Standard Project

Experimental Report template

Proposal title: Structural study of Pt/ZrO$_2$/TiN and Pt/Ti/ZrO$_2$/TiN OxRRAM memories by XANES			**Proposal number:** MA-1851
Beamline: ID21	**Date(s) of experiment:** from: **11th July 2013** to: **16th July 2013**		**Date of report:** 15th October 2013
Shifts: 18	**Local contact(s):** Dr. Murielle SALOME		*Date of submission:* *15th October 2013*

Objective & expected results (less than 10 lines):

Samples : the bottom electrode (TiN layer) was grown by Physical Vapor Deposition (PVD) on Si(100) substrate and the ZrO_2 layers were grown by Plasma-Enhanced Atomic Layer Deposition (PEALD), at the Leti (CEA Grenoble). For this study, two kinds of devices were realized : one with a top electrode of Pt and one with a top electrode of Pt/Ti. Applying a voltage at the electrodes causes the device to switch its electrical resistive state from high resistive state to low resistive state and vice versa. The current models explaining this switching are based on the creation of conductive filaments, created by migration of oxygen in the oxide layer.

Consequently, we expected to see a change of the Zr oxidation state between the pristine and the written state in the region where the filaments grew. Besides, we expected to see a global change in the valence of the zirconium for the Ti/ZrO2 samples, Ti being known as an oxygen getter.

Results and the conclusions of the study (main part):

According to the literature, we took the decision to work at the L_{II} and L_{III} edges of zirconium, looking for at least energy shifts due to a change of Zr oxidation state. We also measured references samples for comparison. In a first time, we focused our analysis on reference samples.

Reference samples

Sample ZrO2/TiN

A pristine sample with a 8 nm thick ZrO_2 layer was used as a reference. The XAFS spectra was very similar to the one obtained with our 10 nm thick ZrO_2 pristine sample. Then, we used a specific sample prepared by conductive AFM.

Sample prepared by conductive AFM

We measured a 8 nm thick ZrO_2 region in which filaments were created with a step of 1 µm on a 10 x 10 µm2 grid by using a conductive AFM, as indicated in figure 1.
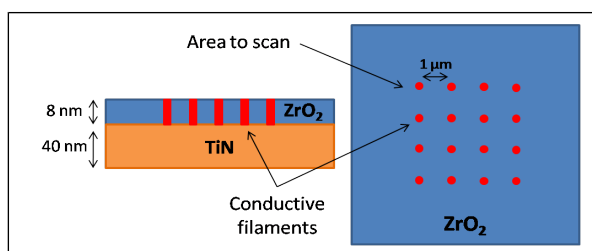

Figure 1: AFM prepared sample

Reference samples

Fluorescence XANES spectra were obtained with a zirconium foil and a single crystal of oxide zirconium (ZrO_2 bead).
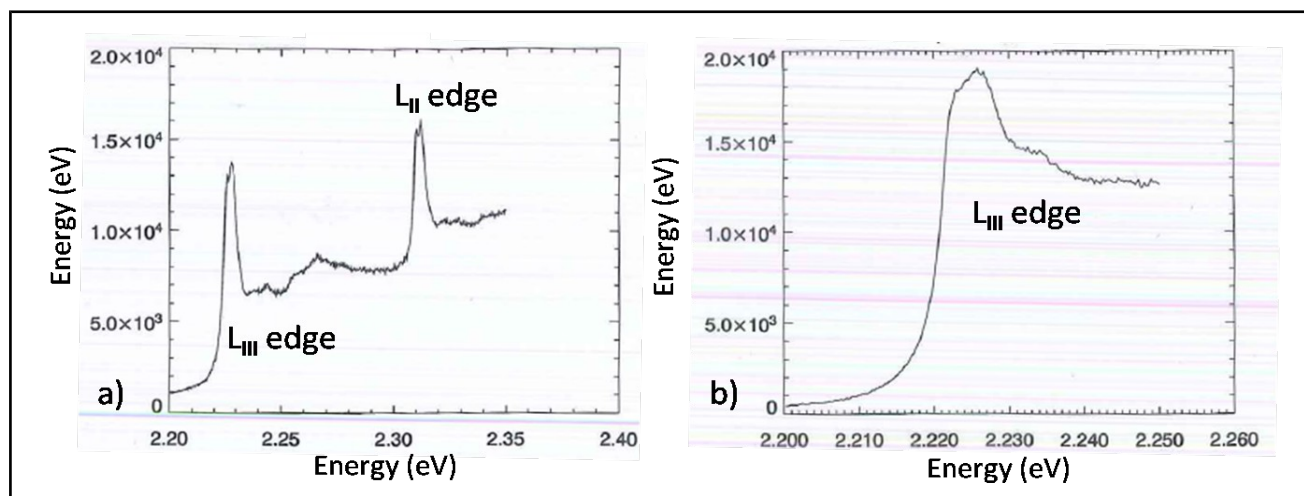

