Electroresistance in non-tunnelling ferroelectric junctions

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Abstract: Ferroelectric materials are of potential interest for their integration in memristive devices. Polarization switching in ferroelectric thin film junctions might lead to a change of the electronic band diagram of the device, which can result in important changes of resistance. This effect is known as electroresistance. Electroresistance in 12.2, 24.3 and 36.5 nm BTO thin films junctions is investigated. It is observed that electroresistance decreases with thickness. In addition, ferroelectric characterization allows to conclude that switchable ferroelectric polarization also decreases with thickness. Thus, we conclude that electroresistance is intimately linked to the ferroelectric switching process.

I. INTRODUCTION

Memristor devices behave like an analogic multi-state resistance and have a strong potential for implementation in large-scale neuromorphic circuits [1]. The term is used to describe devices which resistance can be stabilized at multiple different values upon application of an applied external field. Ferroelectrics are insulators by definition; however, in nanometre thick ferroelectric layers thermally activated current and electronic tunnelling from quantum mechanical origin can take place. Ferroelectric materials display spontaneous polarization in absence of applied electric field. Spontaneous polarization can be commuted between different states by the application of adequate external electric field. The ferroelectric switching can influence the mentioned different electric transport mechanisms (tunnelling or thermally activated current), which can result in changes of the electrical resistance that can mimic the memristor behaviour. The effect of the change in resistance by ferroelectric polarization switching is known as electroresistance.

Ferroelectric polarization dependence on electric field shows the archetypical hysteretic curve shown in Figure 1(a). When all the electric moments are oriented in the same direction, the system is said to be saturated. In this region (AB interval), the polarization increases linearly with the field like in normal dielectrics. If we now reduce the intensity of the electric field, instead of heading back to zero polarization the system follows the BC line. Some domains are still aligned with the field, and the system presents spontaneous polarization at zero external field known as remanence. To cancel this polarization, we apply an electric field in the opposite sense. When the field generates a state with the same amount of moments oriented in opposite directions, the polarization of the ferroelectric is zero. This field is known as coercive field and provides an insight of the height of the local energy barriers which trap the domains. Increasing the electric field originates a negative polarization that takes it again to saturation following DE. Taking the field back to positive values following EFB will close the cycle.

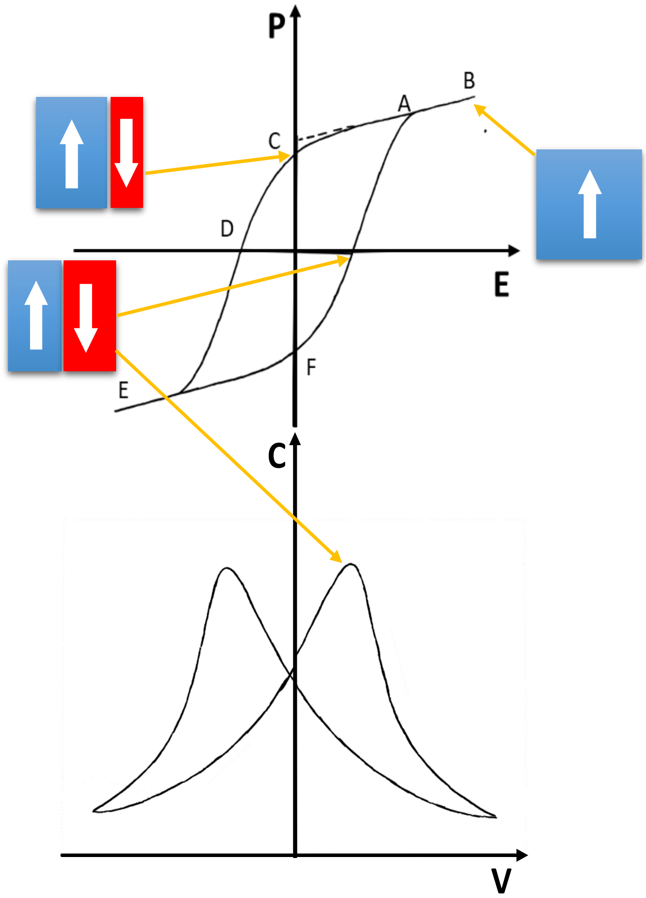

FIG. 1: (a) Polarization dependence on electric field for an archetypical ferroelectric material. (b) Capacitance dependence on applied voltage for an archetypical ferroelectric material. Sketches correspond to domain configuration.

