Sign and magnitude of electroresistance in BaTiO$_3$ ferroelectric thin film capacitors are modulated by modifying the duration of the writing electric field pulses and the measurement temperature. The results are explained in the framework of electronic band structure reconfiguration caused by the polarization switching and electric-field-driven ionic motion in the ferroelectric.

**Keywords**: ferroelectric junctions, BaTiO$_3$ films, resistive switching, ionic motion, memristors.

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**Synergetic electronic and ionic contributions to electroresistance in ferroelectric capacitors**
Synergetic Electronic and Ionic Contributions to Electroresistance in Ferroelectric Capacitors

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Advanced use of ferroelectric capacitors in data storage and computing relies on the control of their electrical resistance (electroresistance, $ER$) by the change of the electrostatic potential profile across the capacitor occurring upon electric field-driven polarization switching. Here we report on the observation that BaTiO$_3$-based capacitors, sandwiched between metallic Pt and La$_{12/3}$Sr$_{1/3}$MnO$_3$ electrodes, display a large $ER$, whose magnitude (up to $10^4$ % at room temperature) and sign ($ER > 0, ER < 0$) are determined by the writing pulse duration and temperature. Temperature-dependent measurements have been instrumental to obtain evidence of the presence of a thermally activated process coexisting with the electronic changes produced by ferroelectric polarization switching, both contributing to $ER$.

Detailed analysis allows concluding that the thermally activated process can be attributed to field-assisted ionic motion. It is argued that the relative balance between purely electronic and ionic diffusion processes modulate the height of the interfacial Schottky barriers and, consequently, are responsible for the observed variations of magnitude and sign of electroresistance.
1. Introduction

Ferroelectric tunnel capacitors are considered promising candidates for next generation low consumption memory devices and building blocks for circuits with endless potentialities in present and future applications, from multilevel data storage to neuromorphic computing.[1-3] Essentially, these devices consist on a metal/ferroelectric/metal (M/FE/M) structure, where two different states of electric resistance are obtained by switching the direction of the polarization ($P$) of the ferroelectric barrier. Indeed, huge resistance changes (so called Electroresistance, $ER$) as large as $10^4 \%$ have been recorded in metal/BaTiO$_3$ (BTO)/metal capacitors or similar structures.[1,2,4-15]

In spite of the simplicity of the device, deep understanding of its response is challenging. Shortly, if only electronic processes are considered, the scenario for a ferroelectric tunnel device (few nanometer thick ferroelectric barrier) is as follows.[16-18] The ferroelectric material is embedded within two metal electrodes ($M_{1,2}$) of given work-functions creating an energy barrier ($E_0$) for electrons to cross the ferroelectric. The $M_{1,2}$ electrodes also provide charges to screen the ferroelectric surface charge. If different metallic electrodes are used, the electronic screening length ($\delta_{1,2}$) is not identical at both sides of the junction, and an electric field ($E$-field) is created within the ferroelectric layer of permittivity $\varepsilon$ that reverses its direction when $P$ is reversed. The internal $E$-field changes the height [$\Delta \phi \approx \pm P(\delta_1 - \delta_2)q/\varepsilon$] (q is the elementary charge) of the barrier ($E_0$). Therefore, two different barriers $E_0 \pm \Delta \phi$ are obtained when reversing $P$ and consequently the junction resistance differs for both states [$R(P^\downarrow) \neq R(P^\uparrow)$]. The corresponding change of junction resistance named $ER$ [$ER = R(P^\downarrow) - R(P^\uparrow) / \min (R(P^\downarrow), \ R(P^\uparrow))$] is the figure of merit of the junction. The exponential dependence of the tunneling current on the barrier height accounts for the large ER values observed and its sign is dictated by the screening lengths of the electrodes. This simple model has been widely used to describe ER of ferroelectric
tunnel junctions, most commonly fabricated by growing epitaxial ferroelectric layer (perovskite oxide structure) on lattice-matching (La$_{2/3}$Sr$_{1/3}$)MnO$_3$ (LSMO) or SrRuO$_3$ metallic perovskite electrodes.$^{[4,18–20]}$ In presence of defects, such as oxygen vacancies, the ferroelectric layer can be viewed as a doped semiconductor and the polarization-dependent internal $E$-field can change the width of the depletion layer in Schottky barriers at interfaces.$^{[7,21–23]}$ thus changing also the effective barrier width. In this case, $P$ reversal induces a simultaneous change of barrier height and width, both contributing to ER.$^{[7]}$

Alternatively, metal/ferroelectric/semiconducting (M/FE/SC) structures have also been explored. Interestingly, it has been reported that the polarization-dependent depletion-layer width within the n-doped semiconducting electrode, Nb:SrTiO$_3$, results in large $ER$, which may reach a giant $ER$ ($\approx 10^5\%$).$^{[24]}$ Therefore, the electronic nature (p or n-type) of the ferroelectric$^{[25,26]}$ and the electrode$^{[27]}$ modulates the magnitude of $ER$ and its sign.

Whereas the models above collect fundamentally electronic reconstruction processes, the potential role of ionic motion under $E$-field was put forward by D. J. Kim et al.$^{[28]}$ or R. Soni et al.$^{[29]}$ by claiming that the $E$-field could promote redox processes at interfaces. The presence of mobile oxygen vacancies within the ferroelectric layer may largely impact $ER$.$^{[30]}$ Indeed, M. Li et al.$^{[31]}$ and others$^{[32]}$ observed largely different $ER$ depending on the growth conditions (oxygen pressure) of the ferroelectric layer (BTO), and argued that a key ingredient was the oxygen-vacancy screening of $P$ and the resulting modifications of the interfacial Schottky energy barriers. The picture was expanded further by Q. H. Qin et al.$^{[33]}$ by claiming that the observed $ER$ basically comes from an electronic reconstruction at the LSMO electrode: an $E$-field controlled oxygen motion within the LSMO layer produces a hole-depletion, which results in a metal to insulator transition with the concomitant increase of the tunneling width. Consequently, it was argued that the observed $ER$ is not primarily related to the ferroelectric polarization but it results from purely ionic motion within the electrode.
This brief summary illustrates the existing debate between purely electronic and ionic processes, and how challenging is to discriminate them in the \textit{ER} response of ferroelectric capacitors. Understanding the mechanisms contributing to \textit{ER} is crucial for a proper engineering of ferroelectric switching devices as those considered in advanced applications such as crossbar resistive switching devices\textsuperscript{[34]} or as a building blocks for neuromorphic computing.\textsuperscript{[35]}

