Unraveling Ferroelectric Polarization and Ionic Contributions to Electroresistance in Epitaxial Hf$_{0.5}$Zr$_{0.5}$O$_2$ Tunnel Junctions

Milena Cervo Sulzbach, Saúl Estandia, Xiao Long, Jike Lyu, Nico Dix, Jaume Gàzquez, Matthew F. Chisholm, Florencio Sánchez, Ignasi Fina,* and Josep Fontcuberta*

Tunnel devices based on ferroelectric Hf$_{0.5}$Zr$_{0.5}$O$_2$ (HZO) barriers hold great promises for emerging data storage and computing technologies. The resistance state of the device can be changed through use of a suitable writing voltage. However, the microscopic mechanisms leading to the resistance change are an intricate interplay between ferroelectric polarization controlled barrier properties and defect-related transport mechanisms. The fundamental role of the microstructure of HZO films determining the balance between those contributions is demonstrated. The HZO film presents coherent or incoherent grain boundaries, associated to the coexistence of monoclinic and orthorhombic phases, which are dictated by the mismatch with the substrates for epitaxial growth. These grain boundaries are the toggle that allows to obtain either large (up to ≈450%) and fully reversible genuine polarization controlled electroresistance when only the orthorhombic phase is present or an irreversible and extremely large (=10$^3$–10$^5$%) electroresistance when both phases coexist.

1. Introduction

Ferroelectric tunnel devices are attracting attention as resistive switching devices due to its low energy consumption, fast writing/reading, and small cell size.$^{[1,2]}$ A ferroelectric tunnel junction (FeTJ) has a capacitor-like structure in which a nanometric ferroelectric layer is sandwiched between two metallic electrodes. The height of the energy barrier (Φ) across the ferroelectric depends on the direction of the ferroelectric polarization (P) and the difference of electrodes (i and j) screening lengths (δ$_i$, δ$_j$). For a given pair of electrodes, having δ$_i$ ≠ δ$_j$, Φ(P↑) and Φ(P↓) are different; therefore two distinct resistance states can be obtained for the device when polarizing the ferroelectric barrier in opposite directions.$^{[3]}$ The change in resistance, so-called electroresistance (ER), is quantified by ER = (R(V↑)−R(V↓))/R$_{\text{min}}$(V↑)., where R(V↑) and R(V↓) are the resistances after polarizing the junction with writing voltages $V_W$ and $V_W$ and R$_{\text{min}}$(V↑) is the minimum resistance among these states. Accordingly, binary high (OFF) and low resistance (ON) states can be written in a ferroelectric memory cell and read by probing its resistance. It has also been shown that by performing minor polarization loops, ferroelectric tunnel devices can store information in different resistive states, mimicking the functioning of a memristive element.$^{[4,5]}$

The discovery of ferroelectricity in HfO$_2$-based thin films$^{[17]}$ being CMOS-compatible, has created expectations that new functionalities could be implemented in current silicon-based platforms.$^{[18,19]}$ Epitaxial growth of ferroelectric Hf$_{0.5}$Zr$_{0.5}$O$_2$ (HZO) thin films has been achieved.$^{[20–26]}$ opening the door to engineer epitaxial FeTJ and magnetic-FeTJ.$^{[25]}$ The ferroelectric character of ultrathin (few nanometer layers) epitaxial HZO films has been assessed by piezoelectric force microscopy and by recording P-E loops on micrometric electrodes.$^{[20–26]}$ Thus, a natural question arises: can ferroelectric-related ER be observed in epitaxial Hf$_{0.5}$Zr$_{0.5}$O$_2$ tunnel barriers and exploited to create HfO$_2$-based FeTJ?

A key point is that the ER of the ferroelectric tunnel junctions is not only sensitive to polarization effects described above, but may also be affected by ionic or other defect-related charge motion at the barrier. In the most studied ferroelectric tunnel barriers involving BTO and BiFeO$_3$, for instance, it has been recognized that ionic motion plays a role in ER.$^{[4,27–29]}$ Indeed,
electroresistance in non-ferroelectric oxides, including HfO₂, has been largely explored to create resistive switching,[18] memories, and logic elements,[31,32] taking advantage of the high (OFF) and low (ON) resistance states that can be obtained by applying suitable voltage pulses.[32,33] It has been shown that after a voltage-induced forming step, reversible OFF and ON states can be obtained (set and reset) by cycling the external voltage. The microscopic mechanisms for forming and set-reset processes have been much discussed. For example, Bersuker et al.[34] showed that, in monocrystalline HfO₂, the ER can be modeled by a forming step related to the dielectric soft breakdown in a filamentary shape. In the formation of conductive filaments, the HfO₂ grain boundaries show a crucial role. The filaments produced by the soft breakdown are formed at HfO₂ grain boundaries, which involves oxygen dissociation (oxygen vacancy generation) and the creation of a conducting channel.[35] Electric-field driven oxygen vacancies accumulation at the electrode forms a conducting layer which corresponds to the ON state. When the electric field reverses the polarity, the oxygen vacancies diffuse through the oxide, restoring the insulating character of the interfacial layer and ultimately producing the OFF state.[34]