Metal/Ferroelectric/Metal (MFM) junctions are based on 3-layer structures: a thin layer of a ferroelectric sandwiched between two metal electrodes. At the ferroelectric metal interface, the polarization of the ferroelectric points towards one of the two electrodes and attracts the compensation charges of the metal. Compensation charge screens the surface charge of the ferroelectric. However, compensation charges are spread over a finite length originating an imperfect screening inside the ferroelectric. Imperfect screening gives rise to presence of electric fields and concomitant electrostatic potential and energy band discontinuities.

In a symmetric MFM junction, the screening lengths of both electrodes are the same, so the energy band will be symmetric upon ferroelectric polarization switching. The impedance is the same in both states of polarization and consequently there is no electroresistance. If the screening lengths of the different electrodes are different, the electrostatic potential will be asymmetric. Therefore, upon ferroelectric polarization switching the electronic energy band will change. This results in two resistance states depending on the direction of the polarization and gives rise to electroresistance.

When there is an applied voltage across the MFM to measure the resistance, many conduction mechanisms can take part: Direct Tunnelling (DT), Fowler–Nordheim tunnelling (FNT) and thermionic injection (TI).

A. Direct Tunnelling

Carriers can tunnel through the energy barriers of the ferroelectric by direct quantum tunnelling. Current density is exponentially dependent on the applied voltage which tunes the heights of the barriers. Tunnelling probability increases with a reduction in the effective length of the barrier. Thicker samples have a thicker energy barrier which limit quantum tunnelling effects.

B. Fowler–Nordheim Tunnelling

FNT is an extension of direct tunnelling mechanism. At high voltage, the slope of the energy barrier lies beneath the Fermi energy of the electrode. This forms a triangular-shaped potential barrier from the trapezoidal barrier. It reduces the effective width of the barrier and increases tunnelling current, allowing an increase in tunnelling in thicker junctions.

C. Thermionic Injection

At finite temperatures, thermal energy excitation provide the carriers a non-zero probability of jumping the energy barrier of the junction. This probability increases with increasing temperature. TI is an interface phenomenon which is independent of the width of the barrier thus is independent of the thickness of the ferroelectric so the mechanism is more prominent in thicker films.

Our aim is to study the electroresistance effects and its relation to ferroelectricity at thicknesses near above 10 nm, where tunnelling currents are expected to be suppressed, and thermoionic injection becomes dominant [2].