Here, we contribute to solve this puzzle by reporting on the \textit{ER} measured on Pt/BTO/LSMO capacitors. The bottom line of our strategy is that polarization-controlled electronic reconstructions and ion motion can both contribute to the electroresistance under the influence of the applied \textit{E}-field. Ions or other charged-defects, most likely oxygen vacancies (V\textsubscript{O}), may drift under the effect of \textit{E}-field,\textsuperscript{[36,37]} and modify the electrostatic boundaries conditions including polarization screening and Schottky barrier at interfaces.\textsuperscript{[22]} As ionic drift is temperature and time dependent, instrumental for the proposed research is to explore the influence of the duration of the writing voltage (so called \textit{writing time}, \( \tau_w \)) and the temperature on \textit{ER}. Therefore, we report on the \textit{ER} of Pt/BTO/LSMO capacitors where the BTO thickness has been varied gradually (\( \approx 35 - 110 \) nm) and compared with \textit{ER} of ultrathin thin (few nanometers) BTO barriers. It turns out that for (relatively) thin films (\( \approx 35 \) nm), \textit{ER} is observed to be positive (\( \textit{ER} > 0 \)). However, negative \textit{ER} is observed in thicker barriers (\( \approx 110 \) nm). In fact, for films of intermediate thickness (\( \approx 70 \) nm), at room temperature, a change of sign of \textit{ER} (from \( \textit{ER} > 0 \) to \( \textit{ER} < 0 \)) is observed depending on the duration of the writing pulse. A key discovery is that the critical time where the \textit{ER} sign reversal occurs (\( \tau_{\text{CRIT}} \)) depends on the measuring temperature and on the film thickness. These findings allow disentangling purely electronic from ionic effects in a device and to achieve a more complete understanding of the \textit{ER} phenomenon in ferroelectric capacitors.

2. Results

We will first describe the results obtained from a Pt/BTO/LSMO capacitor of BTO intermediate thickness (\( t_2 = 70 \) nm). The sample has been connected to the voltage source and measuring set-up via a
top Pt electrode; the bottom electrode LSMO was grounded (Figure 1a). We first focus on the change of conductivity (evaluated from the I-V characteristics) as a function of the amplitude (V) and duration \( (\tau_w) \) of the writing voltage pulse \( V_w \) (sketch in Figure 1b). In Figure 1c, we show the reading I-V curves collected on junction \( J_1 \) \( (J_N \) is the junction code in the sample) after prepoling the device with +8 V (red) and -8 V (black) pulses of duration \( \tau_w = 20 \mu s \) (solid lines) and \( \tau_w = 20 \) s (dotted lines). Notice that the current scale for \( \tau_w = 20 \) s (dotted lines) has been multiplied by 1/100. Inspection of data in Figure 1a provides important insights. First, there is a significant change of conductance of the device depending on the sign of prepoling voltage. Second, after a short writing pulse \( (\tau_w = 20 \mu s) \) the resistance is smaller for \( V_w = -8 \) V than for \( V_w = +8 \) V. That is, the OFF state is observed for \( V_w > 0 \). This result is similar to that obtained in ultrathin tunnel barriers,\(^ {1,2,7,28,38,39} \) although here direct tunneling is disregarded due to the film thickness. Third, after a long writing pulse \( (\tau_w = 20 \) s) the resistance of the junction is radically reduced (roughly \( \approx 1/100 \)). The resistance reduction indicates that the application of a long writing pulse generates a kind of soft breakdown (see Supplementary Information S1), likely associated to ionic motion (see below), which gives rise to \( ER \). Fourth, for \( \tau_w = 20 \) s, the resistance is smaller for \( V_w = +8 \) V than for \( V_w = -8 \) V. That is, the OFF state is observed for \( V_w < 0 \). We quantify the electroresistance by \( ER = (R^+ - R^-)/\min(R^+, R^-) \) where \( (R^+, R^-) \) indicate the resistance measured for \( V^+ \) \( (V > 0) \), \( V^- \) \( (V < 0) \) and \( \min(R^+, R^-) \) their minimal value. Accordingly, \( ER > 0 \) is positive for \( \tau_w = 20 \mu s \) but the \( ER \) sign is reversed \( (ER < 0) \) for \( \tau_w = 20 \) s. Therefore, data indicates that, contrary to the common wisdom, the sign of \( ER \) is not simply dictated by the nature of the electrodes, and different \( ER \) sign can be observed in the same sample.
Figure 1. (a) Sketch of the Pt/BTO/LSMO junctions and electrical measurement configuration. (b) Sketch of the I-V measuring protocol, for writing and reading junction resistance. The delay time ($\tau_D$) is fixed to 1 s for all the experiments of the present work. I-V characteristics of the 70 nm – BTO sample after voltage pulses of $V_w = \pm 8$ V and $\tau_w = 20$ $\mu$s (black and red solid lines), and $\tau_w = 20$ s (black and red dotted lines, note the current has been divided by 100).

To gain insight into this intriguing change of sign of electroresistance, we first explored the ER as a function of poling voltage $ER (V_w)$ using suitable voltage-pulses train (see Supplementary Information S2). In order to put into context the results and main message of the present manuscript, we first show in Figure 2a,b the $ER (V_w)$ loops of the 4 nm BTO barriers, written with $V_w$ pulses of duration $\tau_w = 20$ $\mu$s and $\tau_w = 20$ s, respectively. We note that the junctions display a remarkably large ER ($\approx 8 \times 10^4$ %) irrespective of $\tau_w$. We stress that this ER value is among the largest values reported for similar junctions at room-temperature.$^{[7,38,39]}$ It can also be appreciated that the loops are anticlockwise for any writing time and have a remarkable squareness, reflecting the stability of the ON/OFF states and the quality of the films.