Recently, ER in tunnel junctions involving ferroelectric HfO₂ barriers have been reported.[25,26,36,37] However, available data do not allow indisputably to conclude if the observed ER is directly governed by polarization-related effects or it results from electric-field induced charge motion as commonly observed in non-ferroelectric HfO₂ barriers.[38] For instance, Wei et al. reported current–voltage curves (I–V) of 2 nm HZO barriers and argued that data can be described using the Brinkman model,[18] indicating direct tunnel transport across the barrier.[25] However, the dependence of the barrier properties on the polarization direction was not analyzed, thus the connection between the measured ER and P remained undisclosed. Ambriz-Vargas et al.[36,37] reported also I–V measurements on HZO (2.8 nm thick) barriers. It was shown that the I–V curves are dramatically different after a writing voltage of ±2.2 V. Nonetheless, the data were analyzed in a narrow voltage region, in which the I–V curves were almost linear, and precluding robust extraction of barrier parameters and its possible change due to polarization reversal. Yoong et al.[26] also reported I–V data on HZO epitaxial tunnel barriers about 10 nm thick and their polarization P(V) loops. Transport data were analyzed in term of thermionic emission over a polarization-modulated barrier. The use of a thermionic model was adequate because direct tunneling across such thick barrier is prohibited. It was observed that the properties of the barriers were significantly different depending on the magnitude of the writing voltage, whereas, in the same voltage range, the polarization loop appeared to be saturated. This observation suggests that barrier properties are not only dictated by polarization but other mechanism may come at play.

Here we address this crucial issue, recording at room temperature, the polarization P(V) and ER(V₉₀) loops of epitaxial ferroelectric HZO tunnel barriers grown on single crystalline cubic substrates with different structural mismatch with HZO. The rationale behind this is the following. First, we take advantage of the recent discovery by Estandía et al.[40] that the structural mismatch between HZO and strained LSMO-coated substrates determines the microstructure of the HZO films. This structure must be interpreted as the relative abundance of orthorhombic (o-HZO) (ferroelectric) and monoclinic (m-HZO) (non-ferroelectric) phases and the fine details of the unavoidable coherent and incoherent grain boundaries. Second, incoherent grain boundaries in polycrystalline HfO₂ are known to be instrumental for electric field controlled resistive switching.[34] Therefore, varying the relative amount of coherent and non-coherent grain boundaries, the latter arising from the coexistence of o- and m-HZO phases, and their respective role on electroresistance can be disentangled. It will be shown that HZO films grown on GdScO₃ and TbScO₃ display genuine polarization-related electroresistance (up to ±450%) developing at the coercive voltage of the film. Whereas HZO films on SrTiO₃ display a coexistence of ferroelectric and non-ferroelectric resistive switching channels, operating at different voltage ranges and with electroresistance of up to 450% and 10⁵–10⁶%, respectively. Therefore, ferroelectric polarization and defect-related effects contribute to the ER in HZO ultrathin ferroelectric films. The structural mismatch between HZO and substrate and the resulting HZO microstructure are the toggle that sets the balance between polarization-related and defect-related mechanisms governing the device ER.

2. Results

Epitaxial HZO films with nominal thickness of 4.6 nm were grown on LSMO (22 nm thick) conducting buffer (001) single crystalline substrates SrTiO₃ (STO), GdScO₃ (GSO), TbScO₃ (TSO) (pseudocubic setting is used for scandates), and (LaAlO₃)₀.₁(Sr₂Ta₂O₇)₀.₇ (LSAT) by pulsed laser deposition (PLD). Ex situ sputtered circular Pt top electrodes of 20 μm of diameter were grown through masks. The heterostructure is sketched in Figure 1a. In Figure 1b, we show an X-ray diffraction 2θ–θ scan of the sample
grown on STO. The intense (00l) reflections of substrate and LSMO can be observed as well as the (111) reflection of the ferroelectric o-HZO, indicating its prevalence in the film. No other reflections can be seen. The I–V curve recorded on a fresh Pt/HZO/LSMO/STO device (junction J₁) (Figure 1c) and the corresponding P(V) loop (Figure 1d) assess the ferroelectric nature of the film. The coercive voltage extracted from the position of the switching peaks is $V_C^+ = V_C^- = 2$ V. Data indicate a remnant polarization $P_R = 16 \mu$C cm$^{-2}$. These ferroelectric characteristics are consistent with previous reports.[21–23]

In Figure 2a, we show I–V curves collected at 5 kHz (junction J₂). This measurement frequency allows meaningful comparison with the ER measurements recorded using writing pulses of 100 µs. The polarization switching current peak occurs at about 2 V, indicating $V_C^+ = 2$ V. The current peak observed at around $V_{max}$ in Figure 2a is a spurious effect due to high frequency used in these measurements (Figure S1, Supporting Information). The ER measurement (junction J₂) sequence is first applying a writing triangular pulse of amplitude $V_W$ and duration $\tau_W = 100$ µs as indicated in Figure 2b and using the electrical contact configuration shown in Figure 1a. Then, I–V curves are collected, after a delay time $\tau_D = 0.5$ s, by applying a linear $V_R(t)$ pulse in a small voltage range (from $-1$ V to $+1$ V). The resistance is determined at $V_R = 0.9$ V. Notice that, to avoid ferroelectric switching during the reading, the maximum reading voltage is smaller than $V_C$ ($=2$ V). The ER data collected cycling $V_W$ up to ±4.5 V is shown in Figure 2c. Data clearly display noticeable changes of resistance developing at about ±2 V, which closely coincide with $V_C^{+/-}$ observed in Figure 2a (as indicated by dashed lines). Moreover, it can be appreciated in Figure 2c that the $R(V_W)$ is reversible (three consecutive loops are shown) and the ER is 410% and no forming steps are necessary. In contrast when increasing $V_W$ (±6 V), the ER becomes larger (>10%) but irreversibility emerges (Figure 2d). Therefore, data in Figure 2 clearly indicate that different ER mechanisms occur depending on the writing voltage. The close correspondence of polarization and ER in Figure 2a,c strongly suggests that ER is due to polarization-controlled tunnel transport across the HZO barrier if voltages up to $V_W \leq 4.5$ V are used. Ferroelectric switching and ER coexists at larger $V_W$, but these are not consequence one from the other, as reported in polycrystalline HfO₂ thin films.[38]

