Growth and characterization of memristive manganite thin films

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Resistive switching effects were studied on manganite based devices at room temperature. Thin films of Laₐ₀₆₆Ca₀₃₃MnO₃ were grown using the pulsed laser deposition technique on top of conductive silicon substrates. Top contacts were deposited either by hand (Ag paint) or by sputtering (Cu). The Mn valence (which is correlated with the oxygen content) was probed by means of XPS experiments. Obtained devices were characterized electrically by means of pulsed I-V curves, and the remnant resistance state was measured after each voltage pulse. In all samples we observed bipolar resistive switching with sharp SET and RESET transitions. Typically, around 20 switching cycles could be repeated, with an OFF/ON ratio of 2-3 orders of magnitude. We found different SET and RESET voltages for Ag and Cu top electrodes. In addition, we found a correlation between the amplitude of the ON/OFF ratio and the oxygen content of the films, suggesting that oxygen vacancies play a key role in the switching mechanism. Finally, the electrical response of a Cu/LCMO sample was studied after a controlled damage process (irradiation with 25 MeV oxygen ions with a fluence of 3E10 ions).

Researches on Ferroelectrics in SFB 595 project as of 2011

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The center of excellence in advanced functional ceramics at the “Technische Universität Darmstadt” develops and characterizes a wide spectrum of functional ceramics. In the core of the center lie eight working groups within the framework of SFB 595 project sponsored by the German Science Foundation and the state-funded Center for Adaptronics. Over the last decade, synergic collaborations among the groups encompassing relevant fields in the Materials Science, i.e., processing, electrical characterization, structural analyses, and theoretical modeling, has proven highly successful with noticeable outcomes. Representative achievements by the eight working groups on the mechanistic studies of the reliability of ferroelectric materials and the development of new lead-free materials are presented.
Electronic transport mechanisms in metal-manganite memristive interfaces

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We studied a La₀.₃₂₅Pr₀.₃₀₀Ca₀.₃₇₅MnO₃-Ag memristive interface. We present a pulsing/measuring protocol capable of registering both quasi-static i-v data while pulsing and non-volatile remnant resistance after pulsing. This protocol allowed distinguishing two different electronic transport mechanisms coexisting in the memristive interface. These two mechanisms appear to be space charge limited current and thermionic emission limited current. We introduce a 2-element electric model that accounts for the obtained results and allows predicting the quasi-static i-v relation of the interface as a simple function of the remnant resistance. Each of the elements of the electric model is associated to one of the electronic transport mechanisms found. This electric model may result useful for developing time-domain simulation models of metal-manganite memristive interfaces.

Optimization of resistive switching performance of memristive metal manganite oxide interfaces by a multipulse protocol

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Non volatile memory concepts for electronic applications are presently based on resistance change rather than in charge storage. Electric pulse induced resistance switching (RS) was shown to produce useful retention time capability for massive applications. Several basic and applied research teams are presently devoted to the study of transition metal oxides contacted through metal electrodes driven by appealing fast switching and scalability.

Evidence for an oxygen diffusion mechanism by means of electric transport measurements was recently obtained by means of a Hysteresis Switching Loop (HSL) procedure in which pulses of varying amplitude determine the state of the interface, and a small bias is used to test the remnant state. We performed HSL’s in manganite La₀.₃₇₅Pr₀.₃₂₅Ca₀.₃₈₅MnO₃ at various conditions. We study the characteristics of non common higher resistance states than the usual high and low resistance states accessible through bipolar pulsing. We found that these higher resistance states can be obtained by repeatedly pulsing with a single polarity. The accumulative action of successive pulsing drives the resistance towards saturation, the time constant being a strong function of the pulsing amplitude. These results can be explained by oxygen vacancy detrapping in the interface oxide-metal. In this work we analyze the different vacancies profiles obtained through numerical simulations which give insight in the resistive switching dynamics.
Resistive Switching in multilevel TiO₂ memory devices

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Non volatile memory concepts for electronic applications are presently based on resistance change rather than in charge storage. Electric pulse induced resistance switching (RS) was shown to produce useful retention time capability for massive applications. Several basic and applied research teams are presently devoted to the study of transition metal oxides contacted through metal electrodes driven by appealing fast switching and scalability. In the present work, we study Au / TiO₂ / metal (Cu and Al) junctions in a crossbar pattern which exhibit resistive switching characteristics (†). We study its physical-chemical mechanisms and its response in aggressive environments. We perform its electrical characterization, both, IV (dynamic measurement) and HSL (remnant measurement) curves. Besides we compare the evolution of the RS response with / without protons and oxygen ions irradiation.

In devices with Cu top electrode we obtain evidence of a copper metallic filament for negative electroforming, while for positive electroforming the filament is presumably TiO₂ - Magnelli phase based. From the comparison of both states we discuss the role of the defects involved in the oxide matrix, which are responsible for the multilevel states observed.

In devices with Al top electrode, after the negative electroforming process we observe the presence of micrometer sized “craters”. We study the effect of changing the current compliance Icc to control the area where these craters appear. The resistance of the two resistive states decreases when Icc is increased. Based on these trends, we suggest that the change in the affected area (due to the different Icc’s) is related to the number of formed filaments at the oxide matrix.

