Resistance switching in silver - manganite contacts

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Abstract. We investigate the electric pulse induced resistance switching in a transition metal oxide-metal contact at room temperature - a non volatile, reversible and multilevel memory device. Using a simple multiterminal configuration, we find that the complementary effect - in which the contact resistance of each pulsed electrode displays variations of opposite sign - is strongly influenced by the history of the pulsing procedure. Loops performed by varying the magnitude and sign of the stimulus at each pulsed electrode allow to disentangle their sole contribution at different stages of the process. Electromigration of oxygen ions and vacancies is discussed as participating at the core of the underlying mechanisms for resistance switching.

1. Introduction

Electric pulse induced resistance switching (RS) is the focus of intense basic research nowadays. [1,2] This non-volatile electrically-induced and electrically-sensed memory effect has definite technological interest due to fast switching and scalability. Although RS has been observed in many different metal-oxide couples, a significant part of the community focusing this scenario is presently devoted to the study of transition metal oxides contacted through metal electrodes. [3,4,5] Among several families, perovskite based structures are being systematically studied [6] due to additional attractive features based on multifunctionality. [7] Manganites, cuprates and titanates exhibit bipolar type RS in which electrochemical migration of oxygen ions and vacancies is regarded as the driving mechanism. [1,8] In this case, RS takes place at the interface between the metal electrode and the oxide, in an interface – type path, as described thoroughly by A.Sawa [2] and references therein.

Evidence towards an oxygen diffusion mechanism by means of electric transport measurements [9] were recently obtained following a Hysteresis Switching Loop (HSL) procedure. The feasibility to induce related reversible switching at the nanoscale by means of conducting atomic force microscopy probe measurements has been recently shown. [10] Here, we take advantage from a simple multiterminal configuration design to systematically explore -under different pulsing protocols including HSL- differences between electrical behavior of complementary pulsed electrodes, i.e. each single electrical contact that suffered the pulsing discharge. We show that unveiled differences are directly related to the electric field established along each metal-oxide junction. Electromigration of oxygen ions and accumulation of vacancies are shown to play a role at the core of the underlying mechanism of the RS effect.

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2. Experimental

We performed a systematic study on a manganite sample, with hand painted millimeter sized silver paste electrical contacts. As schematically shown in the Inset of Figure 1, electric pulses and bias current are always injected through terminals A and D, while voltage can be (simultaneously) measured at AB, BC and CD contacts by means of floating voltmeters. All experiments and data to be shown here were performed at room temperature under ambient pressure and magnetic field, on a polycrystalline sample of \( \text{La}_{0.325}\text{Pr}_{0.300}\text{Ca}_{0.375}\text{MnO}_3 \) (LPCMO) with average grain size 2 microns. Growth details, as well as temperature and intermediate range magnetic field dependences of the RS phenomena on LPCMO were previously reported. [7,11,12]

3. Results and Discussion

Initially, all contacts displayed comparable resistance values, as expected for a symmetric device, i.e. one in which all electrodes are made with the same metal and having similar dimensions. After repeatedly pulsing, a history dependent forming asymmetry was induced, hereafter we call it the "formed sample". Figure 1 exhibits panels displaying a) the pulsing sequence; b) AB, c) BC, d) CD measurements on each pair of contacts. Pulsing consisted of groups of 10 single pulses of 2 ms time width and 3.2 V amplitude. "Positive" means that positive carriers are injected through terminal A, producing a positive voltage drop across AB electrodes. After pulsing, nonvolatile voltage from each pair of electrodes were acquired sequentially using a small bias current (+1mA).

As observed in Figure 1, robust switching between Low Resistance (LR) and High Resistance (HR) nonvolatile states is obtained at electrodes AB and CD upon pulsing with alternate polarities. Note that a positive stimulus switches AB electrode to LR, and switches -in a complementary way [11]- the CD contacts to HR. Complementary electrodes are defined to be sole electrical contacts that suffered the pulsing discharge, A and D in this case. The complementary character of the voltage drop at AB and CD terminals refers to the sign of the change [11], i.e. it is not a numerical cancel of values, in agreement with (but seldom discussed at) previous reports in the area using a multiterminal approach. Resistance of the LPCMO sample (~0.08 ohm), as measured through BC terminals (standard 4 probe method) was unaffected by pulsing at our detection level.