We now describe the corresponding results obtained on the Pt/BTO/LSMO capacitor having a BTO layer of intermediate thickness ($t_2 = 70$ nm). The results for $\tau_w = 20$ $\mu$s and $\tau_w = 20$ s are shown in Figures 2c,d. The $ER (V_w)$ loops in Figures 2c and 2d clearly bear some similitudes with those observed in tunnel devices. However, consistently with data in Figure 1c, two main differences emerge: a) the electroresistance of the shortly-written junction (Figure 2c) is only of about 200 %, which is about $10^2$ smaller than that of tunnel barriers (Figures 2a,b) and the loop is substantially pinched, and b) the loops are anticlockwise for $\tau_w = 20$ $\mu$s, as in tunnel barriers, but clockwise for $\tau_w = 20$ s (Figure 2d),
reflecting the change of sign of the ER, already noticed in Figure 1c. When using \( \tau_w = 20 \text{ s} \) the OFF state is written after \( V_w < 0 \), the ER increases up to about \( 4.6 \times 10^3 \% \), the squareness of the ER\( (V_w) \) loop is definitely improved and the ON/OFF states robustly persists until \( V_w \approx \pm 6 \text{V} \) (Figure 2d). On the other hand, from the comparison of the resistance values in Figures 2c and 2d, it is obvious that when using longer writing pulses, the device resistance is reduced as already observed in Figure 1c.

![Figure 2](image_url)

**Figure 2.** (a,b) ER loops collected with \( \tau_w = 20 \mu \text{s} \) and \( \tau_w = 20 \text{ s} \), respectively for the \( t \approx 4 \text{ nm} \) BTO sample. (c,d) ER loops collected with \( \tau_w = 20 \mu \text{s} \) and \( \tau_w = 20 \text{ s} \), respectively for the \( t = 70 \text{ nm} \) sample. (e,f) \( J-V \) loops following the -8 V to +8 V to -8 V path measured at 25 kHz and 10 Hz.

To disclose the mechanism behind the distinct response of the junctions depending on \( \tau_w \) observed in Figures 2c and 2d, we recorded the \( J-V \) loops up to 8 V at different frequencies \( (f) \). The results
collected using \( f = 25 \text{ kHz} \) and 10 Hz are shown in Figure 2e and 2f. The selected frequencies were chosen by finding a compromise between being similar to the writing time \( \tau_w \) used in Figures 2c and 2d, and large enough to produce a sizable displacive current contribution. In the \( J-V \) curve recorded at 25 kHz (Figure 2e) one can appreciate the polarization switching peaks. It can be noticed that the voltage values at which the switching peaks occur (dashed lines around +4 V and -3.5 V), fingerprints of the coercive fields (\( V_{C^+} \) and \( V_{C^-} \)) of the ferroelectric film, are closely coincident with the voltages where the corresponding \( ER(V_w) \) loop (Figure 2c) display the largest change of resistance. Further analysis allows to conclude that the current peaks of Figure 2e correspond to ferroelectric switching (see Supporting Information S3). The shift of \( J-V \) along the positive voltage indicates the presence of an internal \( E \)-field favoring upwards polarization state (see Supporting Information S4). Therefore, we conclude that the \( ER \) recorded at high frequency (25 kHz) (short writing time) is intimately connected with the ferroelectric polarization switching. Interestingly, this conclusion is at odds with what is observed in the \( J-V \) curves recorded at lower frequency (\( f = 10 \text{ Hz} \)) of Figure 2f. Indeed, the switching peaks appear at \( \approx 2 \text{ V} \) and \( \approx -1 \text{ V} \). The fact that the ferroelectric switching peak occurs at lower voltage when reducing the measuring frequencies is in agreement with the well-known dependence of \( V_C \) of frequency observed in ferroelectrics. More interesting is the observation that the abrupt change of conductance in the \( J-V \) curves of the junctions occurs at significantly larger voltages that the corresponding \( V_{C^+} \) and \( V_{C^-} \) (see Figure 2d). This observation suggests that when junctions are driven by long voltage pulses, the observed changes of resistance are not primarily ruled by the polarization switching. Data in Figures 2c,d,e,f correspond to junction J1. Similar \( ER \) data have been collected in other junctions on the same sample (see Supporting Information S5).

To get a further insight, we determined the electroresistance of the samples as a function of \( \tau_w \) and temperature. In Figure 3a, we show data recorded at room temperature (RT), using writing times \( \tau_w \) spanning more than 9 orders of magnitude (from 80 ns to 100 s). It can be appreciated that \( \tau_w \) longer
than \( \approx 100 \) ns are required to produce visible changes of the junction resistance. Note that the \( \tau_w \approx 100 \) ns time limit is below the time constant of the measuring circuit (see Supporting Information S6). Therefore, the time constant of our circuit limits the observation of switching. Indeed, \( ER \approx 0 \) for \( \tau_w = 100 \) ns and \( ER \) gradually increases up to 10 ms. In this \( \tau_w \) range, \( ER \) is positive and the corresponding \( ER(V_w) \) loops are similar to that of Figure 2c. Data in Figure 3a also indicate that \( ER \) reduces in magnitude when \( \tau_w \) is further increased above 10 \( \mu s \) until zeroing at some critical writing time \( \tau_{CRIT}(RT) \approx 200 \) ms. \( ER \) eventually increases again for \( \tau_w > 200 \) ms but now having a negative \( ER \), that is: \( R^+ < R^- \). This behavior is in agreement with data in Figure 2d, where the \( ER(V_w) \) loop collected \( \tau_w > 10 \) s was depicted.

**Figure 3.** Resistance times area after prepolarizing the junction (writing) with \( V_w = -8V/+8V \) pulses of different duration \( \tau_w \) at different temperatures: (a) RT, (b) 200 K and (c) 420 K (junction J3). The arrows indicate the critical writing time (\( \tau_{CRIT} \)) where \( ER \) changes of sign.

Data collected at higher temperature follow the same trend, that is: \( ER \) changes its sign when increasing \( \tau_w \), as illustrated in Figure 3c where data collected at 420 K are shown. When comparing to data collected at room temperature, the most perceptible variation is that the critical writing time for the change of sign of \( ER \) shortens when increasing temperature; in fact reduces by about 3 orders of magnitude at 420 K (\( \tau_{CRIT}(420 \) K) \( \approx 1 \) ms). See in Supporting Information S7 similar data and behavior in other junctions. In contrast, data recorded at lower temperature (200 K, Figure 3b) does not show any change of sign of \( ER \) but only indications of junction failure at the longest writing time. Overall,
these data suggest that different mechanism may contribute to the ER of the junctions, whose relative weight would be temperature-dependent.

