ESRF	**Experiment title:** HAXPES to investigate novel metal/oxide stacks on III-V substrates for future CMOS applications	**Experiment number**: MA-1902
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Report:

HAXPES experiments were performed to investigate novel metal/oxide stacks for CMOS applications. No full stacks could be deposited on III-V substrates for this experiment. The analysis were carried out on CMOS stacks prepared in a gate-first integration scheeme on 300 mm Si(100) wafers. HAXPES measurements were performed at 12 and 15 keV on the structures detailed in figure 1. They include a 20 nm-thick a-Si capping layer, a TiN metal gate, an active LaO layer (0.4 and 1 nm thick) as well as an high-k oxide layer (HfSiON).

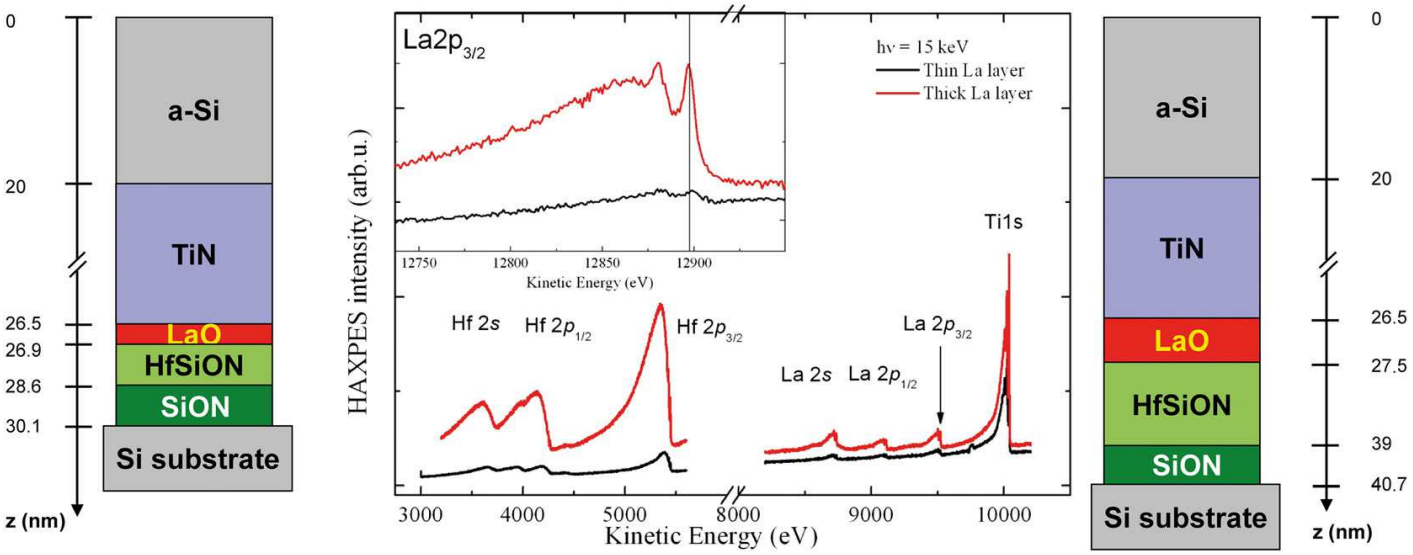

Figure 1: HAXPES spectra measured at 15 keV for the high-k/metal gate stacks detailed at the left and rigth sides.

HAXPES is used for a non-destructive and depth sensitive chemical analysis, thanks to higher probing depths compared to laboratory XPS, since the photoelectron mean free path increases with kinetic energy. This technique allows to probe the full stacks without further removal of the a-Si and TiN thick capping layers. This is of upmost interest to preserve the thin underlying layers (LaO and HfSiON) which are the critical layers of interest. The analysis is thus fully representative of the sample itself without any possible artefacts due to previous remocal of capping layers by sputtering or chemical etching. To go beyond the limits of HAXPES and further extend the probing depth, we combine these experiments with quantitative inelastic background analysis using the Tougaard method [1]. It has already been implement on CMOS stacks with careful optimization of the inelastic scattering cross sections to follow La diffusion after annealing [2].