In order to get an insight on the origin of reversible and irreversible ER observed, Figure 3a shows the resistance (junction J₂) after increasing positive and negative $V_W$ writing steps (pulse sequence is sketched in Figure S2, Supporting Information). Stability of resistance after a certain number of pulses of the same amplitude are shown in Figure S3, Supporting Information. Resistance $R(V_{W})$ data in Figure 3a display two clear regions (I and II) separated by a vertical line. In region I, for $2 \leq |V_W| < 5$ V, the resistance increases with $V_W^+$ ($V_W > 0$) and decreases for $V_W^-$ ($V_W < 0$). Further increase of $V_W$, irrespective of its polarity, produces a large decrease in resistance (region II, Figure 3a) and ER reduction. Between regions I and II, $ER(V_W)$ displays a well pronounced maximum, as shown in Figure 3c in which data collected up to $V_W = 7.5$ V are depicted. The ER values in region I amount up to +340% ($V_W = 4.5$ V) and increase up to 2000% when entering region II. Note that these ER values are slightly different from those in Figure 2c due to the different pulse train used for the measurements in

![Figure 2](image_url)

**Figure 2.** a) I–V loop of Pt/HZO/LSMO/STO measured at 5 kHz before performing $R(V_{W})$ measurement cycles up to $V_W = 4.5$ V, b) Sketch of the writing/reading measuring protocol. The amplitude of the writing pulse ($V_W$), its duration ($\tau_W$), and dwell time ($\tau_D$) before the measuring pulse of amplitude $V_R$ are indicated. c) Dependence of the junction resistance ($R$) on the writing voltage $V_W$ ($|V_W| < 4.5$ V); three consecutive cycles are shown to illustrate reversibility. d) $R(V_{W})$ cycles for $|V_W| > 6$ V; two consecutive cycles are shown illustrating irreversibility. Dashed vertical lines indicate the coercive voltage ($V_C$) of the HZO film extracted from (a).

![Figure 3](image_url)

**Figure 3.** a) Resistance (at 0.9 V) of the device (J₂) in Pt/HZO/LSMO/STO sample after positive ($V_W > 0$) and negative ($V_W < 0$) writing pulses. b) Electroresistance calculated from data shown in (a). c) I–V curves measured (symbols) in Pt/HZO/LSMO/STO (junction J₃) after writing with $V_W = +4.5$ and $-4.5$ V as indicated. The solid red lines are the results of the fit as described in the text. d) Sketch of the energy barrier profile of the device, upon P reversal, based on the $\mathcal{O}_{LSMO}$ and $\mathcal{O}_{HZO}$ energy barrier heights and thickness parameters derived from the fits of I(V) curves in Region I. For convenience, the effective thickness decrease upon polarization reversal has been sketched in the Pt/HZO side, although it may occur at the LSMO/HZO side or in both.
Figures 2c and 3a (see Figure S2, Supporting Information). It is worth mentioning that after these measuring cycles (|V_W| ≤ 7.5 V) the junctions remain ferroelectric, as shown in Figure S4, Supporting Information. However, increasing V_W to 8 V leads to irreversible changes in the junction, which shows a smaller resistance and no evidence of ferroelectric switching (see Figure S5, Supporting Information). The presence of two regions (I and II) and similar R(V_W) and ER(V_W) trends have been found in most of junctions in the sample and are insensitive to the duration of the writing pulse (τ_W) and the dwell time (τ_dwell), within the explored range (τ_W = 10–500 μs and τ_dwell = 0.25 s–1.0 s) (Figures S6 and S7, Supporting Information).

