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# Anomalous time relaxation of the nonvolatile resistive state in bipolar resistive-switching oxide-based memories

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We have studied long time relaxation effects on the nonvolatile resistance state produced by resistive switching in devices composed by ceramic $YBa_2Cu_3O_{7-\delta}$ and $La_{0.7}Sr_{0.3}MnO_3$/metal (Au, Pt, Ag) interfaces. The time relaxation can be described by a stretched exponential law that is characterized by a power exponent ($n$) close to 1/2. We found that the characteristic time ($\tau$) increases with increasing temperature and applied power. The origin of the relaxation effect can be related to oxygen diffusion processes, which were recently associated with the mechanism of bipolar switching in complex oxide interfaces. We argue that the anomalous behavior can be understood in terms of diffusion of oxygen ions (or oxygen vacancies) on a two-dimensional surface with a temperature-dependent density of trapping centers, which may correspond, physically, to the diffusion along grain boundaries.

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## I. INTRODUCTION

The search for new memory devices is one of the key points for the development of information and communication technologies.[1] The Si-based devices are reaching limitations in information density, capacity of retention, and power consumption.[2] Among the possible candidates, resistive memory devices (RRAM) based on the resistive switching (RS) mechanism have shown promising results that could confirm them as the future replacement of nonvolatile memory devices.[3,4] One feature that a memory device must comply to is to maintain, over time, the stable retention of the high or low state. To highlight the parameters that control the stability of the obtained resistive state is therefore a task of interest to achieve stable memories. On the other hand, a detailed characterization of the relaxation effect can help us to gain a deeper understanding of the mechanism beneath the resistive switching. Nian *et al.*[5] have analyzed the time relaxation of the remnant resistive state in manganite-metal interfaces. Their results were interpreted as clear evidence of the relation between RS and oxygen diffusion.

In order to gain insight into the particular characteristics of this diffusion process, in this paper we present studies of the relaxation time observed in the electric-pulse-induced resistance switching of complex-oxide ceramic/metal interfaces. We found that immediately after the new resistance level is obtained by the electric-pulse switching process, the remnant value of the resistance relaxes following a stretched exponential law. Interestingly and unlike ordinary thermal diffusion processes, we observe that the characteristic relaxation time *increases* with increasing both temperature and applied power. We shall present data for two different compounds, the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO) and the colossal magnetoresistant $La_{0.7}Sr_{0.3}MnO_3$ (LSMO), which nevertheless show similar qualitative behavior, therefore pointing to a generic phenomenon within the context of resistive switching. As we shall argue below, this peculiar dependence of the characteristic time indicates that the resistance's relaxation is not related to a standard oxygen (or oxygen vacancy) diffusion process but rather to one where the dominant physics is that of particles diffusing in a sea of traps.

## II. EXPERIMENT

In order to study the time relaxation of the switched resistive state on oxide-metal junctions, we sputtered different metals (Au, Pt) on the surface of a optimally doped ceramic YBCO sample [$T_c \simeq 90$ K and $J_c(77\text{ K}) \simeq 10^3$ A/cm$^2$] by using a shadow mask. The YBCO sample was prepared following the same procedures described elsewhere.[6] The sputtered electrodes, depicted in Fig. 1, have a width of 1 mm and a mean separation between 0.4 and 0.8 mm. They cover the entire width of one of the faces of the YBCO slab ($8 \times 4 \times 0.5$ mm$^3$). Finally, silver paint was used carefully to fix copper leads without contacting directly the surface of the sample. By using a similar geometric arrangement, we also studied a LSMO ceramic sample with Ag hand-painted contacts.

