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Chap. 26 : Resistance Switching Effect in Octahedral framework oxide

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Abstract: Resistive Random-Access Memories (ReRAM) are an alternative way to create new memory devices. This is physically possible due to the existence in the material, of two resistive states clearly discreditable, as a function of voltage value and polarity first parameter under control to pass from one state to another one. However, the mechanism of the resistance switching is not simple and is under debate. We present in the present chapter all the factors entering in the switching process in tetragonal tungsten bronze (TTB) type structure oxide thin films deposited by PLD technique onto MgO or STO substrates. Results show that $\text{GdK}_2\text{Nb}_5\text{O}_{15}$ (GKN) thin films deposited on MgO and STO substrates are resistively switchable. It was found that the nature of the substrate strongly affects the resistance ratio: GKN on SRO/LSCO/MgO showed a large hysteresis compared to GKN on SRO/STO. Substrate effect and oxygen vacancy on resistance switching in GKN thin film were studied in the same experimental conditions. The study of resistance switching in the GKN/MgO and GKN/STO thin films has confirmed that for low voltages, below the threshold value of 1.3 V, the electric transport is dominated by the formation of a Schottky type barrier, which allows a minimum leakage current. Resistance switching in GKN is attributed to the oxygen vacancies migration which can be controlled by the substrate or the frequency sweep.

Keywords: ReRAM, TETRAGONAL TUNGSTEN BRONZE, $\text{GdK}_2\text{Nb}_5\text{O}_{15}$, GKN, RESISTANCE SWITCHING, MEMORY DEVICE, THIN FILM, PULSED LASER DEPOSITION, PLD

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I. Introduction

Leakage current has always been considered as one of the main problems for ferroelectric memories. However, recent studies on electrical conduction in ferroelectric and ferroelectric tunnel junctions suggest the possibility of using this undesirable leakage current (in dipole analysis) for the creation of resistive memories. Nowadays technologies had been developed based on this property of materials such used in EPROM, Flash,....

After a brief description of the resistance switching effect, as well as a brief presentation of state of art on the resistance switching in oxides, in particular ferroelectric oxides, we present the results obtained in the case of the GKN thin film grown on MgO and STO substrates. To do this, we used SRO as the bottom electrode and Pt as the upper electrode. Several parameters have been taken into account; such as the frequency of the applied field, the surface of the electrode and the epitaxial stress and/or oxygen gaps, in order to determine the origin of the resistance switching effect and we open debate on the mechanisms and general understanding will be highlighted.

The technology of non-volatile memories is currently dominated by Flash memories (semiconductors based on silicon). This technology is used with great commercial success, notably in the portable devices (digital cameras, USB keys, laptop disk, etc...). The American giant Apple has just replaced, in all of its products, the traditional magnetic hard disks by Flash SSD memories, stronger than a traditional hard disk, because of their robustness to shocks and vibrations, much greater than classical discs, and also to their relatively low consumption^[1–4]. Figure 1 shows the classification of existing memory devices and the used physical property. However, Flash memories still have limits compared to their low endurance (10^3 to 10^6 cycles), their long writing time (μ s) and their high voltage used for writing process.

Furthermore, the drastic reduction in the dimensions of elementary devices comes up against, in particular, the physical performance of the materials integrated into the architecture of memory from a critical size^[5,6]. It is then necessary to consider other technological solutions.

As opposed to FeRAM memories in which the accumulation of charges on the armatures of a ferroelectric capacitor shape is used (memories with charge storage), resistive memory technologies (MRAM, PCM and ReRAM ...) are based on concepts in which the discrimination of the two memory point states is ensured by a change in resistance^[7,8]. In recent years, special interest has been shown in OxRAM memories.

The limitation in terms of size in current devices, for example, a reduction in thickness of the ferroelectric oxide in the FeRAMs promotes conduction by tunnel effect and consequently degrades the ferroelectricity. So increased miniaturization can be obtained more easily in resistive devices^[7,9].

Figure 1 : Some examples of existing memory devices and used physical properties.

II. Resistance switching

Resistance Switching (RS) is defined by the passage of a material from a high resistance (HR) state [ON or 1] to low resistance (LR) state [OFF or 0] under applied electrical field. The two states must be very stable, and the transition from one state to the other one is obtained by the application of a voltage which polarity may be or not be reversed (bipolar or unipolar or modes, respectively)^[10–12].

The Figure 2 schematizes the principle of a resistance switching (RS) between two states of resistance in the I(V) characteristic, typical of a bipolar switching of resistance.

Figure 2 : Principle of Resistance Switching

The RS occurs via two characteristic phenomena. In fact, the switching of resistance seems to differ from one system to another, the $I(V)$ characteristics indicate two types of behavior: unipolar (non-polar) and bipolar^[7,13]

The SET operation: this is the operation which switches the material from its high resistance state (OFF or 0) to a low resistance state (ON or 1). The write voltage must therefore be at least equal to the threshold voltage “SET”, while the read voltage must imperatively be lower than the threshold voltage, ie : $V_{wr} \geq V_{thr}$ and $V_{re} < V_{thr}$

The RESET operation: it is the operation which allows the system to be switched back from state 1 to state 0. This operation can be performed with a voltage greater than the V_{set} voltage in unipolar systems, or with a $-V_{set}$ voltage for the bipolar systems.

One of the characteristics of RS is the resistance ratio between the state of high resistance and that of low resistance. Recall that only a ratio of 1.2 is sufficient to make ReRAM type devices^[14,15]. However, a ratio of 10 is necessary to be competitive with Flash technology.

II.1 Unipolar Switching

As its name suggests, the switching of unipolar resistance requires only one polarity of the applied voltage. In this unipolar mode, the transition from one state of resistance to another depends on the amplitude of the applied voltage and not on its polarity; the two voltages V_{set} and V_{reset} are in the same polarity; the SET voltage is always greater

than the RESET voltage, but the RESET current is always greater than the so-called compliance current during the SET operation. $I(V)$ characteristic shows symmetry and we find the same behavior in the two polarities (positive and negative) as indicated in Figure 3.

Figure 3: Unipolar type Resistance switching
(inspired from Ref [7])

This behavior is advantageous because it requires only one polarity of the applied field to operate.

A last state commonly called "forming" is often necessary to initiate resistance switching in unipolar RS. This step takes place during the first power-up of the sample: it involves switching of the sample from its state of very high resistance (so-called virgin state) to a state of low resistance. This step requires relatively high voltages and requires a current limitation to avoid breakdown of the oxide. This behavior has been observed in several binary oxides^[16,17].

