Resistance switching induced by electric fields in manganite thin films

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Abstract. In this work, we investigate the polarity-dependent Electric Pulses Induced Resistive (EPIR) switching phenomenon in thin films driven by electric pulses. Thin films of $0.5\text{Ca}0.5\text{MnO}_3$ (manganite) were deposited by PLD on Si substrate. The transport properties at the interface between the film and metallic electrode are characterized in order to study the resistance switching. Sample thermal treatment and electrical field history are important to be considered for get reproducible EPIR effect. Carriers trapping at the interfaces are considered as a possible explanation of our results.

1. Introduction

Materials showing Electric Pulses Induced Resistive (EPIR) switching are attractive for today’s semiconductor technology [1-4 and references therein]. So far, significant progress has been achieved in recent years in fabrication techniques such as pulsed laser deposition (PLD), for the growth of metal–insulator–metal (MIM) structures that display different types of resistance switching. These devices are prototypes for two-terminal non-volatile random access memories and the resistance switching is obtained through the application of a short voltage or current pulse. The insulator in these MIM structures is usually a transition metal oxide in which the electron correlations might be expected to play an important role. Although experimental results, reported for different compositions of manganites, show the EPIR effect when the applied voltage was higher than a critical value, a condition to observe this phenomenon is to train the sample. Normally, that training consists of cooling and heating cycles and pulsed current-voltage (I-V) curves at low temperatures, performed to the sample. Only after that training, can the EPIR effect can be achieved, at least in manganite films. Thus, it is not clear if that response is intrinsic to the nature of the film, or if it is due to structural or electronic changes, defects in the interface with the electrodes or any other effect produced by the training. Regardless, the experimental evidence shows that training is essential to obtain a reproducible and long lasting effect.

In a previous work [4], we have found in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ thin films that the conductivity of the films was diode-like and the application of electric fields resulted in resistance switching to low resistive states. In this work, we focus in the origin of the EPIR effect in that manganite, trying to identify the causes that “activates” the EPIR effect in this samples.
2. Experimental

Thin films of La_{0.5}Ca_{0.5}MnO_{3} were fabricated using pulsed laser deposition (PLD). A Nd:YAG laser beam, operating at 266 nm and 10 Hz, was focused on a rotating target of the same composition to yield an energy density of ~ 2.5 J/cm². The manganite films were deposited on Si_{3}N_{4} buffered Si substrate and deposition was carried out at 700 °C under 10 Pa oxygen pressure. After deposition, the ablation chamber was back-filled with O₂ to atmospheric pressure and the sample was cooled to room temperature at a rate of ~ 10 °C/min. The thickness of the sample is about 80 +/- 2 nm. The x-ray diffraction patterns of the La_{0.5}Ca_{0.5}MnO_{3} films showed a polycrystalline nature, with a slight texture in the (100) direction.

For electrical measurements we employed a two-probe scheme in the setup, using constant-voltage mode or constant-current mode. Au electrodes were sputtered on the film, and Cu wires were attached on them with Ag epoxy.

Fig. 1 shows a schematic diagram for electrical measurement used in this work. Electric current or voltage from electrode A (or B) to electrode D (or C) are defined as positive (+) direction. We will show here only the response when voltage multipulses of +20 and -40 V, were applied between B and C electrodes. The normalized response between A and C, A and D and B and D electrodes is essentially the same.

![Figure 1. A schematic diagram of the Au/LCMO/Si3N4/Si system and direction of the applied pulse voltage](image)

3. Results and Discussion

Figure 2 (open circles) shows the sample resistance response at room temperature when alternate voltage multipulses of -40V and +20V were applied, using the scheme showed in Fig. 1. Each multipulse is a sequence of 10 pulses of 40 ms. A small reading voltage of +0.1V was held between pulses. As can be seen, the EPIR effect was not observed in this sample at this stage. After cooling the sample down to 140K and holding it at this temperature for two hours, the room temperature resistance response was the one shown in Fig. 2 (closed circles). We can see that the first pulse switches the resistance of the film, but subsequent pulses do not produce a clear EPIR effect. The inset of figure 2 shows the two-point resistance as a function of the distance between contacts: A-B, A-C, and A-D before and after cooling the sample. The contacts resistance can be obtained from the linear extrapolation to zero distance. We can see from Figure 2 that the contacts resistances are increased after the cooling – heating cycle. In order to separate the contribution of the manganite film from the contacts resistances, the resistance of the manganite film was measured using the four-point technique. We obtained that the manganite resistance remains almost without changes: 27.5 KΩ and 28.5 KΩ before and after the thermal cycle, respectively.

