STUDENT RESEARCH REPORT
Ferroelectric tunnel junctions based on correlated oxides

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1 Introduction

1.1 Ferrolectricity

Ferroelectrics are materials which exhibit a spontaneous electric polarization switchable by external electric fields. This polarization results from the transition into a polar state with a lattice distortion which breaks inversion symmetry.

A paradigmatic ferroelectric material is Barium Titanate ($BaTiO_3$, also referred to as BTO), member of the *perovskite family* (from the mineral perovskite $CaTiO_3$). Over 393 K, BTO's crystal structure is cubic and can be described in terms of the five following base ions: one Ba^{2+}, one Ti^{4+} and three O^{2-}, as depicted in figure 1a. This state features zero polarization as a consequence of its symmetrical arrangement of ions. However, as temperature decreases, BTO exhibits three less symmetrical structures (tetragonal [from 278 to 393 K], orthorhombic [from 183 to 278 K] and rhombohedral [lower than 183 K]), all of them characterized by an off-centre position of Ti^{4+} which originates polarization. Figures 1b and 1c show two different polarization states of the tetragonal phase with titanium's displacement taking place along [001] (for orthorhombic and rhombohedral this direction changes to [011] and [111] respectively).

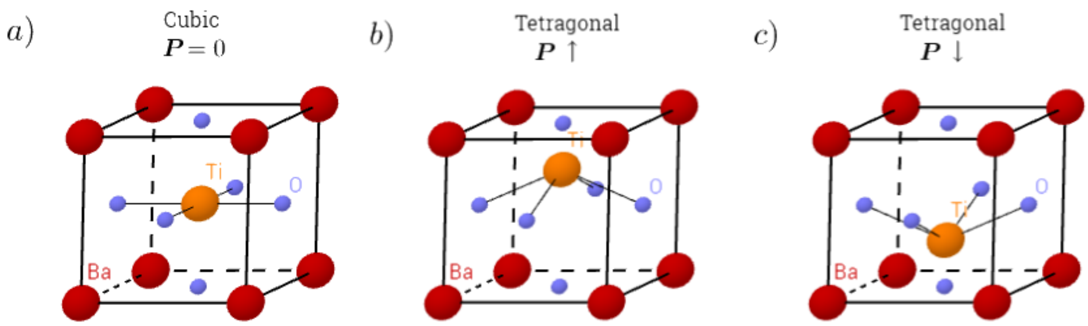

Figure 1: Two BTO's phases. a) Cubic phase ($T > 393$ K) with zero polarization due to its symmetry. b) and c), tetragonal phase ($278 < T < 393$ K) with two different polarization orientations.

1.2 Ferroelectric tunnel junctions

Tunnel junctions are structures where an ultrathin insulating layer is sandwiched between two conductors. Transport in these devices is mainly due to the tunnel effect in the dielectric barrier, being the resistance determined by the form of the barrier. *Ferroelectric tunnel junctions* (FTJs) add a degree of freedom to conventional tunnel junctions by choosing the dielectric barrier to be ferroelectric: depending on the polarization orientation, the tunneling conductance varies, thus leading to an *electroresistance effect* (currents originate a change in electrical resistance).

More in detail, the so called giant electroresistance mode [1] can be described as follows. When a dielectric is sandwiched between two conductors C1 and C2, polarization charges at the interfaces repel or attract electrons from electrodes until their fields are screened. If conductors feature similar work functions and different screening lengths $\delta_1 < \delta_2$, the effective barrier height is higher when polarization points towards C1 than in the opposed situation (schematized in figure 2). As a result, resistance is lower in the former case than in the latter. From a practical perspective, resistance states can be written in FTJs through the application of electric (coercive) fields which change polarization orientation, and can later be read with weak currents. Interestingly, here, as in ferroelectricity, asymmetry (now concerning the electrodes) is responsible for this effect.