**Figure 4.** (a) Dependence of the electroresistance \[ ER = (R^+ - R^-)/\min(R^+, R^-) \] on writing time \( \tau_w \) at some selected temperatures, of \( J_3 \) junction of the \( t_2 = 70 \) nm sample. Note that the negative sign of \( \log(ER) \) corresponds to negative ER sign. (b) Invers temperature dependence of \( \tau_{\text{CRIT}} \). The dashed line is a guide-to-eyes. (c) Dependence of ER dependence on the writing time \( \tau_w \) of samples having different BTO thicknesses \( (t_1 = 35 \) nm (purple), \( t_2 = 73 \) nm (black) and \( t_3 = 110 \) nm (pink)), measured at a fixed temperature (450 K).

To derive the temperature dependence of \( \tau_{\text{CRIT}} \), we have explored the temperature dependence of ER in the 200 - 450 K range. In Figure 4a we show \( ER(\tau_w) \) data collected at 200, 300 and 450 K. Data for other temperatures are included in Supporting Information S8. Data in Figure 4a indicate that the change of sign of ER occurs at progressively shorter (longer) writing times when the sample is warmed (cooled). In fact, at the lowest temperature, \( ER \) remains positive for all explored \( \tau_w \). Notice that, as mentioned, using writing times longer than 10 s, typically produces irreversible damage of the junction.

In Figure 4b, we plot the temperature dependence of \( \tau_{\text{CRIT}} \) recorded on the same junction. The corresponding raw \( ER(\tau_w, T) \) data are in Supporting Information S8. The strong \( \tau_{\text{CRIT}} \) dependence on temperature suggests that thermally activated mechanisms could be at play.

If the observed variation of the \( ER \) with \( \tau_w \) and temperature reflect the dynamics of the electronic and/or ionic species within the BTO barrier eventually modifying the electronic properties of the metal/ferroelectric interfaces, one could suspect that at some fixed temperature, \( \tau_{\text{CRIT}} \) should depend the
BTO thickness. Therefore, we have performed similar measurements on capacitors having different BTO barrier thicknesses ($t_1 = 35$ nm and $t_3 = 110$ nm). In Figure 4c, we show the dependence of $ER$ on $\tau_w$ for $t_1$, $t_2$ and $t_3$ samples at 450 K (raw data in Supporting Information S9). This particular temperature value is selected because at this temperature, the $t_1$ and $t_2$ barriers display the change of sign of $ER$ within the available $\tau_w$ range and allows monitoring the thickness dependence of $\tau_{\text{CRIT}}$. Data in Figure 4c, show that the change of sign occurs at progressively shorter time, which is: $\tau_{\text{CRIT}}$ get shorter, when increasing BTO thickness. In fact, for the thickest sample ($t_3 = 110$ nm) only the $ER < 0$ state can be seen at the selected temperature. In short, the room temperature $ER(\tau_w)$ data display a fully consistent behavior with the 450 K data (see Supporting Information S10).

3. Discussion

Overall the experimental results strongly suggest that the ER of BTO capacitors of thicknesses within the 35 – 110 nm range, appears to be ruled by two different mechanisms that dictate either $ER < 0$ or $ER > 0$ and whose strength depends on the duration of the writing pulse and measuring temperature. To rationalize these observations, we start by analyzing first the temperature dependence of $\tau_{\text{CRIT}}$, which fixes the lower bound for the time scale where the slowest process governs the resistive switching mechanism of the junction.

The strong dependence of $\tau_{\text{CRIT}}$ on temperature suggests that a thermally activated process, probably associated to ionic motion, f.i. oxygen vacancies$^{[41–46]}$ are responsible for the negative $ER$ at $\tau_w >> \tau_{\text{CRIT}}$. If one assumes that $\tau_{\text{CRIT}}$ corresponds to the diffusion time of charges across the whole BTO film thickness to reach the interface, then $\tau_{\text{CRIT}} \approx 100 \mu$s (as observed for the $t_2$ films at 450 K) corresponds to a mobility $\mu \approx 5 \times 10^{-8}$ cm$^2$/Vs, at $V_w = 5$ V. This value is orders of magnitude smaller than typical electronic mobilities in similar oxides ($\approx 1$ cm$^2$/Vs),$^{[44]}$ thus allowing to identify ionic drift, usually oxygen vacancies in titanates,$^{[41]}$ as the main mechanism responsible for the observed change of sign.
Therefore, we should build band diagrams for the LSMO/BTO/Pt structures where electronic reconstructions are governing the response at short writing pulses and where ionic motion plays a role at long writing pulses. We start by recalling that Schottky barriers shall be formed at the interfaces in the LSMO/BTO/Pt capacitor. A Schottky barrier shall produce a rectifying response (Schottky diode). The experimental data, see for instance Figure 1c, does not show a rectifying response but slightly asymmetric non-linear conductance. Therefore, the LSMO/BTO/Pt device cannot be modeled as a single Schottky diode. Indeed, the measured device structure corresponds to a back-to-back arrangement of Schottky diodes formed at the corresponding LSMO/BTO and BTO/Pt interfaces. However, in this case, if only thermionic injection over the Schottky barrier is considered, the \( I-V \) curves should display an error-function like behavior, with a saturation current (corresponding to the reverse current of each diode) occurring for both polarities because one of the diodes is always reversed and limits the charge flow across the device.\(^{[47]}\) Again this is not the shape of the \( I-V \) curve in Figure 1c. This simple analysis shows that other charge transport mechanisms are involved in the 70 nm LSMO/BTO/Pt devices. It can be shown that including a thermionic tunnel channel for charge transport across the depletion layer in BaTiO\(_3\), as early observed in heavily doped semiconductors,\(^{[47-49]}\) allows to simulate \( I-V \) curves that mimic the experimental ones\(^{[50]}\) (See Supplementary Information S11).