Following our previous studies,[7–9] at a fixed temperature ($77\text{ K} \leqslant T \leqslant 320$ K), we apply trains of 20 000 square pulses to electrodes 1–2, with an amplitude up to +10 V and 0.1 ms width at a frequency of 1 kHz, to obtain a reproducible

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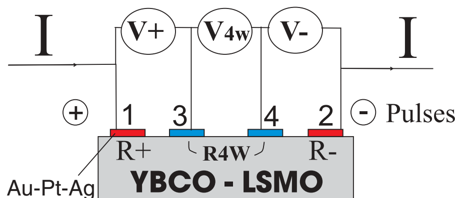


FIG. 1. (Color online) Contact configuration used to study the time relaxation of the remnant resistance state after producing a RS on a YBCO or a LSMO/metal interface.

switching state. Immediately after that, in order to measure the remnant resistance, a small bias current (10 $\mu$A) was applied to electrodes 1 and 2 to measure different resistances, using a standard dc technique: by measuring the voltage in electrodes 1 and 3 we essentially evaluate the resistance near the interface corresponding to electrode 1, as both the YBCO and the LSMO bulk resistance between electrodes are, when compared, negligible (as confirmed by measuring the four-terminal resistance $R_{4W}$). Similarly, when we measure the voltage between electrodes 4 and 2 we essentially evaluate the resistance near the interface of electrode 2. We arbitrarily call $R_+$ the former resistance ($V_{13}/I_{12}$) as it follows the polarity of the applied pulses while the latter corresponds to $R_-$ ($V_{42}/I_{12}$). The initial resistance of contacts was in the range of 20 to 50 $\Omega$, while the bulk YBCO resistance was about 0.1 $\Omega$ for $T$ above $T_c$. Thus, as already mentioned, the bulk contribution was always small or negligible. Temperature was measured with a Pt thermometer well thermally anchored to the sample. In this way, self-heating effects can also be detected. The amplitude of the square pulses was also varied in order to modify the applied pulsing power on each interface (0.4 W to 2 W). For pulsing treatments where the applied power exceeds 1 W, an increase of 2–4 K due to self-heating was observed, followed by a 20–30 s decrease of the temperature to its settled value. After that transient period, temperature was controlled to remain constant within a $\pm 0.5$ K interval during all over the relaxation measurement (up to $\sim$300 minutes).

## III. RESULTS AND DISCUSSION

The time evolution of the remnant resistance of $R^+$ corresponding to a YBCO/Pt interface after a pulsing treatment is shown in Fig. 2. A similar behavior was obtained for $R^-$ and also for YBCO/Au and LSMO/Ag interfaces. It is clear that after each pulse, the resistance relaxes towards its previous resistance state. Self-heating can be easily ruled out by considering the semiconductinglike temperature dependence of the resistance for each state (see the inset of Fig. 2). If the main reason for the evolution of resistance over time was related to this effect, then we should always observe a sudden reduction and a slow increase in resistance after applying pulses as a consequence of the sudden increase of temperature and its slow reduction as the Joule heating dissipates, regardless of the state of resistance considered. As this is not the case, we can consider that the observed evolution is related to a metastable state. Relaxation effects were previously reported in manganite-metal junctions[5] and interpreted as an evidence of oxygen diffusion in these complex oxide systems.

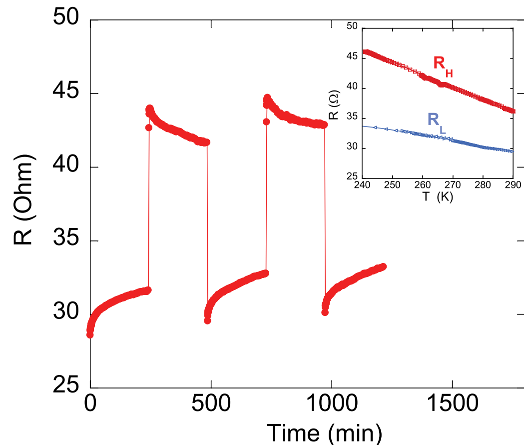


FIG. 2. (Color online) Time relaxation of the resistance state (high or low) after a series of switching processes of the contact labeled $R^+$ for a YBCO/Pt interface. The inset shows the typical semiconductinglike temperature dependence of the interface resistance of the high ($R_H$) and low ($R_L$) resistive states.