![Figure 1](image1.png)

**Figure 1.** Switching on the "formed sample" at room temperature: a) the pulsing sequence; b) AB, c) BC, d) CD resistance measurements at each pair of electrodes. Inset: schematics of the multiterminal configuration.

![Figure 2](image2.png)

**Figure 2.** Switching with varying stimulus I on the "formed sample" as a function of time: a) the pulsing sequence; b) AB, c) CD, d) AD resistance measurements performed after pulsing.
The next experiment corresponds to an electrical pulsing protocol which scans in a loop mode the current during pulsing, the procedure hereafter referred to as HSL. The initial state for this HSL is unambiguously defined after repeatedly cycling (3 or more times) the stimulus—a single pulse of 2 ms time width—within +/− 1A amplitude with 10 V as limiting voltage. Then, the starting point of the loop is defined by injecting the stimulus at -1 A. The stimulus is then increased/decreased in steps of +/− 0.05 A, so as to describe a loop from -1 A to +1A, and then back to -1A. Remanent (i.e. nonvolatile) voltages at each pair of electrodes as well as the stimulus are depicted in Figure 2, as a function of time. Heating effects are expected to be present during pulsing. However, note that even for the highest I pulsing value (1A) the current density injected remains below 100 A/cm². While pulsing time was maintained small (~ few ms), no tracking of heating was evidenced on nonvolatile resistance values (see Figures 1 and 2).

The HSL response is depicted in Figure 3 as a function of the stimulus. Following the electrode AB, at the beginning of the sequence the HR state at -1A is sustained when I pulsing is decreased, reaching I = 0 with practically the same initial remanent value (see path “I” in Figure 3). Surprisingly, after I changes sign, its value decreases, reaching smoothly the LR state at about +1 A (path “II”). On the other hand, the complementary contact CD switches from LR to HR state in a sudden way and only after the stimulus I surpasses +0.5 A. Upon decreasing I from +1 A towards −1 A, the voltage at CD changes smoothly starting as soon as I changes sign, while AB switches steeply only after −0.5 A are surpassed (path “IV”).

![Figure 3. Non volatile voltage measured after pulsing following the Hysteresis Switching Loop procedure on the “formed sample”, as a function of pulsing stimulus I.](image)

The HSL, a distinctive fingerprint of each pulsed contact, is quite unexpected, evidencing a new aspect of complementary behavior. As seen on Figure 3, although pulsing is simultaneously applied to electrodes A and D, the response is not the same at both pulsed contacts, i.e. RS is obtained with different features at AB and CD electrodes, depending on pulsing history. Remarkably, it is possible to induce RS in one electrode and not in the other. This fact signals that complementarity [11] can be circumvented if certain pulsing protocols are applied. Interestingly, control of multilevel nonvolatile states emerge naturally upon performing the HSL experimental sequence.

When a positive pulse is applied at terminals AD, negative oxygen ions (O−) are ejected from the vicinity of the D electrode leaving the interface with vacancies and therefore interrupting and disturbing electrical transport. Pulsing with decreasing positive values leaves unaffected the HR state as these vacancies remain unfilled. Only when the polarity of the stimulus is changed, a smooth and
gradual filling of vacancies with mobile O-- starts. Conversely: starting with the D electrode plenty of O--, when negative pulsing decreases towards zero, no net change is observed until the positive threshold electric field for detrapping O-- is attained. The observed difference in trapping-detrapping process is the disclosed origin of the RS mechanism.

Next, we applied a direct current of 1 A for 17 seconds (positive polarity). This protocol was a priori expected to produce a severe electric injure to the metal-oxide junction due to self heating at contacts. After this procedure, the “17sec-1A” sample still exhibited switching behavior similar to the previously described “formed” sample. Contact resistance figures appear to be drastically lower. The RS performance of the contacts AB and CD is now much more dissimilar as compared to the behaviour before the “17sec-1A” procedure. As expected, the intrinsic resistivity of LPCMO is unaffected by the electromigration process.

