We investigate the switching kinetics of oxygen vacancies (OV) diffusion in LPCMO-Ag memristive interfaces by performing experiments on the temperature dependence of the high resistance (HR) state under thermal cycling. Experimental results are well reproduced by numerical simulations based on thermally activated OV diffusion processes and fundamental assumptions relying on a recent model proposed to explain bipolar resistive switching in manganite-based cells. The confident values obtained for activation energies and diffusion coefficient associated to OV dynamics, constitute a validation test for both model predictions and OV diffusion mechanisms in memristive interfaces.

Memristive devices (ReRAM) based on oxides compounds are deserving a lot of attention in view of its potential use for next generation of non-volatile memories. Its operation relies in the resistive switching (RS) effect, which is the change in the resistance of the device between two different values, the high resistance state (HRS) and the low resistance state (LRS), by an appropriate electric stimulus. [1, 2] The transition from HRS to LRS is called a set, while the opposite process is defined as reset.

A large variety of oxides has been explored for ReRAM applications, ranging from binary transition metal oxides [3–7] to complex ones – manganites and perovskites-like. [8–14]

In complex oxides based devices the emerged consensus points to the voltage-driven ion migration toward/inward the metal-electrode interfaces, as the relevant mechanisms controlling bipolar RS, i.e the voltage polarity dependent switching mode. [2] In particular, oxygen vacancies (ions) have been proposed as the active agents participating in the bipolar RS effect. [15–19]

Ref. [15] constitutes one of the first evidences supporting oxygen vacancies (OV) diffusion in complex oxides based devices. By electric pulsed $P_{70.7Cao.3MnO_3}$ films deposited in an oxygen-deficient ambient, and analyzing the relaxation in time of the HR state, information on the activation energy for OV diffusion has been obtained.

In addition works searching for ReRAM performance improvement by introducing dopants, have been also reported consistently. As an example, the efficiency of OV migration by Nb doping $Ba_{0.7Sr_{0.3}TiO_3}$ (BST) thin films, was tested in Ref. [20]. As stated in that work, the defects distribution is strongly related to the RS properties, assisting the OV migration and making more efficient the ReRAM operation.

Although the exact microscopic origin behind the RS effect remains elusive, a recent phenomenological model, named voltage enhanced oxygen vacancy (VEOV) migration model, [21] succeeded in reproducing many non-trivial characteristic of bipolar RS experiments carried in complex oxides, under different stimulus protocols. [12–14] The VEOV model incorporates as main ingredients (i) the drift/diffusion of OV along the highly resistive metal/oxide interfaces, where strong electric fields developed and (ii) a linear relation between resistivity and OV concentration. Thus, according to the model, the local change in the concentration of OV near the electrodes modifies the contact resistance, as follows from (ii). Depending on the polarity of the electric field during a switching operation, OV might accumulate or void nanosized regions at the metal/electrodes interfaces, giving place to the reset and set transition respectively.

In spite of the success of the VEOV model in reproducing many experimental features of bipolar resistive switching in complex oxides, the drift/diffusion of OV has been only tested indirectly. [12–14]

The goal of the present work is to probe the switching kinetics proposed in the VEOV model, by studying the response of the switched HR state under thermal cycling in a manganite (LPCMO)-Ag memristive interface. As we describe below the experiments are contrasted with numerical simulations based on the VEOV model [21] from which we extract confident values for the activation energies and diffusion coefficient associated to OV dynam-
ics. In this way a new validation test, for both model predictions and thermal activated Ov diffusion mechanisms, is performed.

We conducted experiments on two manganites La$_{5/8}$Pr$_{1/8}$Ca$_{3/8}$MnO$_3$ (LPCMO)-based samples. This compound exhibits bipolar RS when an external stimuli is applied. Contacts were made by depositing drops of silver paint of 1–2 mm diameter over the LPCMO pellet. Each sample was coupled to a different heating stage in order to perform two completely independent analyses in different laboratories. In setup #1 temperature was controlled by a LakeShore 331 Temperature Controller, having an error lower than 1 K. Setup #2 consisted of an ad hoc heating stage based on a Peltier cell controlled by an Arduino board.

In both experiments the HR and LR states of a single interface – the one corresponding to the contact A in Fig. 1(a) – were measured. However in order to extract information about the Ov switching dynamics, we shall solely analyze the temperature dependence of the HR state, $R_A$. -this election will be justified below, when we describe the Ov dynamics at the interface.

The general procedure employed for the experiments consists of applying a writing reset pulse at an initial temperature and then recording the HR state, $R_A(T)$, during several cyclic temperature sweeps. For each temperature, the resistance was measured applying a small voltage drop between A and B.