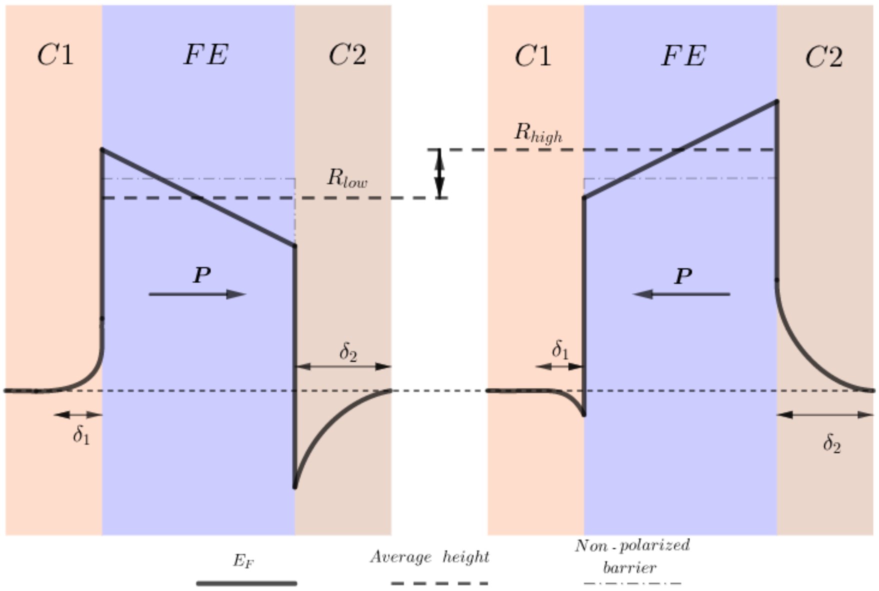

Figure 2: Comparison of tunnel barriers average heights between the two different polarization states in the giant electroresistance model.

The possibility of modulating the tunneling resistance by the orientation of the ferroelectric polarization in what is called *tunneling electroresistance* (TER) [1] has focused much interest in recent years. Notably, a giant electroresistance has been theoretically predicted [1, 2] and experimentally observed [3, 4, 5] for ferroelectric capacitors with metal electrodes with different screening lengths. However, there is a growing debate in the literature on the origin of the large changes in the tunneling conductance driven by the application of moderate electric fields.

Our research is focused on the study of FTJs with $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) bottom electrode (C2), ultrathin BTO ferroelectric barrier (2 nm) and Ag upper electrode (C1). More in detail, we are interested in the understanding of an additional degree of freedom found in these FTJs: oxygen vacancies. These vacancies exist naturally in ultrathin BTO layers and can be furthermore (catalytically) electrogenerated at the Ag interface due to its high oxygen diffusivity and oxygen reduction potential. Oxygen vacancies are positive defects and carry a doping field due to the accompanying neutralizing pair of e^-. In a first approach, vacancies could be considered to be problematic as they might move in the presence of writing fields, and consequently, distort the tunnel barrier in a form which may destroy the two well defined resistance states. Nonetheless, our vision is that these vacancies' movements can be controlled, and furthermore, give FTJs an additional functionality which can be exploited. In this report, we provide measurements that show evidence for the presence of vacancies and that have helped us to characterize the behaviour of both polarization and vacancies.

2 Experimental methods

Ferroelectric BTO has been grown on Sr doped La manganite LSMO epitaxially deposited onto $SrTiO_3$ (STO) substrates using a high (pure) oxygen pressure sputtering technique. Conventional lithography was used to define micron size pillars allowing for the measurement of perpendicular transport. FTJs have been connected to a Keithley SourceMeter to measure I-V curves, as well as to a pulse generator used to switch polarization. Figure 3 sketches the overall arrangement. Reading voltages were constraint to 200 mV in order to minimize polarization changes. The I-V curves obtained are non-linear as expected for tunnel barriers and, although resistance can be inferred through the fitting of these curves to tunnelling models, numeric derivative dV/dI at 100 mV has been used to infer an approximate value, as we are only interested in qualitative variations of the resistance. Measurements were performed at 100 K, so that the BTO phase was rhombohedral with spontaneous [111] polarization. However, epitaxial strain imposes a tetragonal distortion which renders polarization in the [001] direction. It is worth pointing out here that ABF cross section images (not shown) display Ti-O displacements which indicate that, in the virgin state, polarization points towards LSMO.