The time dependence of the contact resistance after each RS, observed in Fig. 2, can be described by the following equation:

$$\frac{R(t)-R(t_0)}{\Delta R} = X = 1 - e^{-(\frac{(t-t_0)}{\tau})^n}, \qquad (1)$$

where $R(t)$ and $R(t_0)$ are the resistances at time $t$ and $t_0$, respectively, $\Delta R$ the total variation of $R$ for $t \to \infty$, $X$ the relative variation of resistance, $\tau$ the characteristic time, and $n$ an exponent. This equation is similar to the one established by Avrami[10] in order to describe the kinetics of a phase transition at a fixed temperature, where $X$ represents the fraction of the volume that has transformed from one phase to another after a time $t - t_0$, and the exponent $n$ is associated with the dimensionality of the growing process.

Equation (1) can be rewritten as follows:

$$Y = \ln[-\ln(1-X)] = n\ln(t-t_0) - n\ln(\tau), \qquad (2)$$

which can be used to fit the relaxation data measured for each interface at different temperatures after applying a pulsing treatment at a fixed power. In this way, we can determine the $n$ and $\tau$ parameters for each case. As can be observed in Fig. 3 the linearized data is well represented by Eq. (2) over two time decades.

A slightly deviation from linearity can be observed for the initial points. As the power applied during pulsing treatments of 20 s was, in most of the cases, higher than 1 W, some evidence of self-heating can be observed, but in a time scale of tenth of seconds. So after several minutes, the effects related to the change of temperature induced by the Joule heating process should not produce any additional effect on the resistance, indicating that the time evolution is essentially related to a long intrinsic relaxation process (lasting in some cases more than six hours). More than 20 curves at different temperatures (77 K $\leqslant T \leqslant$ 320 K) and applied power (0.4 W to 2 W) were fitted with Eq. (2). We obtained a single value for $n = 0.5 \pm 0.05$ in all cases, for both initial resistance states of the sample (high or low). On the other hand, the characteristic time

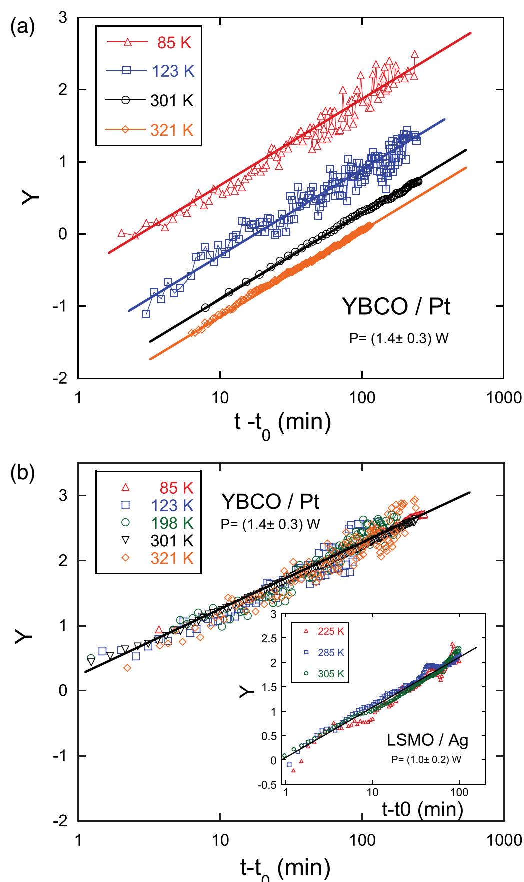


FIG. 3. (Color online) (a) Linearization of the time evolution of the relative resistance variation of YBCO/Pt junctions by following Eq. (2), after producing a RS at different temperatures and at a fixed pulsing power $P$ (not all the measured curves were included for clarity). (b) All the linearized data falls in the same curve just by adding a convenient constant, indicating that $n$ is temperature independent. The inset shows similar results obtained for the LSMO/Ag interface. Lines indicate a slope of 0.5.