II.2 Bipolar switching

As its name suggests it, two polarities of the voltage are essential to switch the resistance from one state to another. In the bipolar mode^[10,12], the switching to low resistance state takes place in a polarity while the transition from the low resistance

state to the high resistance state takes place in the opposite polarity (Figure 4). This behavior was observed in several types of materials^[6,10,18–20].

Figure 4 : Bipolar type Resistance switching

III. Physical mechanisms of resistance switching

We briefly present here the different physical mechanisms proposed to explain the switching of resistance in oxides. Among the origins of the dominant contributions one can distinguish thermal phenomena, oxygen vacancy, space charge transfer, electronic and ionic phenomena (electromigration,...). The list of these hypotheses is not exhaustive because in the literature the debate continues. Only the systems in which the RS is clear are Mott's insulators^[21], where the resistance switching effect is of purely electronic origin. In the initial state the material is insulating, the structure of the bands shows a large gap and an empty conduction band. On the other hand, the application of an electric field induces a total modification of the electronic bands of the system, the lattice contracts and gives rise to a conductive metallic structure. This behavior represents a favorable case for the realization of a nonvolatile memory because the application of electric field leads to switch from HR to LR stable states.

III.1 Thermal effects

Following the application of voltage (greater than or equal to V_{set}), the material undergoes a breakdown (partial short-circuit), the two electrodes (lower and upper) being now linked by a conductive filament. With the control of short-circuit current (compliance current), the resistance in this ON-state can be checked. This filament,

which microstructure is still widely debated, is constituted by defaults such as oxygen vacancies, metallic elements coming from the electrodes.

During the RESET operation, this conductive filament is broken due to a high thermal power density that could reach $10^{12} \text{ W.cm}^{-3}$. This type of RS is similar to a conventional fuse, but at a nanometric scale. Therefore, this type of systems is called fuse-antifuse process. It represents typically a unipolar resistive switching (V_{reset} lower than V_{set}). One of the best-known materials is NiO. Recently, the formation of the conductive path in the ON state has been confirmed experimentally by HREM observation for NiO^[22] and TiO₂^[23] thin layers.

A critical parameter of this unipolar switching effect seems to be the value of the limit current. In fact, it has recently been demonstrated that a thin layer of TiO₂ shows bipolar switching, and this phenomenon can be changed to unipolar switching by changing the limit current to higher values^[24,25].

III.2 Charge effects

The charges seem to play a very important role in the RS process. Many models have been proposed to describe Resistive Switching phenomenon based on charge effects and several mechanisms can coexist in RS process in the same system. Below are some models, proposed in the literature, which have shed light on the switching of resistance in specific materials.

a) Based on Ferroelectricity.

The ferroelectric model was proposed by several authors^[6,26,27]. The same model was theoretically described by Kohlstedt *et al.*^[28,29]. The switching of resistance was observed in ferroelectric oxides such as BiFeO₃ (BFO) and BaTiO₃^[17,19,30,31]. The polarization has therefore been questioned as to be at the origin of the switching of resistance in these materials.

Let us note beforehand, that if the polarization had been at the origin of the switching of resistance, these processes should be bipolar and more or less symmetrical with regard to the two polarities of the applied voltage (the polarization reversal is also bipolar phenomenon). The synchronization between the polarization and the switching of the resistance has been experimentally demonstrated by Wang *et al.*^[32]. As shown in Figure 5 the remnant polarization takes a non-zero value from $U = 4 \text{ V}$, voltage that corresponds to the threshold voltage from which the material passes from its high resistance state to its state low resistance. Unfortunately, this result is not sufficient, because the application of a voltage in addition to the reversal of the polarization,

causes not negligible Joule heating effect; that induces a measured current of about 1 μA . However, this voltage value seems to correspond to the $V_{\text{threshold}}$ value (Figure 5(a)) in $I(V)$ measurements and also to the coercive electrical field (Figure 5(b)).

Figure 5 : Schematic description of $V_{\text{threshold}}$ versus V_{coercive}

The use of low amplitude pulses of short duration proves to be a good solution in order to reverse the polarization and to avoid the local heating of the material. Jiang *et al.*^[33] used pulses amplitude of 18 V of only 5 μs to study this phenomenon in BFO thin films. The results were conclusive: the Joule effect is ruled out and the switching of resistance is well linked to the reversal of polarization. This resistance switching in BFO is of ferroelectric origin and is called “ferroelectric switching of resistance” or “ferro-resistive switching”. Furthermore resistance switching mechanism in bulk BFO has been linked to the polarization as demonstrated in single crystal by Choi *et al.*^[6].

b) Trapping of charges

The effects of injection and/or displacement of electrical charges in the insulator, or at the interfaces, can induce electrostatic modifications of the metal-insulator-metal (MIM) stacks barrier. This mechanism is known in literature as charge-trap model^[4], in which charge injection can be done with a very high electric field, and thus trap charges on some structural defects or existing nanoparticles in the insulation, consequently entailing a modification of the resistance value. In fact, the injection of charges into a dielectric material can be considered as a doping effect which could cause a metal-insulator transition, as in the case of perovskite oxides structure such as $(\text{Pr}, \text{Ca})\text{MnO}_3$ ^[34] and $\text{SrTiO}_3:\text{Cr}$ ^[35].

c) Modification of the Schottky barrier

This model can be envisaged for systems containing a Schottky barrier at the electrode/insulator interface, as is the case for most ferroelectric/metal junctions.

The electric transport in these systems is controlled by this barrier of potential, that being disturbed or modified by the presence of an interfacial layer for example. Furthermore, the measurements on the TiO₂ oxide show that the resistance switching was not intrinsic to the oxide^[9] but to the oxide/metal couple. This effect turns out to be very dependent on the output work of the metal as shown by Wu *et al.*^[36]. All the proposed interface models at this step can be found in Sawa's reported review^[7].

d) Ionic effects

Electrochemical and redox reactions can also be the cause of bipolar Resistance Switching. It is a new field of study where nanoelectronics is becoming intimately linked to nanoionics^[13]. We can distinguish the electromigration of cations from that of anions.

e) Electromigration of cations

By oxidation process of electrochemically active metal electrode such as silver (Ag), the mobile Ag⁺ cations in the solid electrolyte migrate towards the counter-electrode. After reduction process, a growth of an Ag wire occurs. This highly conductive filament can be associated with the ON state of the system. When the polarity of the voltage applied is reversed, an electrochemical dissolution of the filaments takes place with a switching of the system in its OFF state. As a replacement for Ag, it is possible to use copper and other metals with a high diffusion coefficient^[13].

f) Electromigration of anions

The migration of oxygen anions, due to a modification of stoichiometry leads to the oxidation of the electrode. The electronic conductivity is thus modified due to the change in valence of the associated cationic in the subnetwork^[13]. For the main similarities and differences between the electromigration of anions and cations we can refer to the review paper reported by Waser *et al.*^[15].