Additionally we reproduce the experimental results through a realistic model that includes as a main ingredient the oxygen vacancies diffusion under applied electric field. The associated vacancy profiles further unveil the prominent role of the effective electric field acting at the interfaces. These simulations allow to disentangle the microscopic mechanisms behind the resistive switching in metal-transition metal oxide interfaces.

† Samples were grown by sputtering TiO₂ and using standard optical lithography. We acknowledge the MEMS group at CAC-CNEA-Argentina and the Microelectronic Group at INTI- Argentina for assistance and fruitful discussions during fabrication.

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Characterization of charge transport in vanadium oxide V2O₅ thin films obtained by RF sputtering deposition and post-annealing.

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V$_2$O$_5$ vanadium oxide thin films were prepared via RF Magnetron Sputtering deposited at room temperature and then post-annealing on air at different temperatures and characterized via SEM-AFM-XRD-FTIR. Then was tested resistivity and fitted with the charge carrier hopping transport process. The temperature coefficient of resistance obtained was TCR =-3.61%/$^\circ$K with sheet resistivity of 104:5MΩ cm$^2$ @ 25$^\circ$C.

Micro- and nanoprotoyping facilities at INTI

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Sensor technologies and Micro-Electro-Mechanical Systems manufacturing require a wide set of materials and methods, due to the wide range of possible applications: from physical to optical, chemical and biological. Packaging and testing play also a significant role, since they consume the majority of the total fabrication cost.

INTI-CMNB offers several facilities involved with every step in the manufacturing chain: from device nanoprotoyping to wafer level testing. We present here an overview of these facilities and example applications.

Growth and electrical characterization of bismuth ferrite thin films

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Thin films of the room temperature multiferroic BiFeO$_3$ were grown by pulsed laser deposition on top of n-type silicon. The growth was performed at 650$^\circ$C under an O$_2$ pressure of 0.12mbar. The thickness (~100nm) was estimated from scanning electron microscopy cross-view. A moderate amount of particulate was found on the surface. X-ray diffraction suggests a BiFeO$_3$ textured growth, along with the presence of segregated Fe$_3$O$_4$ magnetite phase. Cu top electrodes were deposited by sputtering at room temperature and shaped by standard optical lithography. Resistive switching effects were studied at room temperature. Obtained devices were characterized by means of pulsed I-V curves, and the remnant resistance state was measured after each voltage pulse (Hysteresis Switching Loops, or HSL). We observed bipolar resistive switching, with an OFF/ON ratio of up to 40, depending on the compliance current applied during the SET process. SET and RESET voltages were found at 5V and -5V.
We observed squared HSLs, suggesting that only one interface is active (presumably BFO/Si), while the other one remains ohmic.

**Electric voltage effects on silver-mesoporous titania nanocomposite thin film arrays during conductive tip AFM scannings**

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In this work we present the results obtained with conductive-tip atomic force microscopy (CT-AFM) in silver nanoparticles (AgNP) patterns infiltrated in TiO\(_2\) mesoporous thin films (MTF). The TiO\(_2\) MTF infiltrated with AgNP arrays were fabricated by the *lithography-assisted photocatalysis* method [1]. In these nanostructures, the properties related with the size and the confinement of the Ag-NP and the TiO\(_2\)-Ag interfaces can be explored while the NP remains protected from the environment.

CT-AFM results revealed a conduction contrast of more than two orders of magnitude between the current measured inside and outside the infiltrated regions. The dependence of the electric properties with the thickness, the MTF structure and the AgNP loading confirmed that the electric conduction develops tridimensionally within the film [2]. Here it will be displayed that it is possible to modify locally the electric resistance and the topography depending on the applied voltage during the CT-AFM scanning.

**REFERENCES**


**Electronic transport in ferromagnetic multilayers deposited by pulsed laser ablation**

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Ferromagnetic multilayers with different configurations were deposited by pulsed laser ablation. Spin valves (10nmCoFe2/3nmCu/10nmCoFe2/20nmCoFe2O4/Si) and magnetic tunneling junctions (10nmNiFe/5nmZnO/10nmCo/Si) were fabricated and characterized at room temperature without external magnetic field applied.

The spin valve showed two different bias regimes, with a marked decrease in resistance for applied voltages greater than 0.2 V. We suggest that this could be attributed to the creation of conduction paths with increasing voltage, due to a partially oxidized copper layer during deposition.

Resistive switching and hysteresis in the I-V curve were observed in the magnetic tunneling junction. We propose that the switching effect could be explained by a change in the relative magnetization direction between ferromagnetic layers due to the circulation of spin polarized current (spin-transfer torque). This effect is typically observed in spintronic memristors.

Experiments on noise assisted resistive switching

A. A. García [1], G. A. Patterson [2], P. I. Fierens [2,3], and D. F. Grosz [2,3]


Recently, Stotland and Di Ventra [1] presented simulations, based on a model of resistive switching by Strukov et al. [2], which take into account the interaction of internal (inherent to the sample) noise with the nonlinearity of the device. They showed that there is an optimal noise intensity for which the contrast between high and low resistance values is maximized. They also suggested that externally applied noise should have a similar effect.