In the analysis, we shape the sample of the I–V curves to explore the origin of ER in the reversible region I (junction J1). Figure 3c shows the I–V data collected after writing with V_W = ±4.5 V, corresponding to the resistance after ±4.5 V shown in Figure 2c. I–V data collected after sequential pulses with |V_W| = ±4.5 V obtained sequentially are shown in Figure S7, Supporting Information. Inspection of data in Figure 3c reveals that: a) I–V curves are sigmoidal and asymmetric as commonly found in tunnelized tunnel barriers and b) for V_W<sup>−</sup> (up triangles) the conductance is larger than for equivalent V_W<sup>+</sup> (down triangles), thus reflecting the emergence of ER. The I–V curves in Figure 3c were fitted (solid lines) using the Brinkman model<sup>[19]</sup> to extract the barrier heights (Ω<sub>LSMO</sub> and Ω<sub>Pt</sub>) and the effective barrier width (τ<sub>eff</sub>) of a trapezoidal barrier. Ω<sub>LSMO</sub> and Ω<sub>Pt</sub> refer to the barrier height at the LSMO and Pt interfaces with the ferroelectric layer, respectively. The mean energy barrier has been calculated as: Ω<sub>mean</sub> = Ω<sub>LSMO</sub> + Ω<sub>Pt</sub>/2. The fitted values are Ω<sub>LSMO</sub> = 1.3 ± 0.2 eV, Ω<sub>Pt</sub> = 2.2 ± 0.2 eV, Ω<sub>mean</sub> = 1.86 ± 0.03 eV and τ<sub>eff</sub> = 5.9 ± 0.05 nm for V_W = +4.5 V. For V_W = −4.5 V, they are Ω<sub>LSMO</sub> = 2.5 ± 0.1 eV, Ω<sub>Pt</sub> = 1.4 ± 0.3 eV, Ω<sub>mean</sub> = 1.98 ± 0.07 eV, and τ<sub>eff</sub> = 5.5 ± 0.01 nm. Error bars represent the dispersion of the fitted parameters to I–V data collected after three sequential writing with V_W = +4.5 and −4.5 V. Importantly, repeated cycling of the junction leads to almost identical changes on the barrier properties. I–V data and fitting parameters are shown in Figure S8 and Table S1, Supporting Information. These energy barrier values are larger than those found in similar devices using BTO as ferroelectric barrier,<sup>[41]</sup> which is expected due to the lower electron affinity of HfO<sub>2</sub> (=2.0 eV) compared to BTO (=3.9 eV) and fully consistent with the work functions of electrodes.<sup>[41,42]</sup>

According to the sketch of Figure 1a, V_W > 0 should impose P pointing toward LSMO. This corresponds to a smaller barrier at LSMO (Ω<sub>LSMO</sub> = 1.3 ± 0.2 eV) interface and a higher one (Ω<sub>Pt</sub> = 2.2 ± 0.2 eV) at Pt side. This produces a trapezoidal barrier as predicted by Zhuravlev et al.<sup>[13]</sup> and agrees with results obtained in similar BTO ferroelectric junctions.<sup>[7,15]</sup>

Notice that the height of the energy barriers at LSMO and Pt sides (Ω<sub>LSMO</sub>, Ω<sub>Pt</sub>) changes from ≈(1.3, 2.2 eV) to ≈(2.5, 1.4 eV) when reversing the sign of V_W. However, remarkably, the difference ΔΩ = Ω<sub>LSMO</sub>−Ω<sub>Pt</sub> reverses almost symmetrically when changing V_W polarity. Therefore, although ΔΩ reverses its sign with P, its mean height value Ω<sub>mean</sub> remains constant upon P reversal. This conclusion, derived from the analysis of the I–V curves, at first sight is at odds with the observation (Figure 2c) that the junction resistance (R) is significantly smaller (about 410%) for V_W<sup>−</sup> than for V_W<sup>+</sup>, in spite of the negligible variation of the mean height barrier energy (Ω<sub>mean</sub>) with P reversal. The clue to this unexpected observation can be obtained by inspecting the extracted values of τ<sub>eff</sub>. As indicated above, for V_W = +4.5 V we obtained τ<sub>eff</sub> = 5.9 (±0.05) nm but τ<sub>eff</sub> = 5.5 (±0.01) nm for V_W = −4.5 V. This thickness difference (Δτ<sub>eff</sub> = 0.4 nm) accounts for the observation of a low resistance state for V_W<sup>+</sup> pointing away from LSMO. Therefore, upon V_W reversal, the shape of the energy barrier basically reverses symmetrically, but the width shrinks/expanded as illustrated in Figure 3d. We conclude that the ER observed in Region I can be associated to the modulation of the tunnel barrier properties by polarization reversal. Similar data fitting has been performed in I–V curves collected after |V_W| = 6 V (see Figure S8 and Table S1, Supporting Information) showing a poorer quality of the fits, which indicates that the tunneling conduction might coexist with other conduction mechanisms as discussed in detail below.

We turn now our focus on the abrupt drop of resistance that signals the transition to Region II. It is worth noticing that this abrupt change of resistance occurs in (Pt/HZO/LSMO/STO) around ≈5 V for both writing voltage pulse polarities (V_W<sup>+</sup> and V_W<sup>−</sup>). This behavior is reminiscent of the forming step observed in HfO<sub>2</sub> and other materials in which an electric-field induces the formation of a conducting channel, mostly along grain boundaries.<sup>[44]</sup> Since the structural mismatch between HZO and the LSMO buffer layer is different for the samples grown on STO and GSO substrates, the relative amount of monoclinic and orthorhombic phases is different. Indeed, it has been recently reported<sup>[45]</sup> that the orthorhombic phase is favored with respect to the monoclinic phase in HZO/LSMO samples and substrates with larger lattice parameters than STO (a = 3.905 Å), as it is the case of GSO (a = 3.97 Å). Thus, the HZO film grown on LSMO/GSO contains mainly orthorhombic grains, while the film grown on LSMO/STO is composed of a mixture of orthorhombic and monoclinic grains.