III.3 Filaments and interface effect

The surface of the electrode is an essential element which allows discrimination between the two mechanisms; the formation of nanoconductors and the interface. In fact, when measuring resistance through electrodes of different surfaces, two cases are possible : the resistance decreases with the increase in the electrode surface:

1. The switching effect takes place over the entire surface (interface effect as in the case of Nb:STO)^[15].
2. The resistance remains the same whatever the surface of the electrode: the resistance measured is indeed that of a local nanowire conductor which has roughly the same surface dimension as that of the electrode used, that leads to homogeneous measured current (as in the case of NiO)^[15].

III.4 Resistance switching effect in the GKN

In this section we present the study of the electric transport in a TTB type structure oxide thin film $\text{GdK}_2\text{Nb}_5\text{O}_{15}$ (GKN) in the following configuration:

Pt(50 nm) / GKN (270 nm) / SRO (50 nm) / LSCO (4 nm) / MgO

Recall that the three layers of GKN, SRO and LSCO are grown epitaxially layer-by-layer on the MgO substrate. In order to form a planar capacitor, platinum electrode having a diameter ranging from 0.1 to 0.5 mm have been deposited by pulsed laser deposition (PLD) at room temperature and at very low pressure ($<10^{-6}$ mbar) on the upper face of the layer (Figure 6).

Figure 6 : Upper electrodes with different diameters

The aim is to have much more chance to have a region of sample surface for capacitance shape measurements without short-circuit. Ferroelectricity in this heterostructure has been demonstrated by C(V) measurements; no hysteresis cycle P(E) has saturated for this system in dynamic mode. The current-voltage density (J-V)

was measured at room temperature using a TF analyzer 1000 (aixACCT)^[37,38]. Short duration pulses (100 ns) were applied using Keithley 2635B. All the measurements results carried out under ambient light are presented and described here.

Figure 7 shows the current-voltage density characteristic obtained at room temperature on GKN thin film. To highlight the effect of hysteresis, the voltage is varied according to the procedure: $0 \rightarrow +U_{\max} \rightarrow -U_{\max} \rightarrow 0$. The maximum voltage $V_{\max}$ is 3V in the case of this figure. All the samples showed a non-linear effect for $J(V)$. This characteristic clearly shows a diode behavior^[38,39] while increasing in positive voltages from 0 to 3V. GKN thin film response is similar to that of a direct polarized diode.

During the descent (always staying in positive voltages), the curve $J(V)$ is almost linear and presents a hysteresis comparatively to the rise: the GKN layer is in this second phase completely conductive. When continue this process in the negative voltages ($U = 0$ to $-3V$) the GKN thin film enters in the state of a blocking diode and no transition or hysteresis is observed in this negative voltage state; the GKN layer therefore remains dielectric^[19,38].

The reverse phenomenon is obtained when we reverse the positions of the generator polarities. These two responses of the GKN layer are shown in Figure 7.

Figure 7 : Diode effect in GKN resistance switching

Lee *et al.* [37] attributed this behavior to the formation of a thin layer rich in charge carriers (probably oxygen vacancies) located at the dielectric/metal interface that was activated by first solicitation. This hypothesis is indeed acceptable, and explains well the appearance of hysteresis for a single polarity of the applied voltage.

However, it is still not possible to reverse the diode in our system and it is always blocked in one direction. Note that this effect and diode has been observed several times during studies on oxides with a perovskite structure, such as $\text{Au/PbTiO}_3/\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ [3], BiFeO_3 [9,40] and LiNbO_3 [4].

In the case of stressed GKN thin film under 3V, the resistance ratio between the state of high resistance and low resistance one is approximately 70 with a maximum current of on the order of 10^{-5} A. Thin ferroelectric layers have spontaneous polarization. It seems that during deposition at high temperature, the natural orientation of the downward polarization causes the positive charges to migrate towards the upper surface to compensate the negative polarization charges [5]. This would cause the formation of a layer rich in charge carriers between the upper metal electrode and the ferroelectric layer.

However, if this interfacial layer is responsible for this transition from electrical to conductive, its modification and control should make it possible to control the system. Lee *et al.* [41], in order to have a direct diode for positive voltages and an inverse diode for negative voltages, propose to migrate part of this interfacial layer towards the bottom electrode. They have done this by applying DC voltage for 15 minutes by maintaining the sample at a temperature of 200°C. This was an experimental prove of the existence of this interfacial layer rich in charge carriers.

IV. GKN/electrode junction

When two materials are brought into contact (a dielectric and a metal), the contact could be perhaps ohmic or Schottky type. The characteristic $J(V)$ curves which are the indicator of the type of contact, can be linear or not, respectively. The barrier heights of the two materials forming the junction are, in general, determined by the output work of the metal and especially the nature of interface. In a simple model, where the interface effects are not taken into account, the metal output work controls the properties of the junction. If the output work (W_s) of the metal is more important than ability of electrons to move into the dielectric χ , a potential barrier ϕ (for electrons) is formed at the interface. On the other hand, if the electrons ability in the ferroelectric is higher than the metal output work, ohmic contact should take place, and therefore the barrier does not exist: $\phi = 0$ eV.

The height of this barrier is simply given by the relation:

$$\phi = W_s - \chi \quad (1)$$

In the case of the GKN layer, there is no clear zone of linearity of the J(V) curve. The heterostructure present strongly Schottky-type contacts. The characteristics J(V) are shown in Figure 8, in linear (left) [Figure 8(a)] and semi-logarithmic (right) [Figure 8(b)]. Recall that the two electrodes used in our case (Pt and SRO) have practically the same output work (5.6 eV for Pt and 5.2 eV for SRO^[37,41]). Below 1.3 V, a Schottky type junction appears to be formed at the GKN/Pt interfaces and GKN/SRO (Figure 9) with very low barriers; therefore, a very restricted zone exhibited an ohmic behavior.