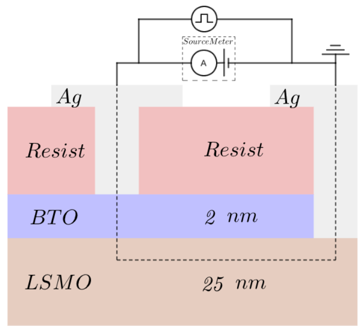

Figure 3: Sketch of the FTJ device connections for reading and writing operations.

3 Results and discussion

Measurement of the differential resistance as a function of the amplitude of 100 ns (write) voltage displayed the well-known *ferroelectric hysteresis loops*. Figure 4a shows one and a half consecutive loops. As illustrated on figure 4b, tunneling conductance changed between the following states. In the virgin state (1) polarization points downwards. Secondly (2), negative bias pulses, which according to the setting in figure 3 correspond to electric fields pointing up, i.e., opposed to virgin polarization, gradually switch the orientation of ferroelectric domains (the non-abrupt change in differential resistance evidences the existence of domains). Stage (3) corresponds to complete polarization switching and determines one coercive field. Finally, the application of positive voltage pulses (electric field pointing downwards) progressively reverses polarization until reaching the final stage (4) with polarization back to its original state. The final result is a one order of magnitude resistance switching. A repetition of half of the cycle is plotted to show that, after finishing the first cycle, the system has apparently recovered to its initial state. However, it must be said that reproducibility is hard to achieve and further work has to be done about how to retain the system in a well defined cycle. In addition, it

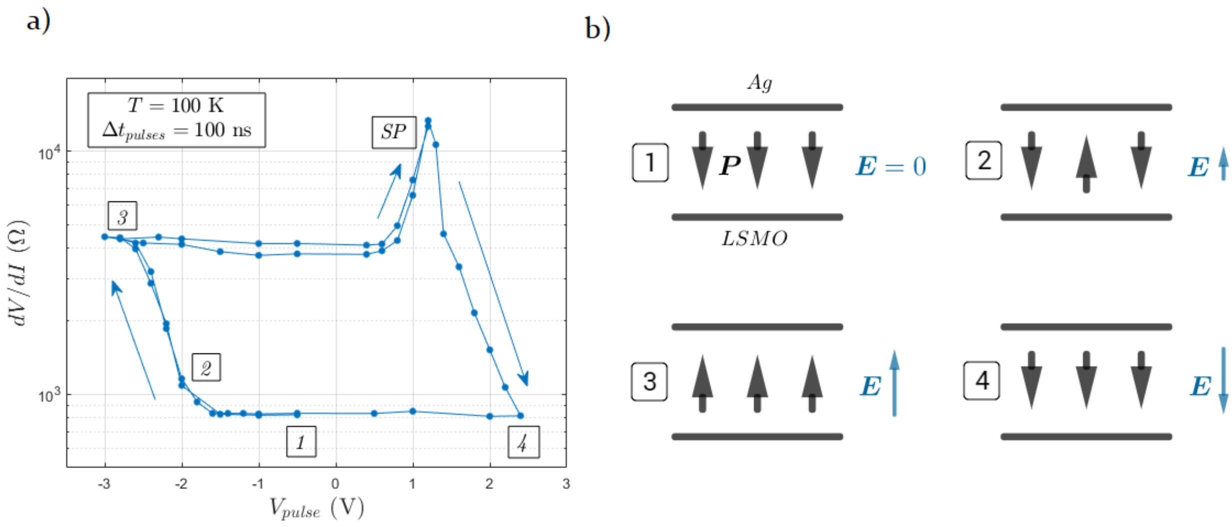

Figure 4: a) Ferroelectric hysteresis measurements with labelled states. b) Sketch of the polarization state for the states labelled in a).

is interesting to note that the coercive field at (3) is higher than in (4) which agrees with the polarization trend to point towards LSMO.