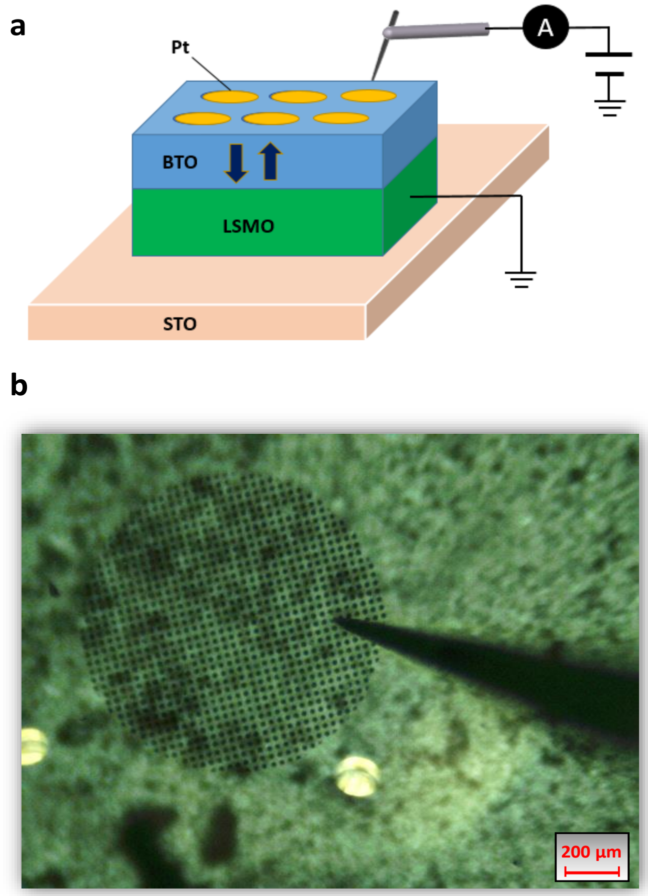

FIG. 2: (a) Cross-sectional view of one MFM sample. A micrometric tip is used to electrically connect the device. Arrows indicate the possible polarization states. (b) Picture of sample. Top Pt electrodes of 20 μm of diameter and the tip to make the contact can be observed. The picture dimensions are 1760x2290 μm.

II. MATERIALS AND METHODOLOGY

Bottom conductive electrode LSMO ($La_{0.67}Sr_{0.33}MnO_3$) of 25 nm of thickness was grown on a STO ($SrTiO_3$) substrate by pulsed laser deposition. BTO ($BaTiO_3$) ferroelectric layers of thicknesses 36.5, 24.3 and 12.2 nm were grown by pulsed laser deposition on top of the LSMO layer. Pt top circular electrodes of 20 μm of diameter were deposited on the BTO layers by sputtering. Further experimental details can be found elsewhere [3].

I-V loops were characterized using aixACCT TFAnalyzer2000 platform. Measurements were performed by applying an electric field between the top Pt electrode and the bottom LSMO electrode using micrometric