Here, we restrict to a qualitative description of the barrier response, detailed as follows.
Figure 5. (a) Sketch of the device and polarization for $V_w > 0$. (b) Sketch of the energy band diagram near the BTO/LSMO interface. If polarization is not taken into account, the band diagram is as indicated by the dashed line. If polarization is taken into account, for $V_w > 0$, it points to LSMO, the band diagram is as indicated by the solid line. (c) Sketch of amplitude and sign of $ER$ loop resulting from the proposed scenario for short writing times when ferroelectric polarization and residual depoling field are relevant; $ER$ is small and positive (d) Sketch of the device and the electric field produced for $V_w > 0$. Accumulation of oxygen vacancies (rhombi) at the BTO/LSMO interface for $V_w > 0$ is also depicted. (e) Sketch of the energy band diagram near the BTO/LSMO interface for no applied voltage (dashed line) and for $V_w > 0$ (solid line). (f) Sketch of amplitude and sign of $ER$ loop resulting from the proposed scenario for long writing times when oxygen vacancies are relevant; $ER$ is large and negative.
If BTO is assumed to be an n-type semiconductor, and resistance measurements are performed with a $V^+$ on Pt, the LSMO interface is in reverse and thus the corresponding Schottky barrier shall dominate the $ER$ of the LSMO/BTO/Pt capacitor. Accordingly, we focus our attention on the LSMO/BTO interface. In Figure 5a, we sketch the LSMO/BTO/Pt capacitor. After prepoling the BTO film with $V_w > 0$, the polarization points towards LSMO ($P^+$, red arrow). In Figure 5b, we sketch a Schottky barrier of height ($\Phi_{SB}$) at the LSMO/BTO interface for unpolarized BTO (Figure 5b, dashed line). When $P^+$ points towards LSMO, the polarization is screened by charges at the LSMO electrode and/or by a charge rearrangement at the depletion layer within BTO. As screening by LSMO is expected to be more efficient, it will rule the changes in the barrier height and will mimic the results obtained in the tunnel barriers (see Supporting Information S12), thus producing an increase of $\Phi_{SB}$ (Figure 5b, solid line) setting the OFF state. Reversing $P$ should result in a reduction of $\Phi_{SB}$ (not depicted) and correspondingly to an ON state. Accordingly, OFF and ON states should be observed for $V^+$ and $V^-$, respectively, as depicted in Figure 5c, which is agreement with our observation (Figure 2c). In this scenario, the time response of the device is mainly dictated by the polarization switching process, which is known to be substantially fast. It thus follows that the observed $ER > 0$ [OFF(ON) for $V^+(V)$] at short writing times, reflects the ferroelectric polarization reversal and the concomitant modulation of the Schottky barriers ($\approx 0.12$ eV and 0.7 eV for LSMO and Pt sides).

We turn now to the response of the junctions to long writing pulses. In Figure 5d, we sketch the LSMO/BTO/Pt capacitor when an external $E$-field ($E_{ext}$) has been applied for a long time. As we have experimentally observed that for long writing time, the resistive switching is not dictated by the polarization reversal, we omit $P$ in the sketch and we only indicate $E_{ext}$. In Figure 5d, we depict $E_{ext}$ (towards LSMO) for $V_w > 0$ (blue arrow). The positively charged oxygen vacancies under the action of $E_{ext}^+$, will be accumulated at the BTO/LSMO interface (solid rhombi) thus producing a reduction of $\Phi_{SB}$ and therefore the ON state is obtained (Figure 5e, solid line). For $V^-$, the reverse situation holds and
thus the device is in the OFF state (Figure 5e, dashed line). It is worth noticing here that local heating associated to the larger thermal energy involved when using longer pulses (Supporting Information S13) could assist and even exacerbate ionic or vacancy motion as it is well documented in some resistive switching devices.\textsuperscript{[55]} The mechanism proposed for negative $ER$ observed at $\tau_w >> \tau_{CRIT}$ is similar to that proposed to describe resistive switching in TiO$_x$\textsuperscript{[56,57]} and SrTiO$_3$ films.\textsuperscript{[58]} Thus for long writing pulses, although the ferroelectric character of the film is preserved (see Supporting Information S3), the observed electroresistance does not stem from polarization reversal but from ionic motion, which produces even larger resistance changes than those produced by polarization switching (see Figures 2c and d). Overall, the resulting, $ER(V_w)$ loop, sketched in Figure 5f, is agreement with our observation (Figure 2d).

The model described above accounts for the reversing of ON/OFF states as a function of $\tau_w$, as observed in the $t_2 = 73$ nm junction, and strongly suggest that polarization reversal and ionic motion processes coexist and contribute to the $ER$. It thus follows that, if the BTO films are thinner (35 nm, as reported here), the prevalence of ionic motion will become perceptible for large $\tau_w$, as its electroresistance for shorter writing times (polarization dominated) is larger. The relatively larger electroresistance of the $t_1 \approx 35$ nm) sample is more visible in the room temperature data (Figure S10a,b in Supporting Information S10). Therefore, the corresponding $\tau_{CRIT}$ is also larger, as observed.

Naturally, the reverse situation should occur for thicker BTO barriers (110 nm in the present case) and consistently, shorter $\tau_w$ is required to write distinct resistance states and the ionic contribution ($ER < 0$) prevails at any practical $\tau_w$. The same picture accounts for the observed dependence of $\tau_w$ on temperature. Indeed, when cooling (warming) the junctions, the activated ionic motion is hampered (reinforced) and thus the electronic response ($ER > 0$) (ionic response $ER < 0$) prevails up the longest (shorter) writing time, as observed in Figure 4a.
4. Conclusions

Overall, the experimental results reported here indicate that the sign and magnitude of the electroresistance on BTO capacitors of intermediate thickness (> 35 nm) reflect different contributions corresponding to different physical processes. Instrumental to this discovery has been the availability of experimental electroresistance data at different temperatures (up to 450 K) which have provided clear indications of a thermally activated process contributing to govern the electroresistance. We have observed that whereas at short writing times, a modest (≈ 10² %) positive electroresistance is observed, its sign is reversed for longer writing times and its magnitude increases, reaching large ER values (≈ 4.6 10³ %) which are comparable to those observed in tunnel BTO barriers, although completely different conduction mechanisms apply. The presence of two time scales for the electroresistance could be of relevance for the design and exploitation of ferroelectric-based resistive switching devices. For instance, the observed ER(τW) response is reminiscence of second-order memristors⁵⁹ such those used to implement biorealistic synapses.⁶⁰ The results presented here, show that temperature-controlled ER provide, achievable exploiting self-heating mechanisms, offer a new toggle to tune the resistive switching and the functionality of ferroelectric capacitors.⁵⁵