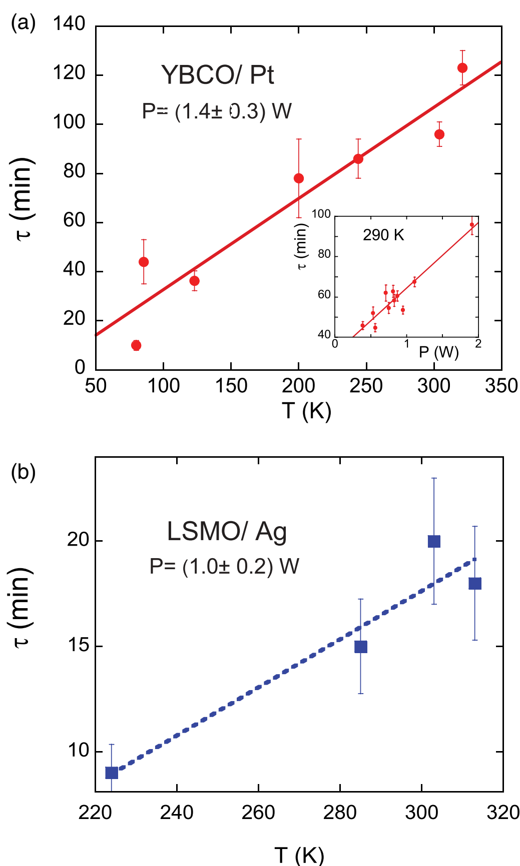


FIG. 4. (Color online) Temperature dependence of the characteristic time $\tau$ for (a) YBCO/Pt and (b) LSMO/Ag interfaces. The applied pulsing power was kept constant in each case, $1.4 \pm 0.3$ W and $1.0 \pm 0.2$ W for the YBCO and LSMO interfaces, respectively. The inset of (a) shows the results obtained for the applied power dependence of $\tau$ for the YBCO/Pt device. $\tau$ error bars were estimated statistically by measuring a set of several curves at similar experimental conditions. Lines are a guide for the eyes.

$\tau$ increases linearly with increasing temperature and applied power, as shown in Fig. 4.

The fact that the characteristic time $\tau$ increases with increasing temperature (and switching power) is quite unexpected and clearly rules out the possibility that we were dealing with a standard diffusion process, mainly governed by a thermal activation energy (Arrhenius-like dependence). An additional ingredient is necessary to take into account. One possibility can be derived by considering that the observed physics properties are not solely related to a diffusion of ions but to a problem of a diffusion with traps. Indeed, oxygen diffusion will not produce local changes of the electrical conductivity if those oxygen atoms are not linked to the crystal lattice: to produce a conductivity change, it is necessary for oxygens to be trapped (or de-trapped) on the crystal lattice, occupying (or liberating) the site of a vacancy. In this way, the observed time relaxation can be related to the physics of a moving particle (an interstitial oxygen ion) in a sea of traps (the vacancies), or its counterpart of a virtual vacancy trapped by a lattice oxygen. In this sense, when negative pulses are applied to one interface, an excess of oxygen vacancies is generated. As far as these lattice vacancies trap oxygens a relaxation to a smaller resistance is observed. On the contrary, if positive pulses were applied, the lattice tends to be fully oxygenated. The resistance then relaxes to higher values as far as oxygens leave the lattice, corresponding to a virtual vacancy trapping process.

By considering the model proposed by Rozenberg *et al.*,[11] the time evolution of the resistivity ($\rho$) can be associated with the time dependence of the oxygen vacancy occupation ($\delta$) near the interfaces [$\rho(t) \sim \delta(t)$]. As the electric pulses produce an out of thermodynamical equilibrium concentration of oxygen ions in the lattice (or vacancies, depending on the pulsing polarity), their diffusion in or out of the lattice will produce a local variation of $\delta$. The time relaxation of the resistance will then depend on their lattice trapping probability. If $P$ is the survival probability, $\delta_0$ and $\delta_\infty$ the initial and the final vacancy occupation after the pulsing treatment, it can be shown that

$$[\rho(t) - \rho(0)]/[\rho(\infty) - \rho(0)] \sim 1 - P(t). \quad (3)$$

Many studies of trapping kinetics[12–15] indicate that the survival probability $P(t)$ of a moving particle in a sea of immobile traps follows a stretched exponential law, as shown

in Eq. (4).

$$P(t) \sim \exp[-C\Delta^{\frac{2}{d+2}}(Dt)^{\frac{d}{d+2}}], \quad (4)$$

where C is a dimension-dependent constant, $\Delta$ the density of traps, $D$ the diffusion coefficient, and $d$ the dimensionality of the medium where the diffusion takes place.