Figure 8 : Schottky effect and threshold voltage

In the case of the Schottky model, the current density depends on the temperature and the electric field:

$$J \approx T^2 \left[\frac{1}{k_B T} \left(\frac{q^3}{4 \pi \epsilon_0 \epsilon} E \right)^{0.5} \right] \quad (2)$$

With q: the electric charge, T: the temperature, ϵ_0 : the electrical permittivity of vacuum, ϵ the electrical permittivity of the material and K_B : the Boltzmann constant.

Among the possible conduction mechanisms, we also find the Space-Charge-Limited Current (SCLC) mechanism, whose current density and voltage are linked by the following relation^[17]:

$$J = \frac{9 \mu \epsilon_0 K V^2}{8 d^3} \quad (3)$$

There is also the Poole-Frenkel model, taking into account the sample volume so the current depends on the thickness of the sample. The increase in the electric field involves the release of the trapped electrons, which are emitted either in the conduction band, or in a nearby (default) trap. We can then write:

$$\frac{J}{E} \approx \frac{1}{k_B T} \left(\frac{q^3}{\pi \epsilon_0 K} E \right)^{0.5} \quad (4)$$

Although the two mechanisms (Schottky and Poole-Frenkel)^[42,43] reflect two different effects, the two relations of current-voltage dependence are similar. In practice, it is not easy to discriminate between these two conduction mechanisms and these two mechanisms can coexist. Figure 9 presents the characteristic J(V) typical (in semi-logarithmic scale) of the GKN layer solicted at a maximum voltage of 3V. The inset of Figure 9 shows the semi-logarithmic representation of J/T² as a function of V^{0.5} for high resistance state (from 0 to +1,6 V process).

Figure 9 : Resistance rate in GKN

Usually a linear variation is obtained in the case of the Schottky model. In the case of the GKN layer, the inset of Figure 9 shows two linear regimes. This indicates that the

conduction takes place, according to two different Schottky modes before and after the threshold voltage. A new slope of the curve $\frac{J}{T^2} \approx f(\sqrt{V})$ appears from the threshold voltage: the Schottky barrier has been modified. Oxygen vacancy or the interfacial layer rich in charge carriers could be at the origin of this barrier modification.

From the adjustment by Schottky's law, the determined dielectric constant is much lower than that of GKN in the solid state ($\epsilon = 80$), although the adjustment by this law is coherent. This shows that the Schottky conduction mode is not the only one to consider in the case of the GKN layer. The coexistence of these two conduction mechanisms was reported by Lee *et al.* in the case of BFO film^[41].

IV.1 Resistance ratio

The ratio of the resistances ON and OFF is calculated from the values extracted from the inverse of the slopes of the characteristic $J(V)$ in the vicinity of the threshold voltage (R_{OFF}/R_{ON}). In order to confirm the irreversibility between the direct and reverse diodes, we studied the effect of the maximum voltage V_{max} on the curves $J(V)$ in GKN. We have performed measurements up to $V_{max} = 8$ V and the GKN/MgO thin film has always shown a hysteresis for a single polarity with an increasing hysteresis more opened with the applied voltage^[37,44]. The hypothesis of an interface rich in charge carriers is reinforced, but the diode is not reversible as shown in Figure 10.

Figure 10 : Voltage effect on RS rate in GKN and evolution of the resistance rate

Furthermore, the resistance ratio increases with the maximum voltage $V_{\max}$ (see inset of Figure 10). This figure shows that the high resistance state is the same, whatever the maximum applied voltage higher than 8V. On the other hand, the state of low resistance changes accordingly up to the maximum applied voltage.

The higher is the applied voltage, the higher are charge carriers that would be entrained by the electric field. We can expect the formation of an increasingly conductive path with the increase in the maximum applied voltage, the resistance at the ON state consequently decreases; that is beneficial to the increase in the resistance ratio (as shown in Figure 10: the variation of resistance ΔR increases almost linearly as a function of the maximum voltage applied). Generally, the compliance current is set to avoid the breakdown of the sample under test. In the case of Figure 10, no compliance current has been taken into account, since the value of the measured current remains very low in the used experimental conditions^[29,45].

IV.2 Role of oxygen vacancies

Several authors have shown that increasing oxygen vacancies density makes it possible to considerably improve of the resistance ratio^[7,44,46]. To confirm this effect, other authors have shown that a reduction in the density of oxygen vacancies leads to reduction in the resistance ratio, and even to the suppression of the hysteresis of the characteristics $J(V)$ ^[7]. In the case of the GKN layer, the mobility of O^{2-} ions (or oxygen vacancies) is very favorable, because of the tunneled structure along the $\vec{c}$ axis. In fact, as shown in Figure 11, the oxygen ions have a small ionic radius comparatively to the other ions forming the crystal and have a significant mobility.

Figure 11 : Oxygen vacancy in GKN structure

To better understand the origin of RS in GKN, we study here in the case of the GKN/MgO layer, the role of oxygen vacancies. To understand the effect of oxygen vacancies, it is interesting to oxidize the GKN layer in order to remove vacancies of oxygen, noting that the GKN deposited layer on this substrate undergoes a non-negligible loss of oxygen and is under compressive stress.

So, the thin layer of GKN was developed under the same conditions, but at the end of growth, the sample was annealed at 400 °C, under pure oxygen atmosphere of 0.3 mbar pressure, during 45 minutes. X-ray diagrams of the sample before and after oxidation are shown in Figure 12. No significant change in the out-of-plane lattice parameter has been observed. The adjustment of Bragg peaks gives an out of plane lattice parameter of $c_{\text{GKN}} = 3,898 \text{ \AA}$. We note the decrease in the mosaic measured around the peak (002)GKN, as well as the decrease in the full width at half maximum of this peak (the (002)GKN line being narrower after annealing)^[37].

