of HRS and LRS, respectively. (b) Temperature dependence of $R(1000\text{ s})/R_0$ and resistance ratio of R_H/R_L . (c) Schematic band diagrams for the HRS and LRS. For the LRS, the vertical short lines at the interface stand for the interface states.

suggests that both the relaxation process and pulse induced resistance switching are related to the oxygen migration.

Figure 3(a) is the resistance ratio between HRS and LRS versus pulse width. It is clear that the ratio reduces with decreasing pulse width. When the pulse width is shorter than 2 ms (marked by the arrow), the ratio reduces very rapidly. This phenomenon indicates that the response time of the resistance switching is much larger than that of the electronic charge transfer time which is in a microsecond scale set by the RC time constant.¹⁵ The slow response of the resistance switching suggests the involvement of oxygen electromigration. The temperature dependences of both the resistance ratio between HRS and LRS and resistance relaxation are summarized in Fig. 3(b). The resistance ratio is about 107 at RT and decreases with decreasing temperature, reaching about 1 around 200 K. The relaxation is large at RT, becomes smaller with decreasing temperature and vanishes below 200 K. Based on the temperature dependent characteristics of I - V hysteresis, pulse induced switching effect and resistance relaxation, we can conclude that oxygen ion electromigration near Ag/LCO interface results in the resistance switching effect. A schematic band diagram is shown in Fig. 3(c) to account for the effect of oxygen ion electromigration on the Schottky barrier. When a negative voltage is applied, the excess oxygen ions migrate toward the interface under high electric field. The oxygen ions accumulate at the interface and create high density of interface states which pin the Fermi level of metal.¹⁶ As a result, the Schottky barrier height Φ_B becomes lower, as shown in the right part of Fig. 3(c). In contrary, when a positive voltage is applied, oxygen ions move away from the interface, so Φ_B changes to a higher value, as shown in the left part of Fig. 3(c). For oxygen ion migration, it has to overcome the energy barrier (roughly 0.78 eV deduced from the resistance relaxation).

The variation of Schottky barrier height with voltage bias and the energy barrier for oxygen ion migration can account for the I - V hysteresis and electrical pulse induced resistance switching effect. The oxygen ions are driven toward the interface under negative pulse voltage, leading to a nonequilibrium ion distribution, so relaxation phenomenon occurs in LRS. It has been mentioned that I - V hysteresis at positive bias is only present at lower voltages, as shown in the inset of Fig. 1(b). It can be explained by considering the disappearance of Schottky barrier due to the removal of band bending under higher positive voltages. In this case, the resistance of the sample is dominated by LCO-M thin film instead of the interface. Thus, the hysteresis of I - V curves disappears. This phenomenon shows Schottky barrier is important for the resistance switching effect in Ag/LCO-M.

In summary, resistance switching effect was studied in Ag/La₂CuO_{4+x} heterostructures. Strong correlations between the resistance switching, relaxation behavior and oxygen migration in the temperature dependence are presented, demonstrating that oxygen electromigration at the interface results in the resistance switching effect. This work will shed light on the mechanism of the resistance switching effect in the metal/oxide heterostructures.

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