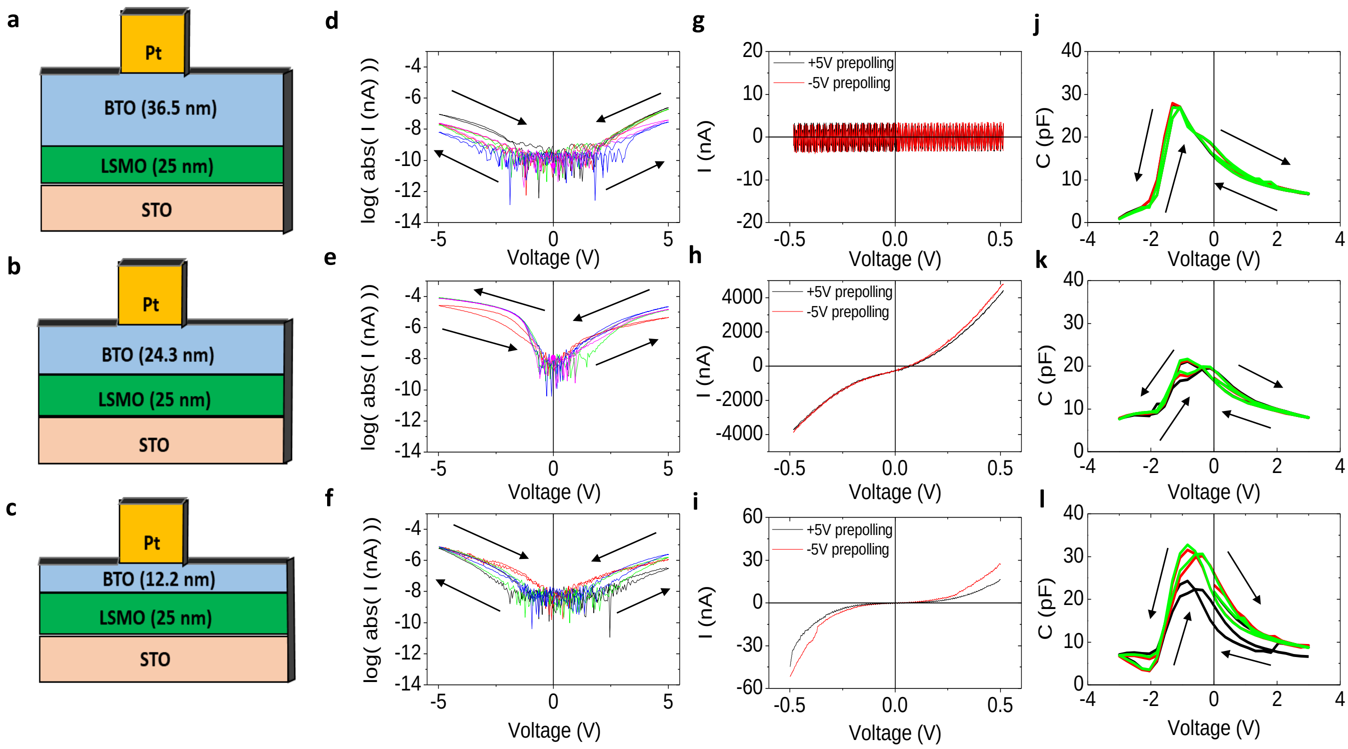

FIG. 3: (a,b,c) Sketches of the cross-sectional view of the samples of different thickness. (d,e,f) I-V loop at a maximum voltage of 5 V. Colours indicate measurements for different electrodes and arrows the direction of variation of applied magnetic field. (g,h,i) Pulsed I-V loop for for 12.2, 24.3 and 36.5 nm thick BTO samples measured for $|V_{read}|<0.5$ V for 1 s after the application of a $|V_{write}|<5$ V prepolling pulse. Black curve indicates positive prepulsed voltage and red curve negative prepulsed voltage. (j,k,l) C-V loop measured at a maximum voltage of 3 V. Colours indicate measurements for different electrodes and arrows the direction of variation of applied magnetic field.

metallic tips. Measurements were performed at a range of 5 V.

Current through the MFM was also measured using prepulsed applied voltage with aixACCT TFAnalyzer2000 platform by applying write voltage prepulses of amplitude $|V_{write}|=5$ V between the tip and the bottom electrode and subsequently measuring the I-V characteristics using small voltage range, $|V_{read}|$ <0.5 V.

C-V loops were measured using an impedancemeter HP4192A LF (Agilent Co.) by using the same contact configuration at a maximum applied voltage of 3 V.

III. RESULTS

Electrical characterization has been performed for the three samples of different BTO thickness sketched in Figure 3(a,b,c).

Figure 3(d,e,f) shows current as a function of voltage for the three samples. In Figure 3(d) hysteresis cannot be observed while in Figure 3(e) some electrodes start to present hysteresis. In Figure 3(f) all the electrodes show hysterical behaviour at the same applied voltage. In brief, BTO layers present an increase in ferroelectric hysteresis as the thickness of the ferroelectric decreases. Notice also that in Figure 3(e), hysteresis sign for the 24.5 nm sample is opposite compared to the other samples for negative voltages. This can be ascribed to small variations on metal/ferroelectric interface, which precise origin goes beyond the scope of the present work.

To get further insight on the consequences of the observed hysteresis in junction resistance, we have performed prepulsed experiments for the three samples which are shown in Figure 3(g,h,i). Figure 3(g) has a lot of noise due to the high resistance of the ferroelectric so the result is not conclusive and will be discussed in more detail in the discussion section. Figure 3(h) shows a larger current for negative prepulse than for positive prepulse. Figure 3(i) also presents a larger current for negative prepulse and the difference between the current at negative prepulse and the positive prepulse becomes larger than that of Figure 3(h). Therefore, lower resistance variation is observed for thicker films upon ferroelectric polarization switching.

Ferroelectric characterization for the three samples has been also performed by means of CV measurements. In

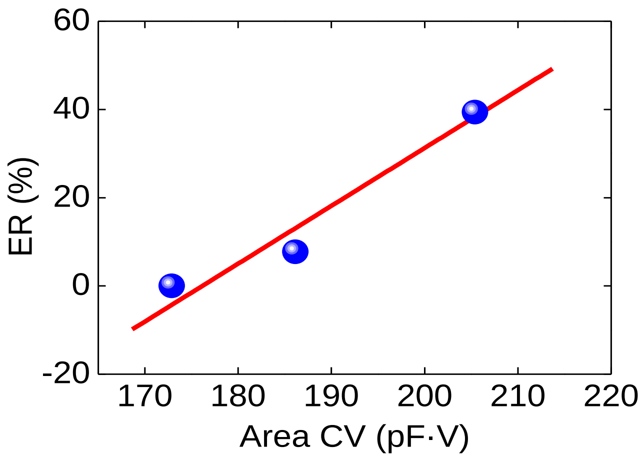

FIG. 4: Dependence of the electroresistance measured at V_{read}=0.5 V with the CV hysteresis area for each sample.