Figure 12 : X-ray diffraction diagram showing oxygen vacancy effect in GKN

The measurement of the characteristics $J(V)$ of two samples (oxidized and non-oxidized) were then carried out under the same conditions. The obtained results are shown in Figure 13. It shows that the characteristic $J(V)$ of the oxidized layer does not present a clear hysteresis and seems to be symmetrical with respect to the y-axis of the coordinates. In the inset of Figure 13 we show the $J(V)$ characteristics of the oxidized layer for different values of the maximum applied voltage V_{max} . We observe that the curves $J(V)$ are symmetrical and the hysteresis is removed. There is no sudden jump in current as is the case for the non-oxidized layer. Furthermore, the very weak hysteresis observed in this figure, for the high voltages, is the same for the two polarities of the applied field, thus indicating that the distribution of oxygen vacancies²¹ is homogeneous in the GKN thin film; the diode is almost blocking for the two signs of voltage. There is, a priori, no interfacial layer at the level of the electrodes (the two

interfaces are similar from the electrical point of view and this up to the highest voltages). This result shows the crucial role of annealing under oxygen pressure.

We can consider, either the role of oxygen vacancies, or the trapping of charges in localized defects at the level of the upper interface (between GKN and Pt), to explain the response of the GKN layer. In both cases, annealing tends to eliminate these defaults and to remove the hysteresis.

Figure 13 : Oxygen vacancy and voltage effect in GKN

IV.3 Frequency effect

In the case of a resistance R_S linked to electromigration, the frequency of the applied field electric field has an important role. In our case, the Pt electrode is not oxidizable easily, and it is not imaginable that an electrode could dissolve and migrate through the GKN layer. Figure 14 shows the characteristics $I(V)$ of the GKN layer at room temperature for different frequencies, the maximum applied voltage being fixed at 5 V.

It is observed that the current passing through the heterostructure decreases drastically when the frequency increases, that means the resistance R_{ON} increases with frequency. The hysteresis disappears at the frequency of 1 kHz. The insets of Figures 14 show the shape of the applied voltage and the corresponding current, as a

function of time for the frequencies of 0.1 Hz and 100 Hz, from top to bottom, respectively^[37]. We note, for the frequency of 0.1 Hz, an asymmetric current of high intensity which indeed becomes weaker and symmetric with the increase in the frequency.

Figure 14 : Frequency effect in GKN thin film

These observations confirm that the electromigration of charges, during the application of the electric field, is the phenomenon which is at the basis for the current vs. tension hysteresis curves. These charges could initially be trapped in defects, at the interfaces or in the core of the sample and begin to migrate under the effect of a higher applied electric field at the threshold value, which contributes to the increase of the current. When the field frequency is too high, these charges carriers can no longer follow the applied field.

IV.4 Effects of the electrode surface

The surface of the electrode is an element which makes it possible to discriminate an interface effect in a filamentary mechanism. We have studied, in the case of the GKN/MgO layer, the effect of the electrode surface on the resistance in the ON and

OFF state. The obtained result is shown in Figure 15: the resistance, especially in the ON state, decreases considerably when d (diameter of the electrode) increases by 0.3 to 0.5 mm, which indicates the increase in current. The larger is the surface of the electrode, the stronger is the current flowing through the sample or exchanged between the two electrodes.

Figure 15 : Electrode effect on GKN with two different surfaces

Furthermore, it is often accepted that the resistance switching does not occur identically everywhere in the sample and can differ from one electrode to another. Figure 15 shows that the resistance in the ON state is inversely proportional to the surface of the electrode; this shows that the resistance switching is established across the entire surface of the electrode and is not of local character. On the other hand, other results observed during this work have shown that the resistance is the same regardless of the surface of the electrode. The filamentary and interfacial characteristics of the GKN layer cannot therefore be separated.

IV.5 Effect of the substrate on RS in the GKN layer

In order to study the effect of epitaxial constraints on the resistance switching in the GKN layer, we have grown thin films on two different substrates (MgO and STO) using the same elaboration conditions. As a reminder, the two thin films undergo out of plane as well as in plane compressive stresses, compared to the same material in the bulk solid state. They are therefore of reduced volume and consequently of oxygen deficiencies; the oxygen deficiencies being more important in the case of the MgO substrate. Furthermore, the GKN microstructure changes depending on the substrate: the GKN layer has elongated rectangular grains in the plane of the substrate in the case of STO while these grains are perpendicular to the plane of the substrate in the case of MgO. Figure 16 shows the $I(V)$ characteristics of the GKN layer deposited on the two different substrates (MgO and STO).

In this figure, a hysteresis is observable in both cases, which means that the resistance of the GKN layer can be switched between two states in a bipolar mode. One notes the presence of the hysteresis for the two signs of the applied voltage in the case of the GKN/STO thin film and only for the positive voltage fin the case of GKN/MgO thin film. The GKN layer behaves like a conventional diode (passing in only one direction) in the case of the MgO substrate and like a passing diode in both directions (Zener) with the STO substrate. Figure 16 shows a clear difference in intensities of the measured currents.

Figure 16 : I-V characteristic of GKN/MgO and GKN/STO thin films : substrate effect

The resistance ratio (R_{OFF}/R_{ON}) has been estimated to be around 70 in the case of GKN/MgO thin film and only around 3 in the case of GKN/STO thin film (4.5 is obtained for the polarity in the negative applied field).

By comparing the state of stresses in the layer of GKN deposited on the two substrates, we note that the lattice volume of GKN is reduced by 0.63% in the case of the substrate MgO, comparatively to its volume on the STO substrate. We also conclude that the opening of the hysteresis is linked to the oxygen vacancies (predominant in the case of the MgO substrate).

IV.6 Thermal effect on RS in the GKN layer

Figure 17 shows the characteristics resistance ratio curve obtained on the GKN/MgO layer as a function of temperature. The two resistances corresponding respectively to the ON and the OFF states, those have been extracted from these $I(V)$ curves allowed us to build this figure. The two resistors R_{ON} and R_{OFF} decrease very slowly, but simultaneously, as a function of the temperature, this reflecting an increase in the current in the material but the ratio remains almost constant. The resistance ratio, on the other hand, is preserved whatever the temperature (between 25 and 140 °C). In the studied temperature range, the two states of resistance remain easily discriminable in favor to applications.

Figure 17 : Thermal effect on RS rate in GKN/MgO thin film

IV.7 Writing time and endurance

According to the requirements of non-volatile high-density memories and to the predictions on technology for the next 15 years, a threshold of requirement has been fixed ^[15]. The write voltage must be a few hundred millivolts to be compatible with current circuits, up to a few 25 volts to compete with Flash technology. It is also desirable that the writing time, which in reality determines the speed of the memory device, is less than 100 ns. As for endurance, Flash technology currently has an average number of write cycles varying between 10^6 and 10^7 . OxRAM technology should provide at least the same endurance, preferably better, in order to be competitive. The protocol used to study the endurance of resistance switching in the GKN layer consists of:

1. apply a voltage of + 5V for a few nanoseconds (writing).
2. read the resistance of the material (reading).
3. apply a voltage of -2V for the same duration of a few nanoseconds in order to switch the system back to its OFF state.
4. read the resistance of the material, using the same reading protocol (low voltage).
5. this operation consists in repeating this protocol (4 previous steps) several times (see the number of cycles on the following Figures, here 10^4).