At this point, we performed another cooling cycle but applying a series of voltage pulses (+/-40V) at 140 K; then, the sample started to respond to voltage polarity at room temperature, switching the resistance, although the response did not properly correlate with the polarity of the pulses. To stabilize the response, pulses of 30 and 40V were applied. After that process, the response followed quite well voltage polarity (see Figure 3), showing a clear EPIR effect. It is possible that a cooling cycle is necessary to induce some phase changes in the sample (like the spatial distribution of charge ordered or ferromagnetic phases) but we demonstrate that the resistance of the film, without the contribution of contacts resistances, does not change.
While the training does not appreciably modify the bulk resistance of the film, however, this could not be valid for the interface with the electrical contacts. Voltage pulses, applied at low temperatures, could enhance "electroforming" of traps and defects at this zone that activate the EPIR effect.

Fig. 4 shows the time evolution of the two-point resistance (between B-C) for an EPIR active sample. The inset of Fig. 4 shows the time evolution of the two-point resistance (between B-C) before the "sample training" (EPIR non-active sample) using the constant-current mode setup (I = +1μA). The slight shift to high resistance values is due to room temperature variations. We observed that after 14 hours, the resistance of the EPIR active sample switches abruptly to a high resistance state (HRS). When the polarity of the current is inverted, the resistance reverses abruptly to a low resistance state (LRS). Resistance switch is not observed if we maintain this polarity for longer times (around 60 hours).

We discuss our results in terms of the "charged domains" (traps, defects, phase separation, etc.) proposed by Rozenberg et al. [5]. The model assumes an insulating medium (middle domain) sandwiched by two metal electrodes. Upon application of a pulse, a large carrier transfer occurs and the occupation of the domains close to electrodes (DCE) is significantly changed due to a large carrier transfer in and out of the large middle domain. The new occupation state of the DCE is reflected in a qualitative change in the read current. A write (negative) V pulse fills up one of the DCE and empties the other. While Vread is continuously applied, the systems remain in a HRS, since the probability of carrier transfer into the already

![Figure 2](image1.png)

**Figure 2.** Alternate voltage multipulses of -40V and +20V, applied at room temperature. Before (open circles) and after (closed circles) cooling the sample to 140K. Reading voltage is 0.1V. Inset: two-point resistance as a function of the distance between contacts: A-B, A-C, and A-D before (open symbols) and after cooling the sample.

![Figure 3](image2.png)

**Figure 3.** Alternate voltage multipulses of -40V and +20V, applied at room temperature after the "sample training".
filled DCE is low and likewise, the probability of carrier transfer out of the emptied DCE to the electrode is also low. On the other hand, an erase (positive) pulse produces a large transfer from the middle domain to the DCE and from the other DCE to the middle domain with concomitant changes in the occupations. The result is that, under the applied $V_{\text{read}}$, the systems now displays a LRS as carriers can be easily transferred to the empty DCE. They argued that the occupation of the domains near the interfaces of the electrodes with injected electrons is responsible for the resistance switching. Then, the HRS and LRS are assumed to be related to domains filling. In our time evolution response of the resistance (Fig. 4), a slow dynamic of the domain occupation filling process is detected (14hs) that leads to the resistance to switch to the HRS without the application of voltage pulses. However, a fast dynamic filling process can be induced by reversing the electric current. These results indicate that the EPIR effect can be associated to occupation domains at the interface between film and electrode.

![Figure 4. Time evolution of the two-lead resistance (contacts B-C) using the constant-current mode setup ($I=\pm 1\,\mu\text{A}$) for an EPIR active sample. Inset: idem for a non-active sample](image)

4. Conclusions
We have studied the effect of voltage pulses and “training” on the electrical response at room temperature of La$_{0.5}$Ca$_{0.5}$MnO$_3$ films. Voltage multipulses and thermal cycles are necessary to activate EPIR effect in this manganite film. An asymmetric time response of the resistance to the polarity of applied current has been reported. This indicates that only one of the electrode interfaces controls the EPIR effect and that the main part of the film only plays the role of mediation between the domains close to metal electrodes. More experiments are necessary to control the observed EPIR effect.

References
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