By comparing Eq. (1) with Eqs. (3) and (4) we can conclude that this framework gives an excellent description of our experimental result for $R(t)$, pointing out the similarity of the involved physics. From Eqs. (1) and (4), the exponent $n$ and the characteristic time $\tau$ can be rewritten as

$$n = \frac{d}{d+2}; \quad \tau = \frac{1}{C^{\frac{d+2}{d}}\Delta^{\frac{2}{d}}D}. \quad (5)$$

Within this approach, our exponent $n \simeq 0.5$ is then indicating that the oxygens (or vacancies) are diffusing in a two-dimensional (2D) medium. Considering than our YBCO and LSMO samples are ceramics, we can infer that diffusion is mainly located at grain boundaries. In fact, the temperature range where we observe the resistance relaxation is in accordance with the relevant temperature interval where oxygen diffusion is particularly noticeable for grain boundaries.[16] Moreover, our previous results affecting the superconducting transition width but not the superconducting onset with a severe pulsing treatment[7] were also an indication that the electromigration was essentially affecting the coupling of the superconducting grains by modifying the oxygen concentration of the grain boundaries.

The linear dependence with temperature of $\tau$ can then be associated with temperature dependence of the effective trap density $[\Delta(T)]$, represented by the following expression:

$$\Delta(T) = \frac{1}{C^2\tau D} \simeq \frac{e^{(\frac{E_a}{k_B T})}}{AT}, \quad (6)$$

where $E_a$ is the activation energy of the oxygen diffusion process, $k_B$ the Boltzmann constant, and $A$ a constant related to $C$ and to $D_0$, the oxygen diffusivity constant. This expression indicates that the density of effective traps is reduced when the temperature is increased. By considering that $E_a \simeq 0.4$ eV for YBCO polycrystals,[17] $\Delta$ reaches practically a null value [$<1\%$ of $\Delta(300\,\text{K})$] for temperatures $T \geqslant 450$ K. This result is in accordance with the fact that the RS is no longer observed in YBCO/metal interfaces for temperatures over this range.[8]

The temperature dependence of the effective trap density can be qualitatively understood by considering a distribution of activation energies that emerges from different oxygen-vacancy migration processes. In the case of YBCO, these processes were identified as point-defect relaxations of oxygen-vacancy pairs between different crystallographic sites.[18] The estimated dispersion in $E_a$ ($\simeq \pm 0.04$ eV) is compatible with the temperature variation range explored by our experiment: as temperature is increased, traps with the lowest $E_a$ are less effective and favors the diffusion process with respect to those with higher $E_a$. Thus, the number of effective traps is reduced by thermal energy.

The observed increase of the relaxation time with deposited power during the electric switching is also consistent with the scenario described above. The higher the power, the higher the local Joule heating of the sample that should induce a modification of the effective trap density. However, one may expect that these local heating effects may be quite spatially inhomogeneous, thus a more detailed study of the dependence of applied power and relaxation time is beyond the scope of the present work and left for future studies.

## IV. CONCLUSION

We have studied the time-relaxation characteristics of the nonvolatile resistance state of two different complex oxide junctions, (YBCO or LSMO)/metal, as a function of temperature and applied pulsing power. We find that the remnant resistance relaxation after the switching event evolves to an equilibrium value following a stretched exponential law, with a temperature-independent and a switching-power-independent exponent $n = 0.5$. Surprisingly, we observe that unlike in ordinary thermal diffusion process, the relaxation time $\tau$ increases with increasing temperature and switching power. We argue that this behavior can be understood as due to the diffusion of oxygen ions (or oxygen vacancies) moving on a 2D surface (grain boundaries) with a temperature-dependent density of trapping centers.

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