Figure 4a shows a resistance peak labelled SP which cannot be explained in terms of ferroelectricity. Our hypothesis is that this peak corresponds to a *Schottky barrier* originated by the accumulation of O^{2-} vacancies in the BTO-LSMO interface, which is reverse biased for electric fields pointing down. The formation of the Schottky barrier increases the height of the tunnel barrier and, accordingly, resistance increases.

Furthermore, it is possible to control the formation of this Schottky barrier by controlling the position of vacancies and their relative electrons: when the applied electric field points towards the Ag-BTO interface (negative voltage pulses), vacancies are moved out from the BTO-LSMO interface, thus removing the Schottky barrier and making the junction less resistive; if the field changes direction, vacancies are generated and the Schottky barrier is restored with the corresponding increase in resistance. The overall process is a *oxygen vacancies' cycle*. Figure 5 shows two consecutive vacancies' cycles, obtained after the first one and a half ferroelectric loops and followed by a half ferroelectric loop. Electric fields necessary to switch vacancies do not surpass the coercive values, so the polarization state remains unchanged. In fact, once the vacancies' cycle has been closed in the Schottky's peak (SP), another ferroelectric hysteresis cycle can be restarted. The vacancies' cycle allows almost an extra order of magnitude change in resis-

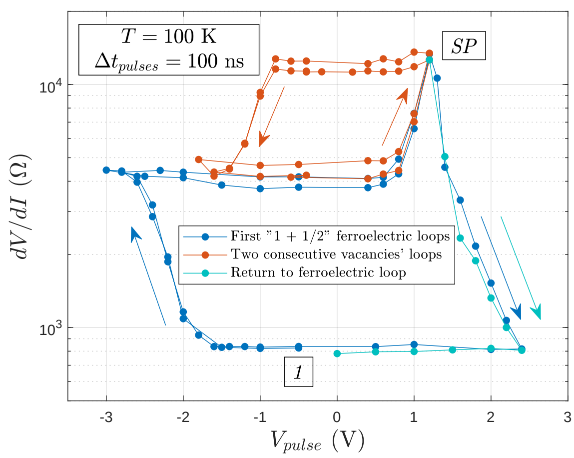

Figure 5: Consecutive loops: one and a half ferroelectric loops, two vancancies's cycles and return to ferroelectric loop. (1) denotes the virgin state and (SP) the Schottky peak.

tance above the high resistance state of the ferroelectric loop. In addition, it is interesting to note the differential fact that ferroelectric loops have a clockwise switching while vacancies' switching is anti-clockwise, and consequently, the two kind of loops differ in the sign of electroresistance.

It becomes clear that the SP is an oxygen vacancy process where the ferroelectric polarization seems to control the ionization of oxygen vacancies which in turn affects ferroelectric switching. The coupled switching of oxygen vacancies and ferroelectric polarization is an interesting new avenue for novel electroresistance effects which may be the seed of novel device concepts in a future oxide electronics.

4 Conclusions

We have studied the effect of oxygen vacancy generation in oxide ferroelectric tunnel junctions with BTO tunnel barriers and LSMO and Ag electrodes. We have found a novel electroresistance effect due to polarization controlled ionization of oxygen vacancies, noticing that ferroelectric and oxygen vacancy switching have opposite sign contributions to the junction electroresistance. This is an important result which may contribute to settle the debate on the role of oxygen vacancy switching in the ferroelectric electroresistance. The concurrent electronic (screening of polarization charges) and electrochemical (generation of oxygen vacancies) processes in a single device is a step towards future neuromorphic devices mimicking operation of whole neurons rather than synapses.

References

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