In Fig. 2 we present results corresponding to setup #1. We swept the temperature from 323 K to 455 K with a rate of ±10 K/min. Results are plotted in semi-log scale vs. $T^{-1/4}$. Indeed, throughout this work we use the variable range-hopping model to account for the semiconductor-like behavior of the samples,

$$R = R_0 \exp \left( \frac{T_0}{T} \right)^{1/4},$$

where the characteristic temperature $T_0$ depends on the localization of the charge carriers and $R_0$ is a scaling factor. It is true that the temperature range of our experiments is far too small to rule out other transport mechanisms; yet, we find that it matches slightly better to our data, and it has been proposed for manganites in the paramagnetic region. The inset of Fig. 2 shows the time evolution of $R_A$ associated to the temperature sweep.

As it can be seen from Fig. 2 during the first heating ramp, the HR state follows an unexpected path eventually arriving to a stable state that matches the VRH behavior Eq. 1. This stable HR state is reached at $T \approx 373$ K.

We repeated the experiment with setup #2, this time with temperature in a narrower range, from 303 K to 373 K with a rate of up to ±6 K/min. Results are presented in Fig. 3. In principle, a qualitative similar behavior is obtained: below $T \approx 373$ K, the resistance deviates from the VRH prediction. However, in contrast to the data in Fig. 2 after the first heating ramp, the HR did not completely match the VRH prediction.

The above results suggest that there is a temperature activated diffusion that changes the local resistivity in the interface.

Based on the VEOV model predictions, our interpretation of the obtained behavior is the following. The negative polarity of the reset pulse forces Ov to move from the bulk to the interface region, increasing its resistance $R_A$. However, the Ov distribution is far from equilibrium; the reset pulse does not succeed in introducing vacancies homogeneously in all the interface and some nanoscale regions remain void of vacancies. After the reset pulse, the dynamics is governed by diffusion. However at room temperature, the diffusion coefficient $D(T)$ for Ov is too small to effectively compensate the density gradient obtained as a consequence of the reset pulse. As temperature is raised, $D(T)$ rapidly increases enabling former void regions to be inflit with Ov, further producing the concomitant increase in the resistance. This process lasts until the steady configuration is attained. A picture of the proposed mechanism is shown in Fig. 1(b).

To be definite we model a nanoscale regions at the interface with defect of vacancies in one dimension, as a nanoscale regions at the interface with defect of vacancies in one dimension, as a

$$n(x, t = 0) = \begin{cases} 0 & x \in (-x_o, +x_o), \\ n_b & x \in (-L, -x_o] \cup [+x_o, +L), \end{cases}$$

Fig. 1. (a) Scheme of the experimental setup. (b) Model description and proposed mechanism described in the text. While the sample is in the LR state, Ov are mostly in the bulk. Under a reset pulse, the Ov move to the interface region and the HR state is attained. When the pulse is switch off, the temperature activated diffusion process can increase even more the interface resistance.
FIG. 2. (Color online) Experimental results for setup #1 showing the temperature behavior of the contact HR, $R_A(T)$. The arrow indicates the starting direction. At $T \gtrsim 373$ K the sample is fully diffused. The solid blue line is the model fit. Inset: time evolution of $R_A(T)$ and model fit.

where $x$ is the 1-D spatial coordinate and $t$ is the time.

We do not expect the results to be qualitatively different for a different choice of $n(x, t = 0)$, as long as it contains a strong discontinuity. In addition the extension to 2D and 3D is straightforward in cartesian coordinates. Vacancy infilling dynamics is governed by Fick’s second law,

$$\frac{\partial n}{\partial t} = D(T) \frac{\partial^2 n}{\partial x^2}, \quad x \in (-L, +L), \; t > 0. \quad (3)$$

The diffusion coefficient $D(T)$ is thermally activated with activation energy $\epsilon$

$$D(T) = D_0 \exp \left( \frac{-\epsilon}{k_B T} \right), \quad (4)$$

where the prefactor $D_0$ is the diffusion coefficient at infinite $T$ and $k_B$ the Boltzmann constant.

We assume that the reset procedure left the interface with a slightly different $R_0 \equiv R_{0,H}$ respect to the final HR state (see Eq. (1)). The small change from $R'_{0,H}$ to $R_{0,H}$ is due to the infill of vacancies. Following the VEOV model assumption, we then consider a linear dependence between the value of $R_0$ and the total number of vacancies in the former void region, $N_i = \int_{-x_o}^{+x_o} n(x, t)dx$

$$R_0 \approx R'_{0,H} + B \; N_i, \quad (5)$$

where $R'_{0,H}$ and $B$ are two arbitrary values.

