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Application for beam time at ESRF – Experimental Method

In operando µ-XANES study of resistive switching in HfO_2/ZrO_2 bilayer RRAM by nano-guided filament (NGF) approach

Proposal Summary (should state the aims and scientific basis of the proposal) :

To date reliability and variability of switching parameters are the major obstacles for the commercialization of resistive random access memory (RRAM). To solve the problem defect engineering approaches such as doping, employing bilayer/multilayer structure have been proposed in order to improve the resistive switching (RS) behaviour through the optimization of defects in conduction filaments (CFs). Versatile resistive switching phenomenon have been reported in binary metal oxides such as HfO_2, ZrO_2 etc. However, the detailed composition and structure of the CFs– responsible for resistive switching (RS) - of Hafnia and Zirconia RRAM are still unknown. This is partly due to the experimental difficulties considering the nano-scale and random nature of the filaments. ***The objective of this proposal is*** therefore to ***in operando*** explore the electronic state and local structure of bilayer Hafnia/Zirconia a) by **nano-guided filament (NGF)** approach in order to find the filament during spatially resolved nano-spectroscopy and b) using ZrO_2 as a sensitive probe (chemical states better detectable by X-ray spectroscopy than for HfO_2) in order to unveil the local physical modification of HfO_2/ZrO_2 bilayer in the forming nano-filament(s).

Scientific background :

The basic RRAM cell structure is generally a capacitor with an insulating oxide, sandwiched between two conducting metal electrodes. The mechanism of RS has been attributed to the formation and rupture of local CFs consisting typically of double positively charges oxygen vacancies ($V_O^{\bullet\bullet}$)[1]. There are several HfO_2 and ZrO_2 bulk polymorphs known, such as monoclinic (*m*, *P2₁/c*), tetragonal (*t*, *P4₂/nmc*) and cubic (*c*, *fluorite*, *Fm3m*) crystal structures. Both HfO_2 and ZrO_2 exist in monoclinic stable phase at the ambient conditions, the presence of *t*-Hf_2O_3, *t*-Zr_2O_3 in the respective O-deficient electroformed HfO_{2-x}, ZrO_{2-x} is a possible explanation of the conductive state of Hf/Zr-based RRAM[2]. However, the composition and structure of CFs in HfO_2/ZrO_2-based RRAM have not been reported because the experimental investigation of CFs suffers from great difficulties. In particular, the impact of electroforming and resistive switching is expected to occur in small ($diameter_{CF}$=50-100 nm)[3] and random CF patches over the capacitor area. The NGF approach is a most promising technical approach and was explored e.g. at IHP in form of geometric confined NGFs by the use of Si nano-tip electrodes (Fig.1) by patterned wafer approaches[4,5]. **NGF approach** is believed as an ideal approach **to locate the nano-filament by cobalt signal coming from the $CoSi_2$ metallization on top of the Si tip** (blue layer in EDX in Fig.1) which is the **"hot spot"** region need to scan to search for ***in operando*** changes as a function of cell status using non-destructive nano-meter scale X-ray beam to obtain bulk-sensitive signals over the whole memory cell dielectric. It will be even better to employ ***in operando*** electrical switching approaches to investigate one and the same RRAM sample in different resistive states, thus allowing to exclude sample variation issues in the final data interpretation. Therefore, ***we suggest using in operando µ-XANES to detect the material modifications on the nanoscale CFs***.

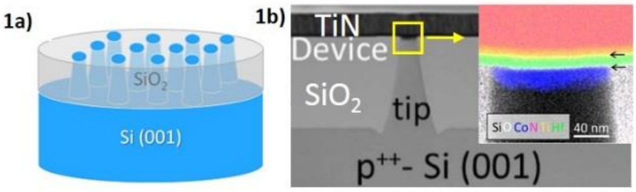

Figure 1: *(a) An illustration of the Si tip wafer structure[4]; (b) STEM image overview showing Si tips. Inset shows the STEM-EDX performed on the cross-section of a TiN/Ti/HfO_2/$CoSi_2$/Si tip device[5].*

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity..etc) :