First experiments of this type have been previously performed at ESRF showing that HAXPES is compatible with inelastic background analysis using the method pioneered by Prof. Tougaard [2]. Here, further experiments were performed on the same structures to retrieve in-depth chemical information, in a quantitative and reliable way with the use of reference sample, consiting in thick films of each constituent of the stacks (Si, TiN, LaO anf HfSiON). Inelastic background analysis including reference spectra acquired with samples of known composition allows to decrease the estimated error of the in-depth elemental distributions [3]. In particular, the depth distribution of La buried up to 30 nm below the surface can be obtained with good accuracy from the inealstic background of the La $2p_{3/2}$ [2,3].

HAXPES experiments were also carried out on stacks designed for advanced resistive memories. Resistive change memories attract lots of interest because of their properties such as high scalability, low power consumption and high switching speed. Conductive Bridge Random Access Memories (CBRAM) store data by creating or dissolving a conductive metal filament through a dielectric. However the switching mechanism is complex and in-situ observation of chemical elements into the stack is difficult. Laboratory XPS does not provide sufficient in-depth sensitivity to probe the layer of interest, i. e. the oxide, which is buried under a thick (~20 nm) top electrode. HAXPES is again of real interest to increase the depth sensitivity. This technique has already been succesfully used to investigate the switching mechanism of resistive memories [4,5]

During this experiment, we have investigated the chemical elements behaviors before and after forming in a CuTe-based/Ta_2O_5 CBRAM stack. For that purpose (TiN top electrode)/CuTe-based/Ta_2O_5/(TiN/Ta bottom electrode) stacks have been fabricated by cosputtering through a shadow mask. Resistive switching was achieved by applying an external electric potential at the two terminals of the memory device, prior to the synchrotron campaign. HAXPES analyses were realized on as-deposited and switched samples to evaluate elemental in-depth distributions and chemical environments. The incident photon energy was set at 15 keV to reach sampling depths of 30 to 40 nm in order to probe the buried Ta_2O_5 active layer. A precise analysis of the $Ta3d_{5/2}$ and Cu2s core levels was done (see figure 2).

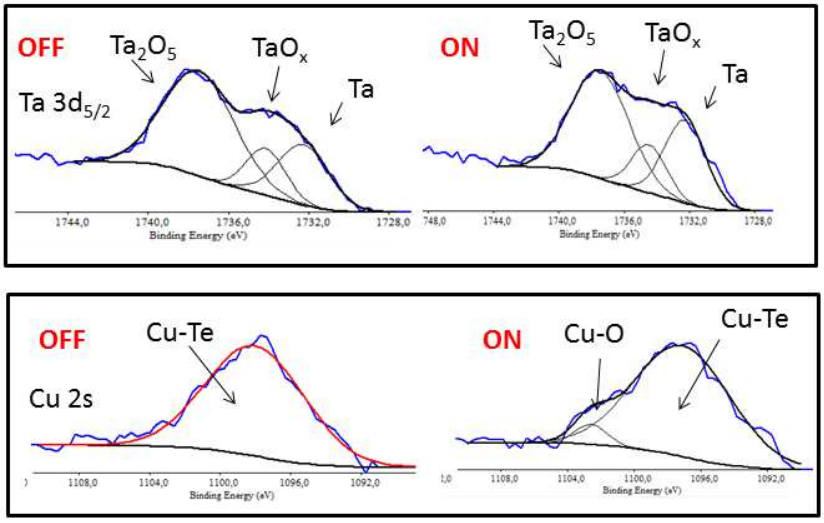

Figure 2: HAXPES spectra measured at 15 keV for the CuTe/Ta_2O_5 stacks designed for advanced CBRAMs before and after ex-situ electrical switching.

Results show that the Tantalum oxide is reduced during electrical stress, as shown by the increase of the Ta^0 component after swithing. Oxygen ions (O^{2-}) diffuse toward the surface, i.e. the anode. Copper oxydation is also observed from an additional component at higher binding energies on the Cu 2s spectra. Cooper ions (Cu^{2+}) are also probably created from the CuTe-based layer and injected through Ta_2O_5 toward the cathode during forming. Therefore, we observe that resistive switching results from the diffusion of both Cu and O indicating a hybrid switching mechanism (i.e. OxRAM with O vacancies and CBRAM with Cu cations). Complementary laboratory measurements such as time of fligth secondary ion mass spectroscopy were performed on the same stacks. Results confirm the copper diffusion inside the oxide toward the bottom electrode [6].

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