5. Experimental Section

Sample preparation. Ferroelectric capacitors are fabricated by pulsed laser deposition by growing thin films of ferroelectric BTO of thicknesses t₁ ≈ 35 nm, t₂ =70 and t₃ =110 nm on top of an epitaxial metallic La₀.₆₇Sr₀.₃₃MnO₃ (LSMO) (30 nm) layer deposited on SrTiO₃(001) substrates. Two series of samples (I & II) are grown under nominally identical conditions and having similar thickness. A nanometric tunnel BTO (t₀ ≈ 4 nm) has also be grown for comparative purposes. Films thickness is determined from the growth rate calibration and the used laser pulses. Details of growth conditions and structural characterization of the films is reported elsewhere.⁶¹–⁶⁴ Square Pt electrodes (20 nm thick,
area 3600 μm² for t₁, t₂ and t₃ samples and 250 μm² for t₀) are subsequently deposited ex-situ, by sputtering, on the BTO film surface by using a shadow mask. About 300 electrodes, labelled Jₙ, where N is the reference number for each electrode, are prepared simultaneously. Data in the manuscript refer to samples of series I. Consistent results are obtained using samples of series II, as shown in Supporting Information S14.

_Electrical characterization._ To perform electrical measurements, the bottom electrode is grounded and the V(t) signal is applied to the top electrode (Pt) as shown in Figure 1a. The polarization state of the junctions is then set (written) by applying a triangular pulse of a given amplitude and duration (Vᵢₚ, τᵢₚ). Afterwards, current-voltage J-V characteristics is collected by sweeping the voltage from -500 to 500 mV as shown in Figure 1b. The junction resistance is calculated at 100 mV after setting the polarization state. When a different reading voltage is used, it is explicitly mentioned in the manuscript. In the experiments reported here the delay time (τ₈) between writing and reading is 1 s. Measurements are done at room temperature using an AixACCT TFAnalyser2000 platform. High temperature measurements are performed using LakeShore EMPX_HF multifunctional probe station. The base pressure of the vacuum chamber reaches up to 10⁻⁶ mbar while performing temperature dependent experiments.

**Acknowledgments**

Financial support from the Spanish Government, through the “Severo Ochoa” Programme for Centres of Excellence in R&D (SEV-2015-0496) and the MAT2017-85232-R, MAT2014-56063-C2-1-R, and MAT2015-73839-JIN projects, and from Generalitat de Catalunya (2017 SGR 1377) is acknowledged. M.Q. is financially supported by China Scholarship Council (CSC) with No. 201406890019. M.Q. work has been done as a part of her Ph.D. program in Materials Science at Universitat Autònoma de Barcelona. I.F. acknowledges RyC contract RYC-2017-22531. The research leading to these results has received funding from “la Caixa” Foundation (code LCF/BQ/IN17/11620051).

**References**

Phys. 2015, 17, 10146.


Supporting Information

Synergetic Electronic and Ionic Contributions to Electroresistance in Ferroelectric Capacitors

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Supporting Information S1. Current versus voltage loop measured up to 8V. The soft breakdown threshold voltage starts much below the maximum applied voltage.

![Figure S1](image1.png)

**Figure S1.** I-V characteristics up to 8V of the 70 nm film.

Supporting Information S2. Voltage pulse train applied for ER loops measurement.

![Figure S2](image2.png)

**Figure S2.** Sketch of the ER measurement sequence following the +8 V to -8 V to +8 V path; the pulse duration is \( \tau_w \).
Supporting Information S3. Ferroelectric characterization of 70 nm BTO thin film capacitor.

Figure S3. (a) $J$-$V$ loops of $J_1$ junction of the $t_2 = 70$ nm BTO capacitor measured at room temperature, at 25 kHz. Polarization values for positive and negative switching, evaluated from the area underneath the switching peak ($= 2 \cdot P_r$, where $P_r$ is the remanent polarization) are 21 $\mu$C/cm$^2$ and 6.4 $\mu$C/cm$^2$, respectively. The lateral shift of the $J$-$E$ loops signals the imprint field. The asymmetry of the polarization values signals the presence asymmetric leakage current contribution, which might have hidden the presence of switching current [see panel b]). This polarization value is smaller than that obtained for bulk BaTiO$_3$ ($2 \cdot P_r = 52 \mu$C/cm$^2$). (b) $P$-$V$ loop recorded at room temperature. The presence of leakage is very important not allowing to extract reliable polarization value as indicated in panel (a). (c) $J$-$V$ loops measured at 100 K at 1 kHz. Here the switching ferroelectric current peaks are well-visible, because the reduced leakage current compared with the measurements at room temperature. (d) $P$-$V$ loop recorded at 100 K at 1 kHz. Extraction of polarization is more obvious from data collected at low temperature. Values near 30 $\mu$C/cm$^2$ ($2 \cdot P_r = 60 \mu$C/cm$^2$) are obtained. Thus, it is confirmed that the switching peaks observed at room temperature [panel (a)], correspond to the ferroelectric switching of the film, somewhat obscured by the presence of the leakage current.
Supporting Information S4. Retention experiments for the 70 nm BTO thin film capacitor after prepolarizing it with short (τ_w = 20 µs) and long (τ_w = 20 s) writing times. The important effect of internal E-field, revealed already in Figure 2d, can be well appreciated in the retention experiment and manifested as faster depoling of the polarization up (V⁺) state. Indeed, in Figure S4a, it is shown that the resistance value for the OFF state decreases until converging with the ON state. This is an indication that the ferroelectric state corresponding to polarization pointing towards Pt is favoured by the mentioned internal electric field. Instead, in Figure S4b, it is shown that both resistance values for OFF and ON state remain constant for the explored τ_D values, illustrating the different origin of the ON/OFF states and the negligible role of the imprint field when the junction response is mainly dictated by ionic motion as argued in the manuscript.