In this work, we present experimental results on the effect of external noise on a sample of La0.325 Pr0.3 Ca0.375 MnO3. We first studied the behavior of the sample resistance under the application of short (~ 1 ms) noiseless current pulses and found that only large amplitude pulses (>~ 500 mA) produced a significant resistance change. We then added white Gaussian noise to the current pulses. In this case we found that noisy pulses with a small mean current amplitude induced similar resistance changes as those observed for much larger noiseless pulses.


Simulating Resistive Switching in Manganite Thin films
We study the resistive switching behaviour in capacitor like structure devices with a transition metal oxide sandwiched between two metallic electrodes using a phenomenological model where the oxygen vacancies migration is enhanced by the local electric field.\(^a\)

We assume that the local resistivity has a linear dependence with the vacancy concentration, and that the metal oxide interfaces are the regions were a high resistance develop. The model\(^a\) consists of a single conductive channel within an insulating dielectric, which is represented by a one dimensional resistive network of N links. Upon applying an external voltage, the local voltage drops at the network domains producing a vacancy drift which determines the total resistance of the device.

We explore the parameter space of the model with the aim of optimizing the ratio between High and Low resistance values. We varied the total amount of vacancies, the width of the interface/bulk region and the magnitude of the external electric field in order to simulate the switching response of a manganite thin film. We obtain two quantitatively different regimes, which are related to the amount of vacancies that could reach the bulk region. We discuss these regimes, and compare obtained results with experimental data obtained on LaCaMnO thin films.


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**Electrical Characterization of MEM’s at the MicroLAB – UNSAM ECyT**

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Nowadays, the most advanced storage devices available known are flash memories. The Metal-Insulator-Metal (Co-HfO2-Ti and Al-TiO2-Au) structures we’re working with are based on the Resistive Switching (RS) concept idea. They’re faster, and, hypothetically, more tolerant to E-M radiations than flash memories. Here we explore this new technology for memory devices, by sourcing interleaved DC pulses, both positive as well as negative. Here we present a promising method based on a technology which may be relevant to the field of spatial electronics, particularly telecommunication satellites, being of extreme importance, for instance, to the satellite’s resetting cycle, due to its hypothetically high tolerance to E-M radiations. We manipulate these memories with three kinds of pulses. The basic experience begins with a one-time
procedure that involves sourcing a series of Set/Reset pulses to a pristine device, this process being known as Forming process. Then, for these memories we determine, as stated above, three different procedures. A Reset Procedure, a Set Procedure and a Reading Procedure. These are conceived as follows: the Reset procedure, changes the memory state into high resistance; the Set procedure, sets the memory into a low resistance state; and the Reading procedure, which bias the DUT in order to get the resistance value. The pulses are as small as necessary to avoid that the resistive state is changed.

Fatigue effects by accumulative pulse application on bipolar RRAM devices
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We have studied the effects of accumulating electrical pulses of the same polarity on the resistance state of interfaces made by sputtering a metal (Au, Pt) on top of the surface of a cuprate superconductor YBa2Cu3O7 - d (YBCO). We show that the evolution of resistance for the high and the low resistance state depends logarithmically on the number of accumulated pulses. We have established a criterion to determine the failure of a device based on the saturation of the relative resistance variation between the high and the low resistance states upon applying pulses of increasing voltage. This criterion is also useful to compare different devices and to determine their optimal working conditions. Our results show the similarity between the physics of the diffusion of oxygen vacancies induced by electrical pulses and the propagation of defects in materials subjected to repeated mechanical stress.

Resistive switching effects in HfO2 based memory devices

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We study capacitor-like structures with HfO$_2$ as the active insulating material, for the implementation of non-volatile memory devices. Arrays of Co/HfO$_2$/Ti devices were fabricated with atomic-layer-deposited HfO$_2$ (20 nm thick) and sputtering of the top (Co) and bottom (Ti) electrodes. Devices were characterized electrically by means of standard and pulsed I-V curves at room temperature. The remnant resistance state was also tested when pulsing.

An hysteretical electric response was observed upon cycling the applied voltage up to +/- 15 V. Obtained I-V curves are “non crossing” type, i.e. two sharp SET transitions (from High Resistance to Low Resistance) are observed at around +/- 5 V. For each polarity, the steep 4-5 order of magnitude switch to a Low Resistance state turns into a High Resistance state upon polarity reversal, suggesting the presence of rectifying junctions. Around a hundred switching cycles could be repeated without device degradation. Besides, the conducting state has a fairly high resistance (~1 E-6 A for 10 volts), a prerequisite for low power consumption.

Samples were irradiated with 20 MeV oxygen ions up to a dose of 3E12 ions. Their electrical response after this controlled damage process is similar to the one obtained at the virgin state. Other radiation hardness tests are in progress.

We discuss a model based on the oxygen vacancy drift to account for the observed experimental results.

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**Clean Room facilities at CAC- CNEA**


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