In Figure 4a,c,e we show HAADF-STEM cross-sectional views of HZO/LSMO//=STO, HZO/LSMO//=GSO, and HZO/LSMO//=LSAT, respectively. Notice that STEM experiments have been conducted on heterostructures containing 9 nm thick HZO layer. A larger field of view in both films can be found in Figure S9, Supporting Information. HAADF-STEM images were obtained along the [110] zone axes of the substrates and show a clear contrast between the HZO film and the LSMO electrode. It can be appreciated in Figure 4a that the HZO film grown on LSMO//STO consists of grains with monoclinic and orthorhombic phases, having a lateral size in the 10–15 nm range. The orthorhombic and monoclinic grains are (111) and (001)-textured on the (001) substrate, respectively, producing non-coherent orthorhombic-monoclinic grain boundaries. They are shown in the higher magnification Z-contrast image of Figure 4b. Notice that the atomic arrangement in these highly mismatched grain boundaries significantly deviates from the structure within the grains which points to a complex atomic reordering at grain boundaries that extends up to several atomic planes. In contrast, the microstructure of the HZO film grown on LSMO//GSO is largely different (Figure 4c). It can be appreciated that the HZO film is also formed by grains, but only (111)-oriented orthorhombic c-HZO grains are present. As expected from the epitaxial growth of a (111) textured film onto (001) cubic substrates, twinning is observed, thus the
grain boundaries between two adjacent orthorhombic grains, having identical out-of-plane texture, can be in-plane rotated and produce coherent grain boundaries. The in-plane rotation is indicated in the higher magnification Z-contrast image of Figure 4d, where coherent grain boundaries are clearly visualized. Notice that these grain boundaries are thinner and less distorted than in HZO/LSMO//STO. In short, o-HZO and m-HZO crystallites can be identified in some regions of the HZO/LSMO//STO sample (Figure 4a,b) and thus incoherent and highly distorted grain boundaries must exist. In contrast, for HZO/LSMO//GSO (Figure 4c,d), the HZO film displays a homogeneous texture corresponding to o-HZO (111) phase and incoherent m-HZO/o-HZO interfaces are absent. The presence of grain boundaries between monoclinic crystallites is also apparent in the images of HZO/LSMO//LSAT film, as shown in Figure 4e.f.

We now analyze the impact of grain boundaries on the junction resistance. We focus our attention on \( R(V_W) \) with increasing \( V_W \) to identify regions I and II of HZO films on different substrates. Figure 5a,c show \( R(V_W) \) on the Pt/HZO/LSMO//GSO and Pt/HZO/LSMO//LSAT samples, respectively. The \( I-V \) loops for junctions grown on these substrates, indicating its \( V_C \), can be seen in Figure S10, Supporting Information. We also include (Figure 5b) data for Pt/HZO/LSMO//STO from Figure 2b for comparison. It is clear that the characteristic abrupt decay of resistance occurring at some \( V_W \) (around 5 V in Pt/HZO/LSMO//STO) is shifted in Pt/HZO/LSMO//GSO for much larger voltage (≈13 V). Instead, \( R(V_W) \) displays two well defined and distinguishable \( R(V_W^+) \) and \( R(V_W^-) \) states developing at \( V_W \approx 4.5 \) V. Their difference remains roughly constant up to ≈13 V, indicating that the energy barrier depends on the sign of the polarizing voltage (\( V_W^+ \) and \( V_W^- \)) but not on its magnitude, as expected for a ferroelectric barrier with saturated polarization. Consistently, \( ER(V_W) \) displays robust loops (\( ER \approx 450\% \)) when cycling the junction up to 6 V, as show in Figure 5d. The fingerprint of ion-related \( ER \) in Pt/HZO/LSMO//GSO sample is shifted to 13 V (Figure 5d), supporting the view that, in this sample, conducting channels along monoclinic-orthorhombic grain boundaries are mostly suppressed. Consistently, the \( ER \) data HZO films grown on...
TbScO$_3$ substrates (Pt/HZO/LSMO//TSO) (see Figure S11, Supporting Information) shows only evidence of the polarization related resistive switching and the absence of the characteristic decay of resistance associated to grain boundaries. Figure 5c,f show the corresponding data for Pt/HZO/LSMO//LSAT. The overwhelming presence of non-ferroelectric monoclinic phase and residual existence of orthorhombic phase is apparent on the observation of a tinny opening of the $R$(V$_W$) loop and a reduced electroresistance (Figure 5f). Both observations are consistent with polarization loops (see Figure S10, Supporting Information).

Finally, we note that the threshold field at which ER develops ($V_W$ $\approx$ 4.5 V) in the Pt/HZO/LSMO//GSO is larger than that observed in Pt/HZO/LSMO//STO (about 2.5 V). If, as argued here, the ER($V_W$) in region I is due to polarization reversal then this would imply that the coercive voltage $V_C$ of Pt/HZO/LSMO//GSO is larger. Indeed, this is what we observed (Figure S10, Supporting Information).