Figure 18 shows the result of the endurance test carried out on the GKN layer. This result shows that a duration of 10 ns is largely sufficient to allow the material to pass from its state of high resistance to its state of low resistance, and vice versa, while preserving a good resistance ratio. Indeed, the two states of resistance remain easily

Figure 18: Writing time and endurance of GKN

discriminable in a large number of write/erase cycles. The system can be read in current (1 μA) or in voltage (0.9 V) without impacting its performance. Furthermore, this study shows that the resistance in OFF state is not very stable like that in ON state.

There is a very small fluctuation in the value of the resistance around a fixed average value. It should be remembered that this resistance was determined by reading the current at a single voltage value (read operation at 0.9 V) and that it is not a true slope (point slope). Figure 18 shows that with a write voltage of 5 V and in ac voltage of -2 (or -3 V), it is possible to write and erase a large number of times with impulses writing 100 ns (or 10 ns).

In fact, after about 10^4 cycles no sign of fatigue has been detected, the resistances corresponding to the ON and OFF states respectively are constant and show great stability while remaining easily discriminated.

IV.8 Retention

By definition, retention being the retention time of a memory state. A duration greater than or equal to 10 years is required for non-volatile memories. In this section, the stability over time of the two resistance states in the GKN layer has been studied.

For the low resistance state, this was written by applying 5 V for 100 ns, then the operation consists of reading in voltage (0.9 V) this state several times, between two successive readings, a pause of 5 s has been respected. For the high resistance state, this was written by applying -5 V for 100 ns. The same protocol was used for resistance reading at 0.9 V every 5 s. The result obtained is shown in Figure 19. We note that the two states of resistance remain relatively stable as a function of time. The resistance ratio decreases very soon after the time elapsed.

Figure 19: Retention in GKN

V. Summary

In this chapter we have studied the electrical properties of GKN, KLN and PKN thin layers deposited on the MgO substrate. A comparative study highlight the substrate effect was carried out by considering the GKN layer deposited on a STO substrate. The dielectric measurements were carried out by impedance spectroscopy and made it possible to define the frequency range corresponding to the best dielectric response. The capacitive character was highlighted in the GKN and KLN layers, but the leakage currents not negligible, did not allow obtaining P-E saturated hysteresis loops. By C-V measurements we confirm the ferroelectric character of these layers. The study of the I(V) characteristics of the GKN layer made it possible to attribute a simple diode behavior to the GKN / MgO layer and zener diode type for GKN/STO. We have studied the influence of temperature, frequency of voltage source and the substrate on the I(V) characteristics of this thin films.

This study allowed us to give precisely each of these effects on the behavior of the layers. The study of resistance switching in the GKN/MgO and GKN/STO thin films has confirmed that for low voltages, below the threshold value of 1.3 V, the electric transport is dominated by the formation of a Schottky type barrier, which allows a minimum leakage current. Above this threshold voltage, the Schottky barrier is modified due to oxygen deficiencies; the material then becomes conductive and passes to a low state resistance. This switching is reversible in bipolar mode. The R_{OFF}/R_{ON} resistance ratio in the GKN/MgO layer has been estimated to be around 180. The resistance ratio found, in the case of the thin layer of GKN/MgO is more important compared to GKN/STO. A switching speed of around 10 ns has been measured. The experimental results show that the electrical transport strongly depends on the nature of the metal/oxide interface. Defects, concentration and distribution of oxygen vacancies in the thin oxide layer strongly influence the resistance of the system. This study shows that it is possible to write and erase a large number of times (around 10^4). In fact, the ON and OFF resistances exhibit great stability, demonstrating the absence of any degradation or fatigue.

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References:

- [1] J.F. Scott, C.A. Paz de Araujo, Ferroelectric Memories, *Science*. 246 (1989) 1400–1405. <https://doi.org/10.1126/science.246.4936.1400>.
- [2] R. Bez, E. Camerlenghi, A. Modelli, A. Visconti, Introduction to flash memory, *Proc. IEEE*. 91 (2003) 489–502. <https://doi.org/10.1109/JPROC.2003.811702>.
- [3] P.W.M. Blom, R.M. Wolf, J.F.M. Cillessen, M.P.C.M. Krijn, Ferroelectric Schottky Diode, *Phys. Rev. Lett.* 73 (1994) 2107–2110. <https://doi.org/10.1103/PhysRevLett.73.2107>.
- [4] Y. Xia, W. He, L. Chen, X. Meng, Z. Liu, Field-induced resistive switching based on space-charge-limited current, *Appl. Phys. Lett.* 90 (2007) 022907. <https://doi.org/10.1063/1.2430912>.
- [5] M.F. Chisholm, W. Luo, M.P. Oxley, S.T. Pantelides, H.N. Lee, Atomic-Scale Compensation Phenomena at Polar Interfaces, *Phys. Rev. Lett.* 105 (2010) 197602. <https://doi.org/10.1103/PhysRevLett.105.197602>.
- [6] T. Choi, S. Lee, Y.J. Choi, V. Kiryukhin, S.-W. Cheong, Switchable Ferroelectric Diode and Photovoltaic Effect in BiFeO₃, *Science*. 324 (2009) 63–66. <https://doi.org/10.1126/science.1168636>.
- [7] A. Sawa, Resistive switching in transition metal oxides, *Materials Today*. 11 (2008) 28–36. [https://doi.org/10.1016/S1369-7021\(08\)70119-6](https://doi.org/10.1016/S1369-7021(08)70119-6).
- [8] D.J. Kim, H. Lu, S. Ryu, S. Lee, C.W. Bark, C.B. Eom, A. Gruverman, Retention of resistance states in ferroelectric tunnel memristors, *Appl. Phys. Lett.* 103 (2013) 142908. <https://doi.org/10.1063/1.4823989>.

