Unraveling the resistive switching mechanisms in LaMnO$_{3+\delta}$-based memristive devices by *operando* hard X-ray photoemission

Oxide-based resistive random-access memories (OxRRAMs) are promising candidates for the next generation of non-volatile memories. The data storage principle is based on the switching, upon applied electrical bias, of the resistivity of an oxide between high (HRS) and low (LRS) resistive states. Devices based on a transition metal oxide, such as the LaMnO$_{3+\delta}$ (LMO), have shown interesting electrical properties such as multi-level data storage [1]. Their resistive switching mechanism is related to the formation and partial rupture of a conductive filament.

Further information concerning chemical changes governing the conduction mechanism are needed to efficiently control and optimize the devices performances. In the past, HAXPES was used to study the critical metal/oxide interfaces of such oxide-based memristive devices [2]. However, standard measurements only provide a static view of the involved phenomena whereas *operando* measurements can bring a more dynamic picture of the mechanisms governing the device behavior [3].

Operando HAXPES under *in situ* electrical biasing has thus been developed to investigate the behavior of memory devices during operation and based on the M/LMO/Pt stack, with M = Au or Pd [4]. We focus here on memory cells fabricated with a chemically inert top electrode, compared to an active TiN electrode [5]. HAXPES measurements were performed at SPring-8 **BL15XU** with a photon energy of 7933 eV.

In order to both match the HAXPES requirements and allow *in situ* electrical activation, the device depicted in Fig. 1(a) was fabricated. The active region consists of a thin (~7 nm) metal layer (Au or Pd) deposited directly on a 100×100 µm² LMO surface. Outside this region, the top electrode was electrically isolated from LMO by a 50 nm-thick Si$_3$N$_4$ insulating layer. A thick current collector was deposited away

from the active area and connected to a sourcemeter (Keithley 2635B).

Figure 1(b) shows the characteristic hysteretic current-voltage (I-V) curve measured *in situ* for the Au top electrode-memristive device, exhibiting an asymmetric bipolar counter-clockwise-type switching. An abrupt RESET from LRS to HRS occurs around 2 V while the SET process requires higher negative voltage (−8 V) and presents several consecutives steps starting at −6 V. The compliance current was set to 10 mA in negative polarity in order to avoid the oxide electrical breakdown at high voltage.

HAXPES measurements were carried out on the Pd/LMO/Pt device after *in situ* switching. By comparing the O 1s spectra measured in LRS and HRS (see Figs. 2(a) and 2(b)), noticeable differences are observed, though partly screened by the large Si−O signal coming from the partially oxidized Si$_3$N$_4$ layer. Two other contributions are identified corresponding to lattice oxygen from LMO (O$_{latt.}$) and to interfacial oxygen (O$_{inter.}$) ascribed to oxygen inserted at the metal/oxide interface. From LRS to HRS, the O$_{inter.}$ contribution slightly increases (from 20.5% to 21.6% of the total area) with respect to the O$_{latt.}$ one (from 7.7% to 6.6%). This result indicates that oxygen is released from the LMO lattice and drifts towards the top electrode during the RESET step (V$_{RESET}$ > 0).

Figures 2(c) and 2(d) show the La 3$d_{5/2}$ spectra recorded in LRS and HRS, respectively. Both spectra exhibit a main peak (cf^0) and two satellite peaks (cf^{1}L), resulting from core-hole screening processes. In our previous study [5], we demonstrated the direct relationship between the oxygen content in the surrounding of La atoms and the ratio of the satellites/main peak areas. From LRS to HRS, a slight decrease of the main peak intensity is observed, thus indicating an increase of the oxygen content in the La
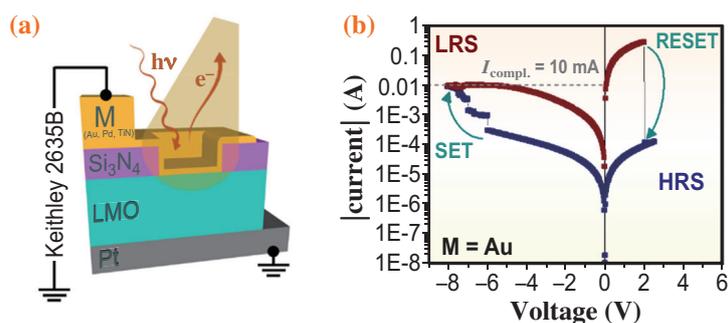