3. Summary

Here, we have reported exhaustive ER($V_W$) and ferroelectric polarization measurements of nanometric (4.6 nm) ferroelectric epitaxial HZO barriers grown on LSMO (bottom electrode) deposited on different substrates (STO, LSAT, GSO, and TSO), which have different lattice mismatch with HZO. We have found that in Pt/HZO/LSMO//STO devices the junction resistance $R$(V$_W$) displays two well-defined regions (I, II) with dependence on the writing voltage $V_W$. In region I, a substantial ER develops ($\approx$410%) giving rise to well defined low/high (ON/OFF) resistance states. Data indicate that the two states are triggered by switching of the ferroelectric polarization of HZO and that the conduction mechanism is tunneling. Therefore, ER develops coinciding with the ferroelectric layer coercive voltage ($V_C$). Interestingly, the polarization reversal affects the barrier energy profile almost symmetrically and mostly modulates the barrier width. This observation suggests that polarization-dependent depletion layers formed at electrode/HZO interfaces have a prominent role in the ER. When increasing $V_W$ well above $V_C$, the junctions enter in the so-called region II at some critical voltage where a large and non-fully-reversible ER develops. It is argued that this second voltage threshold is a fingerprint of the presence of a different ER mechanism not related to polarization but to ionic motion. This effect is commonly observed in non-ferroelectric devices based on HfO$_2$ and other oxide thin films and extensively discussed in the literature. We have argued that the presence of specific grain boundaries in HZO is instrumental for the formation of conducting channels that may mask genuine polarization switching ER. This hypothesis is conclusively assessed by growing and characterizing the microstructure and comparing ER in HZO/LSMO heterostructures on STO and perovskite scandates (GSO and TSO). STEM images with atomic resolution demonstrate that incoherent boundaries (between monoclinic and orthorhombic phases) exist in HZO/LSMO//STO but only coherent grain boundaries are observed in HZO/LSMO//GSO. Consistently, it is found that junctions in HZO/LSMO//GSO remain within region I upon $V_W$ cycling and region II is pushed to larger voltages beyond the explored range ($V_W$ $\approx$ 8 V). Consequently, the use of GSO substrates has allowed to obtain larger ER values (up to 450%) displaying a reversible behavior polarization-switchable ferroelectric tunnel devices based on HZO.

4. Conclusion

We have disclosed here the dramatic role that the microstructure, namely the existence of grain boundaries between orthorhombic and monoclinic phases, has on the ER of...
epitaxial HZO tunnel barriers. The message emerging from this work is that polarization-related and ionic-like conductive mechanisms coexist in a tunnel barrier. Both effects give rise to an ER, although fully reversible behavior (without forming steps) is only observed in the former. In ferroelectric tunnel devices, the ER is commonly rationalized by the change of barrier height upon polarization switching. Interestingly, it has been observed here that, in HZO films, the effective tunneling thickness modulation upon polarization switching rules the tunneling current, indicating the very relevant role of the interface in this system. It has been shown that appropriate substrate selection allows to drastically reduce the grain boundary density, which results in an enhanced and robust polarization-related ER (up to 450%). Probably, reduction of the contact size well below micron size may allow further improvements. These findings should contribute to a faster development and implementation of HfO₂-based ferroelectric tunnel devices.

5. Experimental Section

Sample Growth: Epitaxial HZO films with nominal thickness of 4.6 nm were grown on LSMO (22 nm thick) buffered STO (001), (001)–oriented (pseudocubic indexation) GSO and TSO substrates as described elsewhere.[40] Pt electrodes (20 nm thick) were grown ex situ, at room temperature, by DC-sputtering through shadow mask which allows the deposition of circular top contacts (diameter = 20 µm). Junctions were identified by the code Jn. Single crystalline STO, GSO, and TSO used as substrates have bulk cell parameters (pseudo-cubic) of 3.905, 3.97, and 3.958 Å, respectively. Full structural characterization of HZO films on those substrates has been reported elsewhere.[40]

Structural Characterization: X-ray diffraction 2θ–χ recorded using Bruker Bruker-AXS D8 Advance was equipped with a Vantec 500 detector (Cu-Kα radiation). The corresponding 2θ–2θ scan was obtained by integration within the ±10° angular range.

Electrical Characterization: The electrical contact configuration is sketched in Figure 1a. The bottom LSMO layer acts as electrical ground and was contacted through silver paste contact at the edge of the sample. Top Pt electrodes were biased. Polarization measurements were done by integrating the current through time of collected i–V curves at indicated frequency. Electroresistance measurements were done by using a triangular voltage pulse of variable amplitude $V_{p}$(t) and duration $\tau_{W}$ (10–500 µs) to set the device initial state (writing step). A linear $V_{p}$(t) pulse of maximum amplitude 1 V was subsequently used to read the resistance of the junction. Quoted values of junction resistance correspond to $V_{p}$ = 0.9 V. The delay time $\tau_{D}$ was fixed at 0.5 s. All electrical characterizations were performed with an AixACCT TFAnalyser2000 platform. The P(V) loop in Figure 1d was obtained by integration of the I–V data in Figure 1c (collected using dynamic leakage current compensation protocol[44]) and subtracting the dielectric and series resistance background[45] (Figure S12, Supporting Information). All measurements were performed at room temperature.

Transmission Electron Microscopy Characterization: Aberration-corrected scanning transmission electron microscopy (STEM) was used for microstructural analysis with atomic resolution. Samples were characterized using a NION UltraSTEM operated at 200 kV equipped with a NION corrector and a JEOL JEM ARM200cF operated at 200 kV, equipped with a CEOS aberration corrector. The STEM microscopes were operated in high angle annular dark field (HAADF) imaging mode, also referred to as Z-contrast because the brightness associated to each atomic column scales with its atomic number.[48] Specimens for STEM were prepared by conventional methods: grinding, dimpling, and Ar ion milling.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Financial support from the Spanish Ministry of Economy, Competitiveness and Universities, through the “Severo Ochoa” Programme for Centres of Excellence in R&D (SEV-2015-0496) and the MAT2017-85232-R (AEI/FEDER, EU), and MAT2015-73839-JIN projects, and from Generalitat de Catalunya (2017 SGR 1377) is acknowledged. M.C.S. acknowledges fellowship from “la Caixa” Foundation (ID 100010434; the fellowship code is LCF/BQ/111620051). I.F. and J.G. acknowledge Ramón y Cajal contracts RYC-2017-22531 and RYC-2012-11709, respectively. S.E. acknowledges the Spanish Ministry of Economy, Competitiveness and Universities for his Ph.D. contract (SEV-2015-0496-16-3) and its cofunding by the ESF. J.L. and X.L. are financially supported by China Scholarship Council (CSC) with Nos. 201506080019 and 201806100207, respectively. M.C. acknowledges financial support from U.S. Dept. of Energy. M.C.S. work has been done as a part of her Ph.D. in physics at Universitat Autònoma de Barcelona. S.E. and J.L. work has been done as a part of their Ph.D. in materials science at Universitat Autònoma de Barcelona. The authors acknowledge the ICTS-CNME for offering access to their instruments and expertise. The electron microscopy performed at ORNL was supported by the Materials Sciences and Engineering Division of Basic Energy Sciences of the Office of Science of the U.S. Department of Energy.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