- [9] J.J. Yang, M.D. Pickett, X. Li, D.A.A. Ohlberg, D.R. Stewart, R.S. Williams, Memristive switching mechanism for metal/oxide/metal nanodevices, *Nature Nanotech.* 3 (2008) 429–433. <https://doi.org/10.1038/nnano.2008.160>.
- [10] R. Bruchhaus, R. Muenstermann, T. Menke, C. Hermes, F. Lentz, R. Weng, R. Dittmann, R. Waser, Bipolar resistive switching in oxides: Mechanisms and scaling, *Current Applied Physics*. 11 (2011) e75–e78. <https://doi.org/10.1016/j.cap.2010.10.022>.
- [11] L. Goux, W. Polspoel, J.G. Lisoni, Y.-Y. Chen, L. Pantisano, X.-P. Wang, W. Vandervorst, M. Jurczak, D.J. Wouters, Bipolar Switching Characteristics and Scalability in NiO Layers Made by Thermal Oxidation of Ni, *J. Electrochem. Soc.* 157 (2010) G187. <https://doi.org/10.1149/1.3454199>.
- [12] M.J. Rozenberg, M.J. Sánchez, R. Weht, C. Acha, F. Gomez-Marlasca, P. Levy, Mechanism for bipolar resistive switching in transition-metal oxides, *Phys. Rev. B*. 81 (2010) 115101. <https://doi.org/10.1103/PhysRevB.81.115101>.
- [13] R. Waser, M. Aono, Nanoionics-based resistive switching memories, *Nature Mater.* 6 (2007) 833–840. <https://doi.org/10.1038/nmat2023>.
- [14] X. Xu, H. Lv, H. Liu, Q. Luo, T. Gong, M. Wang, G. Wang, M. Zhang, Y. Li, Q. Liu, S. Long, M. Liu, Investigation of LRS dependence on the retention of HRS in CBRAM, *Nanoscale Res Lett.* 10 (2015) 61. <https://doi.org/10.1186/s11671-015-0771-0>.
- [15] R. Waser, R. Dittmann, G. Staikov, K. Szot, Redox-Based Resistive Switching Memories - Nanoionic Mechanisms, Prospects, and Challenges, *Adv. Mater.* 21 (2009) 2632–2663. <https://doi.org/10.1002/adma.200900375>.
- [16] L. Goux, Y.-Y. Chen, L. Pantisano, X.-P. Wang, G. Groeseneken, M. Jurczak, D.J. Wouters, On the Gradual Unipolar and Bipolar Resistive Switching of TiN\HfO[sub 2]\Pt Memory Systems, *Electrochem. Solid-State Lett.* 13 (2010) G54. <https://doi.org/10.1149/1.3373529>.
- [17] S.-W. Chen, J.-M. Wu, Unipolar resistive switching behavior of BiFeO₃ thin films prepared by chemical solution deposition, *Thin Solid Films*. 519 (2010) 499–504. <https://doi.org/10.1016/j.tsf.2010.08.004>.
- [18] Y. Shuai, S. Zhou, D. Bürger, M. Helm, H. Schmidt, Nonvolatile bipolar resistive switching in Au/BiFeO₃/Pt, *Journal of Applied Physics*. 109 (2011) 124117. <https://doi.org/10.1063/1.3601113>.
- [19] X. Chen, G. Wu, H. Zhang, N. Qin, T. Wang, F. Wang, W. Shi, D. Bao, Nonvolatile bipolar resistance switching effects in multiferroic BiFeO₃ thin films on LaNiO₃-electrodized Si substrates, *Appl. Phys. A*. 100 (2010) 987–990. <https://doi.org/10.1007/s00339-010-5910-y>.

- [20] J. Zhang, H. Yang, Q. Zhang, S. Dong, J.K. Luo, Bipolar resistive switching characteristics of low temperature grown ZnO thin films by plasma-enhanced atomic layer deposition, *Appl. Phys. Lett.* 102 (2013) 012113. <https://doi.org/10.1063/1.4774400>.
- [21] N.F. Mott, The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals, *Proc. Phys. Soc. A.* 62 (1949) 416–422. <https://doi.org/10.1088/0370-1298/62/7/303>.
- [22] D.C. Kim, S. Seo, S.E. Ahn, D.-S. Suh, M.J. Lee, B.-H. Park, I.K. Yoo, I.G. Baek, H.-J. Kim, E.K. Yim, J.E. Lee, S.O. Park, H.S. Kim, U.-I. Chung, J.T. Moon, B.I. Ryu, Electrical observations of filamentary conduction for the resistive memory switching in NiO films, *Appl. Phys. Lett.* 88 (2006) 202102. <https://doi.org/10.1063/1.2204649>.
- [23] B.J. Choi, D.S. Jeong, S.K. Kim, C. Rohde, S. Choi, J.H. Oh, H.J. Kim, C.S. Hwang, K. Szot, R. Waser, B. Reichenberg, S. Tiedke, Resistive switching mechanism of TiO₂ thin films grown by atomic-layer deposition, *Journal of Applied Physics*. 98 (2005) 033715. <https://doi.org/10.1063/1.2001146>.
- [24] B.J. Choi, D.S. Jeong, S.K. Kim, C. Rohde, S. Choi, J.H. Oh, H.J. Kim, C.S. Hwang, K. Szot, R. Waser, B. Reichenberg, S. Tiedke, Resistive switching mechanism of TiO₂ thin films grown by atomic-layer deposition, *Journal of Applied Physics*. 98 (2005) 033715. <https://doi.org/10.1063/1.2001146>.
- [25] K. Tsunoda, Y. Fukuzumi, J.R. Jameson, Z. Wang, P.B. Griffin, Y. Nishi, Bipolar resistive switching in polycrystalline TiO₂ films, *Appl. Phys. Lett.* 90 (2007) 113501. <https://doi.org/10.1063/1.2712777>.
- [26] R. Meyer, R. Waser, Hysteretic resistance concepts in ferroelectric thin films, *Journal of Applied Physics*. 100 (2006) 051611. <https://doi.org/10.1063/1.2337078>.
- [27] X. Chai, J. Jiang, Q. Zhang, X. Hou, F. Meng, J. Wang, L. Gu, D.W. Zhang, A.Q. Jiang, Nonvolatile ferroelectric field-effect transistors, *Nat Commun.* 11 (2020) 2811. <https://doi.org/10.1038/s41467-020-16623-9>.
- [28] E.Y. Tsybal, APPLIED PHYSICS: Tunneling Across a Ferroelectric, *Science*. 313 (2006) 181–183. <https://doi.org/10.1126/science.1126230>.
- [29] H. Kohlstedt, N.A. Pertsev, J. Rodríguez Contreras, R. Waser, Theoretical current-voltage characteristics of ferroelectric tunnel junctions, *Phys. Rev. B.* 72 (2005) 125341. <https://doi.org/10.1103/PhysRevB.72.125341>.
- [30] A. Razumnaia, Y. Gagou, H. Bouyanfif, B. Carcan, B. Allouche, J. Wolfman, C. Autret-Lambert, M.E. Marssi, D. Mezzane, I. Luk'yanchuk, Resistive Switching Hysteresis in Thin Films of Bismuth Ferrite, *Ferroelectrics*. 444 (2013) 183–189. <https://doi.org/10.1080/00150193.2013.790759>.