Figure 3(j,k,l) capacitance as a function of voltage for the three samples is displayed. Figure 3(j,k,l) shows a non-linear capacitance caused by residual hysteresis. Figure 3(j) does not show hysteresis for the thickest sample. In comparison, Figure 3(k,l) shows increased hysteresis, revealing larger ferroelectric polarization switching for decreased thickness.

IV. DISCUSSION

According to previous literature, we ascribe the conduction mechanism origin to thermionic injection because, at the measured thicknesses, tunnelling is expected to vanish [2]. Data in Figure 3 suggests increased resistance variation for larger polarization switching. In these devices, polarization does not switch abruptly from up to down. Ferroelectric switching occurs through the formation of ferroelectric domains of opposed polarity. In thinner ferroelectrics, a larger number of domains switch direction upon ferroelectric polarization switching because, as far as the applied voltage is fix for all samples, the electric field for the thinner ones is most probably much above the ferroelectric switching coercive field. As a result, there will be a larger change in resistance upon ferroelectric polarization switching for thinner samples as Figure 3 exhibits. Research has shown that, resistive switching phenomenon can be caused by charged oxygen vacancies which move under the influence of the electric field [4]. These may release their free charges at the interface and thus modify subsequently the energy profile. To check if the electroresistance effect was caused by these impurities or by polarization switching, we plot in Figure 4 the CV hysteresis area as a function of ER. Since the current depends on the barrier height we can define the electroresistance as

$$ER = \frac{R_H - R_L}{R_H} \tag{1}$$

where R_H is the resistance in the high conducting state and R_L in the low conducting state. The noise in Figure 3(c) does not allow a proper reading of the current. However, in the range of |V|=5 V, 36.5 nm ferroelectric does not yet show hysteresis so the energy barrier is almost symmetrical. The resistance is almost the same for both polarization states and the electroresistance tends to zero.

It can be observed in Figure 4 that the CV area increases with decreasing thickness of the ferroelectric. As the CV hysteresis area accounts for the polarization switching, resistance switching is a consequence of polarization reversal and not caused by free charges released by oxygen vacancies.

V. CONCLUSIONS

We have reported electroresistive effects in MFM junctions with thicknesses of 12.2, 24.3 and 36.5 nm. We have accounted for an increase in ferroelectric behaviour and ER as the thickness of the layer decreased. Therefore, we have observed that there is a direct correlation between ferroelectricity and electroresistance. We conclude that, in our films, data suggests that ER results from ferroelectric switching.

These features qualify MFM junctions based on BTO as potential candidates for the fabrication of memristors for neuromorphic circuits. Moreover, in order to disclose the exact conduction mechanism that allows electronic transport in our films, further experiments at different temperatures are proposed.

Acknowledgments

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[1] M. Prezioso et al, «Training and operation of an integrated neuromorphic network based on metal-oxide memristors,» Nature, **vol. 521**, **pp. 61–64** (2015).

[2] D. Pantel and M. Alexe, «Electroresistance effects in ferroelectric tunnel barriers,» Phys. Rev. B, **vol. 82**, **Iss. 13**, **pp. 41-46** (2010).

[3] F. Mao, «Photoresponse of ferroelectric $BaTiO_3$ thin films.» (Doctoral dissertation). Retrieved from Physics Department [538.9 - Condensed Matter Physics], Universitat Autònoma de Barcelona (2017). (ISBN: 9788449077197)

[4] S. Boyn, «Ferroelectric tunnel junctions: memristors for neuromorphic computing.» (Doctoral dissertation). Retrieved from Materials Science [cond-mat.mtrl-sci], Université Paris-Saclay (2016). (NNT: 2016SACLS089)