ferroelectric tunnel junctions, hafnium oxides, Hf$_{0.5}$Zr$_{0.5}$O$_{2}$, resistive switching, tunnel electroresistance

Received: August 8, 2019
Revised: October 10, 2019
Published online: November 14, 2019

[1] V. Garcia, M. Bibles, Nat. Commun. 2014, 5, 4289.
[2] M. Coll, J. Fontcuberta, M. Althammer, M. Bibles, H. Boschker, A. Calleja, G. Cheng, M. Cuoco, R. Dittmann, B. Dkhil, I. El Baggari, M. Fanciulli, I. Fina, E. Fortunato, C. Frontera, S. Fujita, V. Garcia, S. T. B. Goennenwein, C.-G. Granqvist, J. Grollier, R. Gross, A. Hagfeldt, G. Herranz, K. Hono, E. Houwman, M. Huijben, A. Kalaboukhov, D. J. Keeble, G. Koster, L. F. Kourkoutis, et al., Appl. Surf. Sci. 2019, 482, 1.
[3] J. D. Kim, S. Ryu, C.-W. Bark, C.-B. Eom, E. Y. Tsybalk, A. Grunevann, Nano Lett. 2012, 12, 5697.
[4] E. Y. Tsybalk, H. Kohlstedt, Science 2006, 313, 181.
[5] A. Kanthoubaula, V. Garcia, R. O. Cherifi, K. Bouzehouane, S. Fusil, X. Moya, S. Xavier, H. Yamada, C. Deranlot, N. D. Mathur, M. Bibles, A. Barthélémy, J. Grollier, Nat. Mater. 2012, 11, 860.
[6] V. Garcia, S. Fusil, K. Bouzehouane, S. Enouz-Vedrene, N. D. Mathur, A. Barthélémy, M. Bibles, Nature 2009, 460, 81.
[7] L. Wang, M. R. Cho, Y. J. Shin, J. R. Kim, S. Das, J.-G. Yoon, J.-S. Chung, T. W. Noh, Nano Lett. 2016, 16, 3911.
[8] A. Gruverman, D. Wu, H. Lu, Y. Wang, H. W. Jang, C. M. Folkman, M. Y. Zhuravlev, D. Felker, M. Rzchowski, C.-B. Eom, E. Y. Tsymbal, Nano Lett. 2009, 9, 3539.

[9] M. Qian, I. Fina, F. Sánchez, J. Fontcuberta, Adv. Electron. Mater. 2019, 5, 1800407.

[10] D. Pantel, S. Goetze, D. Hesse, M. Alexe, ACS Nano 2011, 5, 6032.

[11] A. Quindeau, I. Fina, X. Marti, G. Apachitei, P. Ferrer, C. Nicklin, E. Pippel, D. Hesse, M. Alexe, Sci. Rep. 2015, 5, 9749.

[12] M. Hambe, A. Petraru, N. A. Pertsev, P. Munroe, V. Nagarajan, H. Kohlstedt, Adv. Funct. Mater. 2010, 20, 2436.

[13] H. Yamada, V. Garcia, S. Fusil, S. Boynt, M. Marinova, A. Gloter, S. Xavier, J. Grollier, E. Jacquet, C. Carrétéro, C. Deranlot, M. Bises, A. Barthélémy, ACS Nano 2013, 7, 5385.

[14] A. Q. Jiang, C. Wang, K. J. Jin, X. B. Liu, J. F. Scott, C. S. Hwang, T. A. Tang, H. Bin Lu, G. Z. Yang, Adv. Mater. 2018, 30, 113102.

[15] G. Radaelli, D. Gutierrez, F. Sanchez, R. Bertacco, M. Stengel, J. Fontcuberta, Adv. Mater. 2015, 27, 2602.

[16] Z. Wen, C. Li, A. Li, N. Ming, Nat. Mater. 2013, 12, 617.

[17] T. S. Böckle, J. Müller, D. Bräuhaus, U. Schröder, U. Böttger, Appl. Phys. Lett. 2011, 99, 102903.

[18] T. Mikolajick, S. Slesazeck, M. H. Park, U. Schroeder, MRS Bull. 2018, 43, 340.

[19] M. H. Park, Y. H. Lee, H. J. Kim, Y. J. Kim, T. Moon, K. Do Kim, J. Müller, A. Kersch, U. Schroeder, T. Mikolajick, C. S. Hwang, Adv. Mater. 2015, 27, 1811.