- [31] G. Liu, K. Jin, J. Qiu, M. He, H. Lu, J. Xing, Y. Zhou, G. Yang, Resistance switching in BaTiO₃- δ Si p-n heterostructure, Appl. Phys. Lett. 91 (2007) 252110. <https://doi.org/10.1063/1.2821369>.
- [32] C. Wang, K. Jin, Z. Xu, L. Wang, C. Ge, H. Lu, H. Guo, M. He, G. Yang, Switchable diode effect and ferroelectric resistive switching in epitaxial BiFeO₃ thin films, Appl. Phys. Lett. 98 (2011) 192901. <https://doi.org/10.1063/1.3589814>.
- [33] A.Q. Jiang, C. Wang, K.J. Jin, X.B. Liu, J.F. Scott, C.S. Hwang, T.A. Tang, H.B. Lu, G.Z. Yang, A Resistive Memory in Semiconducting BiFeO₃ Thin-Film Capacitors, Adv. Mater. 23 (2011) 1277–1281. <https://doi.org/10.1002/adma.201004317>.
- [34] J. Tikkanen, H. Huhtinen, P. Paturi, Oxygen-sintered (Pr,Ca) MnO₃: Structure and magnetism at high Ca concentrations, Journal of Alloys and Compounds. 635 (2015) 41–47. <https://doi.org/10.1016/j.jallcom.2015.02.098>.
- [35] M. Janousch, G.I. Meijer, U. Staub, B. Delley, S.F. Karg, B.P. Andreasson, Role of Oxygen Vacancies in Cr-Doped SrTiO₃ for Resistance-Change Memory, Adv. Mater. 19 (2007) 2232–2235. <https://doi.org/10.1002/adma.200602915>.
- [36] S.X. Wu, L.M. Xu, X.J. Xing, S.M. Chen, Y.B. Yuan, Y.J. Liu, Y.P. Yu, X.Y. Li, S.W. Li, Reverse-bias-induced bipolar resistance switching in PtTiO₂/SrTiO_{0.99}Nb_{0.01}O₃/Pt devices, Appl. Phys. Lett. 93 (2008) 043502. <https://doi.org/10.1063/1.2965469>.
- [37] B. Allouche, Y. Gagou, F. Le Marrec, M.-A. Fremy, M. El Marssi, Bipolar resistive switching and substrate effect in GdK₂Nb₅O₁₅ epitaxial thin films with tetragonal tungsten bronze type structure, Materials & Design. 112 (2016) 80–87. <https://doi.org/10.1016/j.matdes.2016.09.047>.
- [38] B. Allouche, Y. Gagou, M.-A. Fremy, F. Le Marrec, M. El Marssi, Resistive switching in a (00 $\bar{l}$)-oriented GdK₂Nb₅O₁₅ thin film with tetragonal tungsten bronze type structure, Superlattices and Microstructures. 72 (2014) 35–42. <https://doi.org/10.1016/j.spmi.2014.04.008>.
- [39] Q. Xu, X. Yuan, Y. Cao, L. Si, D. Wu, Bipolar resistive switching in BiFe_{0.95}Mn_{0.05}O₃ films, Solid State Communications. 152 (2012) 2036–2039. <https://doi.org/10.1016/j.ssc.2012.08.023>.
- [40] H. Yang, H.M. Luo, H. Wang, I.O. Usov, N.A. Suvorova, M. Jain, D.M. Feldmann, P.C. Dowden, R.F. DePaula, Q.X. Jia, Rectifying current-voltage characteristics of BiFeO₃Nb-doped SrTiO₃ heterojunction, Appl. Phys. Lett. 92 (2008) 102113. <https://doi.org/10.1063/1.2896302>.
- [41] D. Lee, S.H. Baek, T.H. Kim, J.-G. Yoon, C.M. Folkman, C.B. Eom, T.W. Noh, Polarity control of carrier injection at ferroelectric/metal interfaces for electrically switchable diode and photovoltaic effects, Phys. Rev. B. 84 (2011) 125305. <https://doi.org/10.1103/PhysRevB.84.125305>.

- [42] J.G. Simmons, Poole-Frenkel Effect and Schottky Effect in Metal-Insulator-Metal Systems, Phys. Rev. 155 (1967) 657–660. <https://doi.org/10.1103/PhysRev.155.657>.
- [43] J. Frenkel, On Pre-Breakdown Phenomena in Insulators and Electronic Semi-Conductors, Phys. Rev. 54 (1938) 647–648. <https://doi.org/10.1103/PhysRev.54.647>.
- [44] B. Allouche, Y. Gagou, F. Le Marrec, M.-A. Fremy, M. El Marssi, Oxygen-deficient $\text{GdK}_{2}\text{Nb}_{5}\text{O}_{15}$ ferroelectric epitaxial thin film, EPL. 116 (2016) 67001. <https://doi.org/10.1209/0295-5075/116/67001>.
- [45] S. Deswal, A. Jain, H. Borkar, A. Kumar, A. Kumar, Conduction and switching mechanism in $\text{Nb}_{2}\text{O}_{5}$ thin films based resistive switches, EPL. 116 (2016) 17003. <https://doi.org/10.1209/0295-5075/116/17003>.
- [46] Z. Xu, K. Jin, L. Gu, Y. Jin, C. Ge, C. Wang, H. Guo, H. Lu, R. Zhao, G. Yang, Evidence for a Crucial Role Played by Oxygen Vacancies in LaMnO_3 Resistive Switching Memories, Small. 8 (2012) 1279–1284. <https://doi.org/10.1002/smll.201101796>.