Figure 2: XANES spectra (not normalized) showing a) the Zr-L_{II} and Zr-L_{III} edges of ZrO_2 bead and b) the Zr-L_{III} edge of Zr foil

Samples of interest

The samples presented in the following part are all composed of a substrate of silicon (750 µm) on which is deposited a TiN bottom electrode (35 nm thick) and a ZrO_2 dielectric layer (10 or 20 nm thick). The variable parameter are the thickness of the

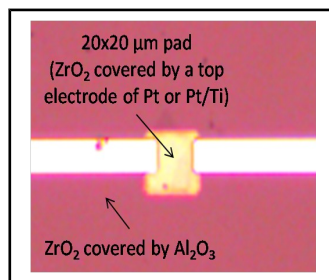ZrO$_2$ layer or/and the composition of the top electrode.

Figure 3:Pad of 20x20 µm^2 to scan

<u>Pt-10nm/ZrO$_2$-10nm/TiN-35nm sample:</u>

This sample was switched *ex situ* from a high resistive state (HRS) of ~1.4 .10^9 Ω to a low resistive state (HRS) of ~200 Ω before the scan. A raster scan of the 20 x 20 µm2 memory cell (pad) was performed with a step size of 1 µm, at each point a fluorescence XANES spectrum was measured at the Zr LIII edge. Considering the size of the memory cell and the step size, the measurement took about 48 hours to be completed. Figure 4 shows a characteristic XANES spectrum measured at the Zr LIII edge.
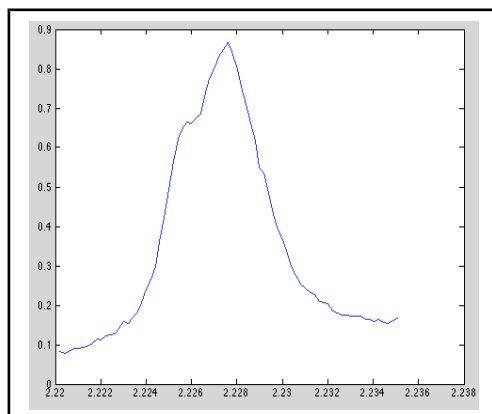

Figure 4: Fluorescence XANES spectrum of the Pt/ZrO$_2$/TiN sample at the the Zr-L$_{III}$ edge. Intensity as a function of the energy.

<u>Pt-5nm/Ti-5nm/ZrO$_2$-10nm/TiN-35nm sample:</u>

We carry out two raster scans on the same sample: one before the switching (in the pristine state) and one after (in the LRS). We selected a sample containing Ti in the top electrode because they presented better switching characteristics. So, at the first time, we raster scanned all the memory cell (pad) of a pristine sample. This scan took about 26 hours. Figure 5 shows the ratio of the Zr/Si fluorescence yields at each point of the pad before in the pristine state.
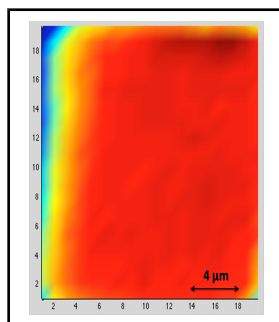

Figure 5:Image of the Zr/Si fluorescence intensity ratio summed in the range of the x-ray beam energy corresponding to the XANES spectrum (see figure 4), before set

After the scan in the pristine state, we take out the sample and switched it from LRS to HRs and vice versa. We checked that this sample was working fine and put it in low resistive state (in which filaments are supposed to be formed). We placed the sample in the chamber as close as possible to its previous position so that we could make a scan of about the same area as in the pristine state. The raster scan took about 26 hours. Figure 6 shows the Zr/Si fluorescence ratio at each point of the pad after the set.
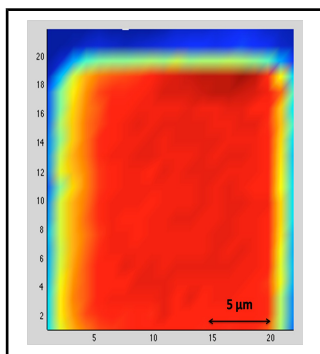
Figure 6: Image of the Zr/Si fluorescence intensity ratio summed in the range of the x-ray beam energy corresponding to the XANES spectrum (see figure 4), after set

Although the samples presented a good switching behavior, we did not observe significant evidences of a valence (or oxidation state) or a structural changes. One hypothesis which can be brought to explain this result is the rather small size of the filaments in comparison with the X-ray beam size. Indeed, the expected size is about 10 nm or more, which is likely too small to affect the signal created by the 1x1 µm2 beam of ID21. Anyway, one still need to perform a more careful image analysis to be sure of that first result. Data analysis is in progress.

To go further in the study, we will decrease the size of the cell down to about 50x50 nm2, this is possible at Leti. Also we will use samples with Ti layers of different thicknesses (Ti at the top electrode is a getter of oxygen atoms). On the other side, we can use a smaller beam like the one at the brand new NINA beamline.