[20] Y. Wei, P. Nukala, M. Salverda, S. Matzen, H. J. Zhao, J. Momand, A. S. Everhardt, G. Agranis, G. R. Blake, P. Lecoeur, B. J. Kooi, J. Íñiguez, D. Kdhil, B. Noheda, Nat. Mater. 2018, 17, 1095.

[21] J. Lyu, I. Fina, R. Solanas, J. Fontcuberta, F. Sánchez, Appl. Phys. Lett. 2018, 113, 082902.

[22] J. Lyu, I. Fina, R. Solanas, J. Fontcuberta, F. Sánchez, ACS Appl. Mater. Interfaces 2019, 11, 6224.

[23] J. Lyu, I. Fina, J. Fontcuberta, F. Sánchez, ACS Appl. Mater. Interfaces 2019, 11, 6224.

[24] J. Lyu, I. Fina, R. Bachelet, G. Saint-Girons, S. Estandia, J. Gázquez, J. Fontcuberta, F. Sánchez, Appl. Phys. Lett. 2019, 114, 222901.

[25] Y. Wei, S. Matzen, G. Agranis, M. Salverda, P. Nukala, T. Maroutian, Q. Chen, J. Ye, P. Lecoeur, B. Noheda, Phys. Rev. Applied 2019, 12, 031001.

[26] H. Y. Yoong, H. W. Wu, J. Zhao, H. Wang, R. Guo, J. Xiao, B. Zhang, P. Yang, S. J. Pennycook, N. Deng, X. Yan, J. Chen, Adv. Funct. Mater. 2018, 28, 1806037.

[27] A. Tsurumaki, H. Yamada, A. Sawa, Adv. Funct. Mater. 2012, 22, 1040.

[28] Q. H. Qin, L. Åkäslompolo, N. Tuomisto, L. Yao, S. Majumdar, J. Vijayakumar, A. Casiraghi, S. Inkinen, B. Chen, A. Zugarramurdi, M. Puska, S. van Dijken, Adv. Mater. 2016, 28, 6852.

[29] M. Qian, I. Fina, M. C. Sulzbach, F. Sánchez, J. Fontcuberta, Adv. Electron. Mater. 2019, 5, 1800646.

[30] D. Ielmini, H. P. Wong, Nat. Electron. 2018, 1, 333.

[31] D. Ielmini, R. Waser, Resistive Switching: From Fundamentals of Nanoionic Redox Processes to Memristive Device Applications, John Wiley & Sons, New York, 2015.

[32] K.-L. Lin, T.-H. Hou, J. Shieh, J.-H. Lin, Y.-J. Lee, J. Appl. Phys. 2011, 109, 084104.

[33] L. Goux, Y.-Y. Chen, L. Pantisano, X.-P. Wang, G. Groeseneken, M. Jurczak, D. J. Wouters, Electrochem. Solid-State Lett. 2010, 13, G54.

[34] G. Bersuker, D. C. Gilmer, D. Veksler, P. Kirsch, L. Vandelli, A. Padovani, L. Larcher, K. McKenna, A. Shluger, V. Iglesias, M. Porti, M. Nafria, J. Appl. Phys. 2011, 110, 124518.

[35] M. Lanza, K. Zhang, M. Porti, M. Nafria, Z. Y. Shen, L. F. Liu, J. F. Kang, D. Gilmer, G. Bersuker, Appl. Phys. Lett. 2012, 100, 123508.

[36] F. Ambriz-Vargas, G. Kolhatkar, M. Broyer, A. Hadi-Youssef, R. Nouar, A. Sarkissian, R. Thomas, C. Gomez-Yáñez, M. A. Gauthier, A. Ruediger, ACS Appl. Mater. Interfaces 2017, 9, 13262.

[37] F. Ambriz-Vargas, G. Kolhatkar, R. Thomas, R. Nouar, A. Sarkissian, C. Gomez-Yáñez, M. A. Gauthier, A. Ruediger, Appl. Phys. Lett. 2017, 110, 093106.

[38] B. Max, M. Pešić, S. Slesazeck, T. Mikolajick, J. Appl. Phys. 2018, 123, 134102.

[39] W. F. Brinkman, R. C. Dynes, J. M. Rowell, J. Appl. Phys. 1970, 41, 1915.

[40] S. Estandia, N. Dix, J. Gázquez, I. Fina, J. Lyu, M. F. Chisholm, J. Fontcuberta, F. Sánchez, ACS Appl. Electron. Mater. 2019, 1, 1449.

[41] S. Monaghan, P. K. Hurley, K. Cherkaoui, M. A. Negara, A. Schenk, Solid-State Electron. 2009, 53, 438.

[42] P. W. Peacock, J. Robertson, J. Appl. Phys. 2002, 92, 4712.

[43] M. Y. Zhuravlev, R. F. Sabirianov, S. S. Jaswal, E. Y. Tsymbal, Phys. Rev. Lett. 2005, 94, 246802.

[44] I. Fina, L. Fábrega, E. Langenberg, X. Martí, F. Sánchez, M. Varela, J. Fontcuberta, J. Appl. Phys. 2011, 109, 074105.

[45] S. González-Casal, I. Fina, F. Sánchez, J. Fontcuberta, ACS Appl. Electron. Mater. 2019, 1, 1937.

[46] P. D. Nellist, S. J. Pennycook, Ultramicroscopy 1999, 78, 111.