Solving Eqs.(2)-(4) and using Eqs.(1) and (5), we obtain that

$$R(t) \approx \left[ R'_{0,H} + B \left( \frac{x_o}{L} - \sum_{k=1}^{\infty} \phi_k \psi(t) \right) \right] \exp \left( \frac{T_0}{T} \right)^{1/4}, \quad (6)$$

where

$$\phi_k = \left( \frac{\sqrt{2} \sin \left( k \pi \frac{x_o}{L} \right)}{k \pi} \right)^2, \quad (7)$$

FIG. 3. (Color online) Experimental results for setup #2 showing the temperature behavior of the contact resistance $R_A(T)$. The arrow indicates the starting direction. The sample continues the diffusion process for more than one cycle. The solid blue line is the model fit. Inset: time evolution of $R_A(T)$ and model fit.

FIG. 4. (Color online) Diffusion coefficient as a function of temperature. The activation energy obtained is $(0.18 \pm 0.03)$ eV. Inset: time evolution of the HR state at $353$ K. Two consecutive diffusion processes are observed at this temperature.
\[ \psi(t) = \exp \left\{ -\frac{(k\pi)^2}{L^2} \int_0^t \exp \left( -\frac{-\epsilon}{k_B T(t')} \right) dt' \right\}. \quad (8) \]

We fit Eq. (6) to the experimental measurements of \( R_A \) (see Figs. 2 and 3). First, \( T_0^{1/4} \) was obtained from stable regions in the experiments presented in Figs. 2 and 3, i.e., long after transients have passed. Fitted values of \( T_0^{1/4} \) were in the range of \([45,57]\) K\(^{1/4}\). Using Eq. (6), we then looked for the values of \( x_o/L, D_0/L^2 \) and \( \epsilon \) which minimized the mean square error between the experimental results and simulated values.\cite{27}

Among different experiments, we obtained \( x_o/L \sim 0.5 \). In the case of \( \epsilon \), the height of the barrier that maintains the system in a metastable out-of-equilibrium condition immediately after the writing pulse- we got values ranging between 0.3 – 1.3 eV. The equilibrium cannot be achieved at room temperature; indeed, it is necessary to increase the thermal energy by \( \sim 25\% \) in order to significantly activate the displacement of Ov. Regarding the dispersion in the values, we hypothesize that it is evidencing a broad distribution of anchoring energies instead of the mono-energetic level considered in our model. Moreover, experimentally we have little control (if any) in the way this broad distribution of states is infilled.

Extracting \( D_0/L^2 \) is not straightforward because it is exponentially affected by the estimated value of \( \epsilon \). In fact, there is a strong nonlinear covariance between \( \epsilon \) and \( D_0/L^2 \) in the proposed minimization method.

Therefore, we estimated \( D(T)/L^2 \) from the measured time evolution of resistance for a fixed temperature and the first term in Eq. (6). In the inset of Fig. 4, we present an example of the evolution of the resistance after setting the HR state at 353 K. We hypothesize that the two successive exponential-like-increase intervals could correspond to the sequential infilling of two vacancy-void regions. Indeed, we also obtained good fits (not shown here) of Figs. 2 and 3 with a two-vacancy-void-region model.

Fig. 4 displays the results for six temperatures (two sets of measurements for each temperature) together with the fit from which we extracted \( \epsilon \sim 0.18 \) eV, \( D_0/L^2 \sim 90 \) s\(^{-1}\).

A value of \( D_0 \sim 2 \cdot 10^{-7} \) cm\(^2\)/s is obtained by setting \( L = 500 \) nm, which is fully consistent with reported oxygen diffusion constant in perovskite- based oxides.\cite{15,28}

In the case of \( \epsilon \) and \( T_0 \), the fitted values are of the order but slightly smaller than those reported in literature.\cite{24}

In summary, by performing temperature sweeps of the stable HR states in a perovskite- based memristive interface, and relying on simple assumptions of the VEOV model, we have extracted confident values of relevant parameters involved in the kinetics of Ov diffusion. We have found that the electric pulse might set the system in a metastable configuration that relax after overcoming a barrier of 0.3 – 1.3 eV. We have also extracted diffusion coefficient values for oxygen vacancies that are consistent with literature, supporting that they are the responsible for the resistance modulation at the interface. Moreover, these findings support a switching dynamics completely in-line with the VEOV model.

Finally, the metastability here reported could be also further exploited in resistive switching binary memories, as it actually increases the resistance of the HR state (i.e., it improves the ON/OFF ratio).

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