	Experiment title: Magnetoelectric Fe/FE-HfO_2 interface	**Experiment number**: HC-3078
Beamline:	**Date of experiment**: from: March, 1 to: March, 6, 2017	**Date of report**: March, 31, 2017
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Report:

The performed experiments aimed at the search for magnetoelectric phenomena at the interface between ferromagnetic (Fe) and emerging ferroelectric ($Hf_{0.5}Zr_{0.5}O_2$) thin films. Specifically, we have monitored *in situ* with Mössbauer spectroscopy the effect of the polarization direction switch in ferroelectric HfO_2 layer, on the magnetic properties of the adjacent few-ML thick isotopically enriched ^{57}Fe marker layer (capped with a Pt layer). In particular, we searched for local magnetic hyperfine field and magnetic moment value and orientation changes. The Mossbauer measurements were combined with *in operando* electrical characterization of the prototype devices under investigation.

Pt (7nm)/^{57}Fe(1nm)/$Hf_{0.5}Zr_{0.5}O_2$(10nm)/TiN(20nm) multilayered structures were grown on Si substrates by combination of Atomic Layer Deposition and Pulsed Laser Deposition techniques followed by rapid thermal annealing to drive $Hf_{0.5}Zr_{0.5}O_2$ crystallization in ferroelectric phase. In order to enable *in situ* experiments, the samples were patterned to define 50x8000 μm^2 area exposed to a grazing incidence X-ray beam and to connect both top and bottom TiN electrodes with remote contact pads (Figure 1). Thus prepared functional prototype memory devices exhibit robust ferroelectric response with the remnant polarization P≈ 10 $\mu C/cm^2$ (*Figure 2*).

The Mössbauer spectrum of ultrathin ^{57}Fe layer on top of FE-HZO is presented in Figure 3. The spectrum consists of 5 components: paramagnetic doublet, corresponding to Be focusing lenses in the beamline (containing some Fe contamination), paramagnetic single line with isomer shift δ~0.26 mm/s, associated with Fe-Pt alloy, and 3 magnetic sextets. Two of these sextets are attributed to the magnetic Fe oxide (Fe_3O_4), while the last one corresponds to α-Fe at the interface. The preliminary fitting reveals the line ratio in the sextets to be around $A_{16}:A_{25}:A_{34} \approx 3:3:1$, indicating sample magnetization between the film plane and the random distribution. The line ratio in ferromagnetic Mössbauer spectra is the signature of the (averaged) magnetic moment direction. This line ratio does change following the polarization reversal (experimental data *not shown*), and therefore, small, but statistically distinct changes in this ratio in a few-ML thick Fe layer adjacent to FE- $Hf_{0.5}Zr_{0.5}O_2$ observed on the same sample following *in situ* reversal of the polarization is the direct evidence of the magnetoelectric effect.

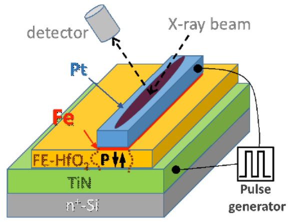

Figure 1. Schematic of the $^{57}Fe/FE\text{-}HfO_2/TiN$ samples used in operando Mossbauer experiments.

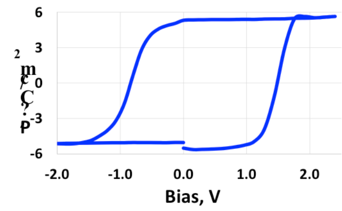

Figure 2. Polarization vs. voltage curve taken from $^{57}Fe/FE\text{-}HfO_2/TiN$ devices during in-operando experiment.

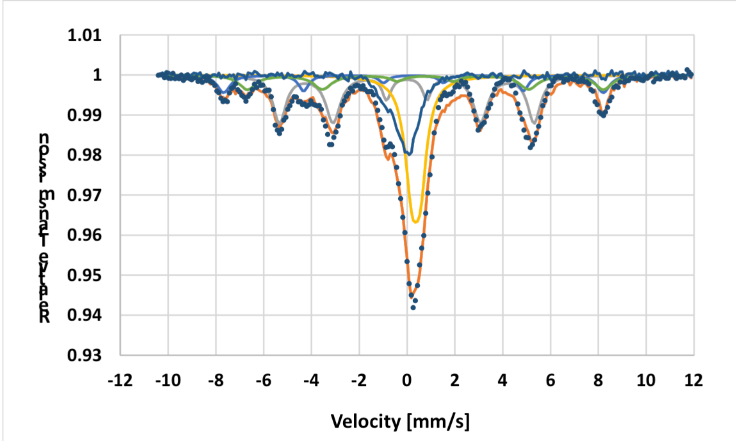

Figure 3. Mössbauer spectrum of a marker ^{57}Fe layer in contact with FE-HZO.

In addition, we have performed same measurements under external perpendicular magnetic field (B ~100 mT), monitoring the 2-d and 5-th component relative intensity changes in ^{57}Fe sextet as the function of both external magnetic field and polarization direction. We have got some evidence that the effect of polarization reversal on magnetic properties of Fe marker layer depends on the direction of external magnetic field, but the error bar is too high to make unambiguous conclusions.

The obtained results perfectly fit the expected outcome from the beamtime. However, before these results can be published in a high impact factor peer-reviewed journal, the additional analyses, such as the accurate identification of exact magnetization direction by SQUID measurements, and the structural characterization of the interface by high resolution transmission electron microscopy have to be performed. This work is currently underway. Another portion of the data related to the effect of external magnetic field on the sign of magnetoelectric effect should be verified by additional Mössbauer experiments with better statistics.