In situ hard X-ray photoemission study of the resistive switching effect in Pt/ZrO\textsubscript{x}/HfO\textsubscript{2-x}/p\textsuperscript{++}-Si

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Reversible resistive switching (RS) effects observed in thin film transition metal oxides have been under intense investigation over the last years considering their applicability in the innovative non-volatile memory (NVM) devices [1,2]. The combination of properties such as high speed (~1 ns), low energy consumption (< 1 pJ), long retention time and good scalability are the advantages making RS concept competitive. The obstacle on the way of commercialization is to elucidate the microscopic physical mechanism(s) behind the observed RS phenomena. In this contribution, HAXPES was used to probe the whole functional MIM structures based on Pt/ZrO\textsubscript{x}/HfO\textsubscript{2-x}/p\textsuperscript{++}-Si stacks upon in-situ biasing (“device under operation”). By observing small chemical changes following the assumed (charged) oxygen vacancies drift we get insight into the processes accompanying the effect of resistive switching in dielectrics based on the transition metal oxides.

Pt/ZrO\textsubscript{x}/HfO\textsubscript{2-x}/p\textsuperscript{++}-Si multilayered stacks were grown by the combination of Atomic Layer Deposition (ALD) and Pulsed Laser Deposition (PLD) techniques on highly doped p\textsuperscript{++}-Si substrates (\(\rho = 0.01\) Ohm-cm). First, HfO\textsubscript{2} layers were grown by ALD, while ultrathin Zr and Pt layers were separately deposited on top by PLD in a single vacuum cycle. The thickness of the Zr interlayer \(d \approx 4\) nm was optimized in terms of resistive switching effect by separately performing I-V measurements on the respective MIM stacks. The thickness of the Pt capping layer serving the top electrode also has to be carefully selected either to ensure both a continuous film coverage and a sufficiently high yield of photoelectrons from the buried HfO\textsubscript{2-x}/ZrO\textsubscript{x}/Pt interfaces. However, an ultrathin Pt electrode has a surface conductivity comparable with that across the HfO\textsubscript{2} functional layer. The substantial electric potential distribution across the sample area upon biasing can result in fluctuations of the resistive switching phenomena in the HfO\textsubscript{2} functional layer. To avoid this detrimental effect, a mesh of thick (~100 nm) 0.1 mm wide conductive metallic (Au, Cu) stripes with a spacing of ~0.1 mm were deposited through a shadow mask on top of the ultrathin Pt electrode. This mesh provides a uniform potential distribution across the sample area of 2x2 mm\textsuperscript{2} during biasing.

Zr 3\textit{d} and Hf 4\textit{f} core-level spectra taken from as-grown Pt/ZrO\textsubscript{x}/HfO\textsubscript{2-x}/p\textsuperscript{++}-Si functional structure are shown in Figure 1a.

\textbf{Figure 1.} Core-level Zr 3\textit{d} and Hf 4\textit{f} spectra taken from the as-grown n\textsuperscript{++}-Si/HfO\textsubscript{2-x}/ZrO\textsubscript{x}/Pt functional structure (a) and subtle changes upon resistive switching following \textit{in situ} biasing (b). The X-ray energy was set to 6.0 keV.

It can be concluded from HAXPES spectra that 4 nm thick Zr layer is partially oxidized while HfO\textsubscript{2} is reduced. By fitting the line shape of the core level spectra of both Hf and Zr, an oxide-to-
metal component intensity ratio $I_{\text{oxide}}/I_{\text{metal}} = 95\%$ for Hf 4$f$ and 32\% for Zr 3$d$ is obtained. To verify the natural assumption that the reaction occurs at the HfO$_2$/Zr interface, the spectra of deeper core level lines Zr 2$p_{3/2}$ ($E_B \approx 2220 \text{ eV}$) and Hf 3$d$ ($E_B \approx 1660 \text{ eV}$) were also recorded (spectra not shown). Due to the smaller kinetic energy and the correspondingly shorter inelastic mean free paths of the photoelectron, these spectra are more “surface sensitive”. In these cases, the curve fitting yields $I_{\text{oxide}}/I_{\text{metal}} = 96\%$ for Zr 2$p_{3/2}$ and 22\% for Hf 3$d$. By comparing $I_{\text{oxide}}/I_{\text{metal}}$ ratios it is evident that ZrO$_x$ forms at the bottom of the metallic Zr layer, while HfO$_x$ forms at the top of HfO$_2$. We conclude that Zr and HfO$_2$ react at the interface, presumably during deposition of Zr on top of HfO$_2$.

To investigate the mechanism of the resistive switching effect in these structures, we employ $\textit{in situ}$ biasing of the sample directly in the HAXPES UHV-chamber. According to previous $\textit{ex situ}$ current-voltage (I-V) measurements, it is known that as-grown Pt/ZrO$_x$/HfO$_{2-x}$/p$^{++}$-Si structure is in a low conductive state (OFF). $\textit{In situ}$ voltage sweep up to $U = 6 \text{ V}$ results in the resistivity switched to the high conductive (ON) state. The measured spectral changes in Zr 2$p_{3/2}$ and Hf 4$f$ lines for OFF and ON states are shown in Figure 1b.

In these spectra, $I_{\text{oxide}}/I_{\text{metal}}$ ratio for Zr 2$p_{3/2}$ line drops from 25 to 20\%, while for Hf 4$f$ it increases slightly from 95 to 96\%. From this analysis, it may be concluded that the switching from OFF to ON state corresponds to a thickness reduction of both the ZrO$_x$ and HfO$_x$ layers at the interface. This evolution of the interface chemistry is schematically illustrated in Figure 2. According to this model, the HfO$_2$ layer adjacent to the interface with Zr is rich in oxygen vacancies due to the initial partial oxidation (reduction) of Zr (HfO$_2$) to form ZrO$_x$ (HfO$_{2-x}$). The concentration of oxygen vacancies defines the conductivity level across the hafnium oxide layer and effectively sets the OFF state. During $\textit{in situ}$ positive biasing the positively charged oxygen vacancies are driven away from the interface effectively enriching it with oxygen and thus facilitating further oxidation of Zr. The latter process produces more oxygen vacancies in HfO$_2$ and dramatically increases the conductivity (ON state). The biasing of the opposite sign results in the reversed sequence of reduction/oxidation steps as confirmed by HAXPES (spectra not shown).

Figure 2. Schematic of the chemical evolution of the n$^{++}$-Si/HfO$_{2-x}$/ZrO$_x$/Pt stack upon resistive switching as obtained from the HAXPES analysis following $\textit{in situ}$ biasing.

In conclusion, the data on $\textit{in situ}$ biasing of Pt/ZrO$_x$/HfO$_{2-x}$/p$^{++}$-Si stacks reveal reversible changes in chemical state of Zr and Hf at Zr/HfO$_2$ interface. Based on these data, we conclude that the switching from OFF to ON states in these stacks correspond to the formation of reduced (and, hence, more conductive) layers close to the Zr/HfO$_2$ interface.

References