We request beamtime to perform *in operando*, µ-XANES experiments at the sensitive K-edges of Zr (18.004keV)[6] and sensitive L_{III} edges of Hf (9.561 keV)[7] over oxygen content on a set of HfO_2/ZrO_2 bilayer thin films using fluorescence detection at the ID 16 B ESRF beamline. The special *in-operando* set-up developed at IHP aims to directly switch the MIM device in the XANES measurements chamber, further followed by the XANES (for valence states) spectra recording. Fig.2 shows the set-up details already realized for *in-operando* hard X-Ray photoelectron spectroscopy studies at PETRA III[8]. One sample (integrated TiN/Ti/HfO_2/TiN device) with a size of **600×600 nm^2** is mounted on a printed circuit board (PCB) and wire-bonded to external electrical connectors. The PCB is then placed on the sample holder and attached to the manipulator. This assembly is finally connected via SMA connectors and vacuum feed throughs to a Keithley 4200 SCS semiconductor characterization system. Subsequently, using the available nano-meter size X-ray instrumentation at ID 16 B, nano-filaments are located using Co signal and HfO_2/ZrO_2 bilayer thin film over nano-filament region will be scanned while Hf/Zr spectra for each point will be saved. By comparing and mapping the Hf/Zr spectra (at certain energy) under virgin, low resistance (LR-) or high resistance (HR-) states, the nano-filament location can be identified and the possible valence state and local structure modification of HfO_2/ZrO_2 bilayer in CFs can be clarified and directly correlated with electrical RRAM results. The experiment (on in total six samples) can be divided into two steps: 1) normal μ-XANES on three HfO_{2-x}/ZrO_{2-x} bilayer samples with different oxygen stoichiometries (x=0, 0.1 and 0.2), which will be used as references for more complex *in-operando* data; 2) *In-operando* μ-XANES on three Si-tip devices: one based on HfO_2/ZrO_2 (x=0), and two based on HfO_{2-x}/ZrO_{2-x} (x=0.1, 0.2) films to check how XANES spectra vary with the oxygen deficiency. Each sample requires three times of detection under virgin-, LR- or HR- states. The thicknesses of ZrO_2/HfO_2 films in total are ~20 nm. A bulk ZrO_2 and HfO_2 sample (*m*-phase) will also be measured as reference. The expected surface ratio between the CF region (~60nm^2) and the nano X-ray beam (~80nm^2) is 0.75.

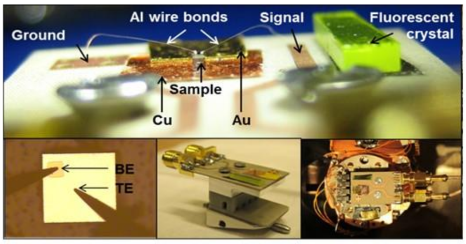

Figure 2: *In-operando XAFS set-up to enable the in-situ study of single RRAM devices in various resistance states, manipulated by electrical pulses from an external semiconductor analyser.*

Beamline(s) and beam time requested with justification :

As mentioned, we request ID 16 B beamline which is ideally equipped to perform these fluorescence detected μ-XANES measurements on the set of thin films at the K-edge of Zr and L_{III} edge of Hf. Based on the mentioned test measurements, we estimate that 18 shifts are required (~1.5 shift per measurement). It should be noticed that we need more than two shifts to install the sample, connect all the cables and pump, align the optics, rebend the KB mirrors and calibrate the system.

Results expected and their significance in the respective field of research :

We expect to determine by in-operando μ-XAS the materials modification in nano-filament of HfO_2/ZrO_2 bilayer as a function of the RS process (virgin-, on- & off-state). XANES mapping will thus provide important, locally resolved information of Zr and Hf valence state changes which will help to elucidate the detailed switching dynamics of HfO_2/ZrO_2 bilayer RRAM. In especial, it will be possible to distinguish the local coordination environment of Hf and Zr atoms in the HfO_2/ZrO_2 bilayer film versus its possible modification within nano-filament. The outcome of this study will be of great importance to understand i) the CFs related RS mechanism and ii) changes in the local environment brought about by the incorporation of oxygen-deficiency. Only by in-operando techniques, the detected, locally resolved materials modifications by μ-XAS can be unambiguously correlated to the electrical state of the RRAM cell. Certainly, such insights are "key" to engineer RRAM cells on the atomic – scale to achieve reliable, universal memory technologies.

References

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