Fig. 1. **(a)** Sketch of the memristive device for operando measurements. **(b)** *In situ* I−V characteristics obtained for an Au/LMO/Pt stack. [4]
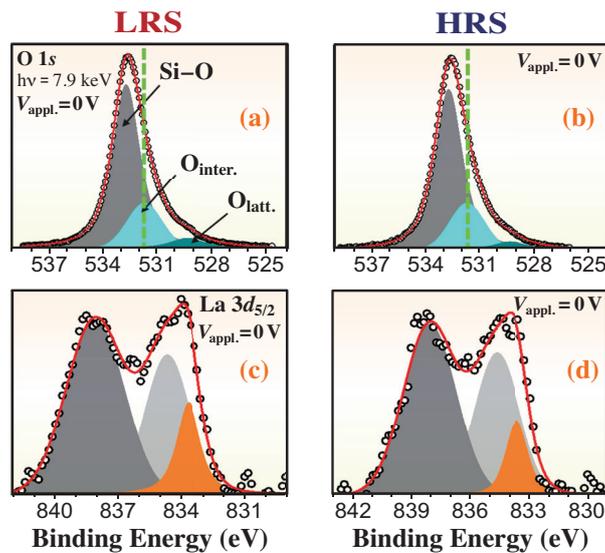
Fig. 2. O 1s and La 3$d_{5/2}$ spectra for the Pd/LMO/Pt stack in (a), (c) LRS, and (b), (d) HRS at 0V. [4]

neighborhood. The La spectra indicate that, in addition to the oxygen release, an oxygen-rich region is formed at the top LMO interface.

Based on these results, we suggest a model of the resistive switching mechanism in the Pd/LMO/Pt system as depicted in Fig. 3. We assume that the conduction in the LMO is related to the formation of filaments with an oxygen-rich composition (see Fig. 3(a)). When a positive voltage is applied (RESET, see Fig. 3(b)), oxygen from the filament drifts towards the top electrode, thus reducing the LMO conductivity. The device is switched to the HRS state. When a negative voltage is applied (SET, see Fig. 3(c)), oxygen is drifting back into the material and conductive paths can be formed again: the device is then set back in its LRS.

In summary, we demonstrated that the switching mechanism of the Pd(Au)/LMO/Pt devices is triggered by oxygen drift phenomena between the LMO and the top electrode, thus locally modifying the conductivity of oxygen-rich regions, so-called filaments. The oxygen is accumulated at the interface with the top Pd(Au) electrode, both in a top LMO oxygen-rich layer, and in the form of gas pockets under the metal electrode.
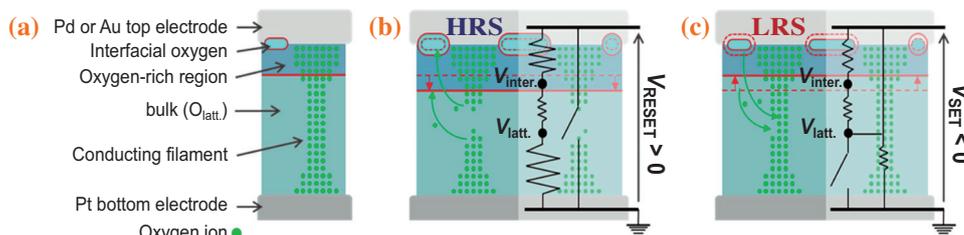

Fig. 3. Sketch of the proposed physical model used to describe the M/LMO/Pt devices (M = Au, Pd) studied by operando HAXPES. [4].

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