Figure S4. Retention measurements for +8 V (red) and -8 V (black) prepoled resistive states after applying a triangular pulse of 20 µs (a) and 20 s (b), respectively. The retention experiment is performed following the procedure described by Figure 1b varying τ_D.
**Supporting Information S5.** Electroresistance of the same $t_2=70$ nm BTO film as reported in the manuscript main body, but collected for another junction ($J_2$) showing a similar result change of sign of $ER$ when increasing the writing time.

**Figure S5.** (a) $I$-$V$ reading pulses recorded of $J_2$ junction of the $t_2=70$ nm BTO capacitor, after prepoling the junction (writing) with a $V_w=-8\, V/ +8\, V$ pulse of $\tau_w=20$ $\mu$s (black and red solid line), and $\tau_w=20$ s (black and red dot line). (b,c) $ER$ loops collected using $\tau_w=20$ $\mu$s and 20 s, respectively. All the data correspond to $J_2$ of the $t_2=70$ nm BTO capacitor.
Supporting Information S6. Determination of the time constant of the circuit. We applied a triangular voltage waveform to determine the circuit time constant for the \( t_1 = 35 \) nm sample. We selected this sample because it is the thinner one; thus, the maximum capacitance and the longest circuit time constant \((\tau = RC, \text{ where } \tau \text{ is the time constant})\) is expected.

**Figure S6.** (a) Applied voltage dependence on time. It corresponds to a triangular bipolar signal of 0.5 V of amplitude with a frequency of 1 kHz. (b) Measured current (empty symbols) in the \( t_1 = 35 \) nm film capacitor. The black thin line is the expected pure displacive current without series resistance and leakage currents contributions. It can be observed that the measured current exponentially approached the expected one. This time-delayed response is due to the circuit time constant. The red thick line corresponds to the fitting of an exponential curve \((I = I_0 e^{-\tau}, I_0 \text{ is the amplitude and } \tau \text{ the circuit time constant})\). We obtained \(\tau \approx 12 \) \(\mu\)s. (c) Zoom of (b) to better visualize the data fit.
**Supporting Information S7.** Dependence of the resistances of the ON and OFF states of $t_2 = 70$ nm sample (equivalent to Figures 3a,b in the manuscript main body), but measured in a different junction of the same sample and at different temperatures, showing similar results.

![Graph](image1)

**Figure S7.** Resistance times area of the $J_4$ junction of the $t_2 = 70$ nm BTO capacitor, after prepoling the junction (writing) with $V_w = -8$ V/+8 V pulse of $\tau_w$ for different length of the writing pulses, of junction $J_4$: (a) room temperature and (b) 400 K.

**Supporting Information S8.** Dependence of the $ER$ on writing time $\tau_w$ for all the measured temperatures of $J_3$ junction of the $t_2 = 70$ nm sample.

![Graph](image2)

**Figure S8.** Dependence of the electroresistance of junction $J_3$ of the $t_2 = 70$ nm BTO capacitor on the writing time at several temperatures, as indicated.
Supporting Information S9. Raw data of the ER dependence on $\tau_w$ for the samples of different thicknesses shown in Figure 4c.

Figure S9. Resistance times area after prepoling the junction (writing) with $V_w = -8 \text{ V}/+8 \text{ V}$ pulse of $\tau_w$ of BTO capacitors with different thicknesses: (a) $t_1$, (b) $t_2$ and (c) $t_3$ measured at 450 K. The resistance of the $t_3 = 110 \text{ nm}$ sample was measured at -1 V due to its lower conductivity.

Supporting Information S10. Dependence of the electroresistance of $t_1$, $t_2$ and $t_3$ samples on $\tau_w$ collected at room temperature. Raw data is also included in panels b,c,d.

Figure S10. (a) Dependence of the electroresistance on $\tau_w$ of $t_1$, $t_2$ and $t_3$ BTO capacitors at room temperature. (b,c,d) Resistance times area after prepoling the junction (writing) with $V_w = -8 \text{ V}/+8 \text{ V}$ pulses of $\tau_w$, for $t_1$, $t_2$ and $t_3$ BTO capacitors, respectively, measured at room temperature. The resistance of the $t_3 = 109 \text{ nm}$ sample was measured at -1 V, as indicated, due to its lower conductivity.
Supporting Information S11. To describe the almost symmetric I-V characteristics of the 70 nm – BTO sample shown in Figure 1c (replicated in Figure S14a after voltage pulses of $V_w = \pm 8 \text{V}$ and $\tau_w = 20 \mu\text{s}$ (black and red solid lines), one needs an appropriate model. A first step on modelling starts by considering a back to back (b-t-b) arrangement of Schottky barriers. If thermionic injection is simply assumed as the conducting mechanism across each Schottky barrier then the I-V curves should show an error-function like shape [Figure R14(b)], as one of them is always in reverse. The I-V curves of Schottky barriers of the 70 nm and other thick films does not show this behavior Figure R14a, but the devices are found to conduct similarly, for positive and negative biases. Therefore, an extended model, allowing conduction in reverse mode, is required. The simplest one is the thermionic tunnel injection. In this case, voltage-dependent carrier injection occurs by tunneling across the depletion layer of the Schottky barrier. The final result is that no significant difference are found for direct bias, but the reverse current is largely enhanced. Consequently, the rectifying behavior of the barrier is reduced and the whole b-t-b displays an I-V curve similar to the one experimentally observed (Figure R14c).

Precisely, in Figure R14c, we illustrate the output of the above model by the I-V characteristics calculated using the model described in ref. [1], by which tunneling injection is described, and using the following plausible parameters for the dielectric and barriers. In this example we assume symmetric barriers.

a. Barrier width, $d = 70 \text{ nm}$
b. Schottky barrier height (LSMO/BTO): $\Phi_B = 0.6 \text{ eV}$
c. Schottky barrier height (LSMO/Pt): $\Phi_B = 0.6 \text{ eV}$
d. Permittivity of BTO: $\varepsilon = 60$
e. Effective mass: $m^* = 1$
f. Temperature: $T = 300 \text{ K}$
g. Carrier density (donors) of BTO film: $N_D = 10^{19} \text{ cm}^{-3}$

Figure S11. a) Measured $I$-$V$ curves for the $t = 70 \text{ nm}$ BTO film for $\tau_w = 20 \mu\text{s}$ and $V_w = \pm 8 \text{V}$, replicated from Figure 1a. b) Calculated $I$-$V$ curves using the b-t-b Schottky model with only direct thermionic injection. The parameters used for the calculation are given in text. Notice the saturation reverse current for both polarities. c) Calculated $I$-$V$ curves using the b-t-b Schottky model with tunnel thermionic injection across the Schottky barrier. Notice the absence of saturation current for any bias polarity.