With the aim of measuring the dynamic resistance (i.e. resistance during pulsing) the HSL was performed using a single pulse having a time width of 60 ms. Under this protocol, the temperature at the contacts raises periodically due to self heating. The decay of their resistance during pulsing reveals the semiconducting like dependence of the tandem metal-oxide interface plus intrinsic LPCMO resistance. Though the maximum density current produces negligible volume heating, dissipative contact power at the interface (~ 100 W/cm²) is undoubtedly high and local heating cannot not be avoided. We used the last voltage value obtained before the end of the pulse as a measure of the resistance during pulsing. After pulsing, the thermal decay occurring for some few seconds could be tracked with a small bias current (data not shown). Thus, in order to allow heat drift, event pulsing was separated by 30 sec intervals. Obtained data for electrodes CD on the “17sec-1A” sample is shown in Figure 4 as a function of time.

![Figure 4](image_url)

**Figure 4.** Resistance at electrodes CD on the "17sec-1A" sample as a function of elapsed time: a) Pulsing sequence; b) $R_{CD}$ during pulsing (i.e., $V_{CD}/I_{AD}$); c) $R_{CD}$ after pulsing (i.e., $V_{CD}/I_{bias}$).
Upon performing the HSL procedure on the “17sec-1A” sample (see Figure 5.a, path “I” starting at I=-1A) the remanent value of $R_{AB}$ does not switch even after reversing and increasing the polarity of the stimulus up to $\pm 0.40$ A, when the RS is initiated. Both vertical edges of this HSL (paths “II” and “IV”) display similar features being almost parallel with smooth corners, thus determining a HSL quite different to the one obtained on the “formed” sample (see Figure 3). On the other hand, as shown in Figure 5.b, the electrodes CD (remarkably displaying a higher contact resistance than the AB contact) exhibited a HSL which appears (at least in its shape appearance) unaffected by the “17sec-1A” process, and resembles the initial HSL of the CD electrodes.

This difference is undoubtedly related to the resistance level at each contact, which determines the effective electric field at the oxide metal junction when pulsing is performed. Note that the $R_{AB}$ value and the amplitude of the HSL are both low, as a consequence of the electromigration produced on the “17sec-1A” sample. The difference above discussed for the HSL of AB and CD electrodes is also apparent studying the dynamic (i.e. volatile) resistance values measured at AB and CD during pulsing (see Figures 5.c and 5.d). These V – I curves exhibit non linear V-I behavior and a two level resistance state. While the curve for the AB contact is almost non hysteretical, data for the CD contact shows a clear jump from the LR to the HR state at $+0.6$ A with hysteresis upon cycling the stimulus in a figure-of-eight mode, evidencing the nonsymmetrical transport behavior related to polarity dependant effects.

**Figure 5.** Comparison of volatile and nonvolatile states on the "17sec-1A" sample as a function of pulsing stimulus $I_{AD}$: a) $R_{AB}$ after pulsing; b) $R_{CD}$ after pulsing; c) $V_{AB}$ during pulsing; d) $V_{CD}$ during pulsing.
Switching is produced at the D electrode when a positive pulsing stimulus (+0.6 A in this case) is applied through AD terminals, as negative oxygen ions are detrapped leaving a HR level at D ascribed to the presence of vacancies at the metal–oxide interface. This oxygen depleted state at D is easily converted to LR level soon upon polarity of the stimulus changes. Note that the negative pulsing in this part of the loop has very low incremental resistance (i.e. ΔV / ΔI ~ 0.1 ohms) related to the easy movement of O-- ions towards empty oxygen vacancies. These results and analysis are in full agreement with previous reports on La0.66Ca0.33MnO3 / Ag contacts. [13] Moreover, with the above described approach and analysis, qualitative understanding is provided for HSL performed with decreased stimulus threshold due to intercalation of ferroelectric layers, as very recently reported. [14]

4. Conclusions

In conclusion, using very simple electrical transport techniques and protocols, we disclosed the core of the mechanism behind resistive switching in silver manganite contacts. We anticipate that similar procedure applied to different metal–transition metal oxide couples could disentangle plenty of data published since pulsing emerged as a possible nonvolatile memory for applications. We speculate that using metals with higher work functions [1] will produce steeper transitions at higher voltages, and that the use of oxides with higher oxygen mobility or an increase of the working temperature will degrade switching and retention capabilities. Besides, an open route for downsampling memory cells is envisaged, as the overall effect still relies on interface type conducting paths.

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