Data in Figure S11(c) show that the computed $I$-$V$ curves reproduce the values of measured current and the main feature of the measured $I$-$V$ curves, namely the conduction for both bias polarities. It is important
to notice that this model and non-analytical calculation behind it,\cite{2} is by far much involved than a simple single Schottky barrier, as typically assumed.

**Supporting Information S12.** Extraction of tunnel barrier parameters from \( I-V \) characteristics of 4 nm BTO thin film capacitor for opposite prepoling voltage.

**Figure S12:** \( I-V \) characteristics measured at room-temperature on BTO junction of 4 nm, and electrode area of 250 \( \mu m^2 \) for: (a) ON and (b) OFF states, respectively. Solid lines across the experimental data are the results of the fits according to the Brinkman model for tunnel transport across trapezoidal potential barriers in the Wentzel–Kramers–Brillouin (WKB) approximation\cite{3,4}. (c) Sketch of the resulting shape of the barrier in the BTO tunnel junction with the fitting results indicated in the sketch. Black line corresponds to +8 V prepoling, and red line to -8 V.

The fitting parameters are:

ON state: \( \varphi_1(ON) = 0.51 \) eV, \( \varphi_2(ON) = 1.30 \) eV and \( d(ON) = 2.1 \) nm,

OFF state: \( \varphi_1(OFF) = 0.63 \) eV, \( \varphi_2(OFF) = 2.0 \) eV and \( d(OFF) = 2.3 \) nm

The results indicate a substantial rising of the average barrier height and its asymmetry and barrier thickness in the OFF state. Note that both barrier heights \( \varphi_1 \) and \( \varphi_2 \) corresponding to LSMO/BTO and BTO/Pt interfaces, respectively, increase after +8 V, which corresponds to polarization pointing towards LSMO.
Supporting Information S13. Power dissipated in the 70 nm BTO sample as a function of voltage.

The average power dissipated in the loop is $P_{\text{ave}} \approx 5\text{mW}$. Therefore, we can estimate the energy dissipated to the sample for representative writing voltage pulses of 8V and $\tau_w = 20\ \mu\text{s}$ and 20 s:

$$E(+8\ \text{V}, 20\ \mu\text{s}) = \frac{P_{\text{ave}}}{2} \cdot \tau_w = 63\ \text{mW}/2 \cdot 20\ \mu\text{s} = 125\ \text{nJ}$$

$$E(+8\ \text{V}, 20\ \text{s}) = \frac{P_{\text{ave}}}{2} \cdot \tau_w = 63\ \text{mW}/2 \cdot 20\ \text{s} = 125\ \text{mJ}.$$

In this estimation, we used half of the power ($P_{\text{ave}}/2$), because unipolar pulses are typically used in the experiments reported in the manuscript. The obtained values indicate that, for the long writing times pulses, significant amount of energy (6 orders of magnitude larger than for the short ones) is dissipated. This might result in an increase of device temperature as reported in oxides-based systems, which might help ionic processes to occur.\cite{5,6}

**Figure S13.** Power as a function of voltage of the Pt/BTO (70 nm)/LSMO junction $J_5$. Data has been collected in quasi-static mode applying constant voltage for each collected power measurement using an integration time of 1 s.
**Supporting Information S14.** Electroresistance characterization for samples of series II. In panels (a,b,c), we plot the \( I-V \) characteristics in the voltage range ±0.5 V after prepolarizing the sample with ±8 V using different writing times (short \( \tau_w = 20 \mu s \) and long \( \tau_w = 20 \) s) for the \( t_1 = 35 \) nm, \( t_2 = 70 \) nm and \( t_3 = 110 \) nm BTO samples. The experiment is equivalent to that shown in Figure 1c. For the the \( t_1 = 35 \) nm sample shown in (a) ON (OFF) states are obtained for negative (positive) prepoling, and their difference increases with \( \tau_w \). For \( t_2 = 70 \) nm sample shown in (b), ON (OFF) states are obtained for negative (positive) prepoling for short writing time, but the opposite for long writing time. For \( t_3 = 110 \) nm sample shown in (c), OFF (ON) states are obtained for negative (positive) prepoling for short and long writing time, although for short writing time the difference is negligible. In panels (d,e,f), the \( ER \) measurement following the sequence of Figure 2a (manuscript) using different writing times (short \( \tau_w = 20 \mu s \) and long \( \tau_w = 20 \) s) is shown for the \( t_1 = 35 \) nm, \( t_2 = 70 \) nm and \( t_3 = 110 \) nm BTO samples. Here, it can be more clearly observed the different sign and magnitude depending on writing time and thickness for electroresistance. For the \( t_1 = 35 \) nm sample shown in (d), positive electroresistance (as defined in the manuscript) is observed irrespective of the writing time, but increasing with it. For the \( t_2 = 70 \) nm sample shown in (e), positive electroresistance is observed for short writing times, and negative (much larger) for long writing times. For the \( t_3 = 110 \) nm sample shown in (f), negative electroresistance is observed for short and long writing times, and its absolute value increases with thickness. Overall, it can be observed that similar trends to those reported in the manuscript are observed for representative junctions in samples of serie II.

**Figure S14.** Electroresistance data of samples of series II. (a,b,c) \( I-V \) reading pulses recorded of \( t_1 = 35 \) nm, \( t_2 = 70 \) nm, \( t_3 = 110 \) nm, respectively, after prepolarizing the junction (writing) with a \( V_w = -8 \) V/+8 V pulse of \( \tau_w = 20 \mu s \) (black and red solid line), and \( \tau_w = 20 \) s (black and red dot lines). Resistance times the area for different prepoling voltages of duration 20 \( \mu s \) and 20 s , measurement sequence following the +8 V to -8 V to +8 V path, for (d) \( t_1 = 35 \) nm, (e) \( t_2 = 70 \) nm and (f) \( t_3 = 110 \) nm.
References