# Insights into defects physics for $HfO_2$-based RRAM

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Low power embedded non-volatile memory (eNVM) constitute an elementary block for the development of wireless sensor networks (WSNs), with crucial applications such as medical health care, green technology and infrastructure control. Oxide-based resistive random access memory (RRAM) is a promising technology for WSNs. RRAM consists of a Metal-Insulator-Metal (MIM) structure, which resistivity can be tuned between high (OFF) and low (ON) resistance state by the application of a voltage. A preliminary electroforming stage, using high voltage, is often required to activate resistive switching (RS). IHP focuses on RS in the CMOS compatible hafnium oxide. Previous *in-operando* HAXPES investigations performed at DESY (P09) [1-4] on Ti/$HfO_2$/TiN microstructures, pointed out the crucial role played by oxygen defects. RS relies on redox reaction at the Ti/$HfO_2$ interface, modulating the oxygen vacancy concentration. HAXPES allowed to overcome laboratory limitations by providing non-destructive measurement with tunable depth of analysis. Based on the latest results, we **pushed further the understanding of RRAM physics**, in order to lower energy consumption and improve reliability (stabilized $R_{OFF}/R_{ON}$ ratio for successive RS) of RRAM. **RS mechanism details and defects physics in engineered structures have been investigated.**

**I- RS mechanism.** Advanced materials insights in RS physics of Ti/$HfO_2$/TiN microstructures have been achieved. Device process was described elsewhere [2]. In reference [5], electrical properties of the device have been directly correlated to chemical modifications at the Ti/$HfO_2$ interface using *in-operando* HAXPES. In Figure 2(a), the $I_C/I_{Hf}$ ratio increases when using higher RS current intensity. Then, 120 RS cycles have been performed on a fresh device. The $I_C/I_{Hf}$ ratio increases when cycling the device (Figure 1(b)). Thus, segregation of carbon at the Ti/$HfO_2$ interface indicates that RS is not limited to oxygen defects, impurities may contribute. Further, the $R_{OFF}/R_{ON}$ ratio degradation responsible for RS failure has been measured after 100 cycles. Photoelectron spectra measured at the Ti/$HfO_2$ interface are currently being processed.

**II- Engineered $HfO_{2-x}$.** Defects engineering by introducing controlled amount of oxygen vacancies has been studied [6]. Stoichiometric $HfO_2$ and sub-stoechiometric $HfO_{2-x}$ were deposited on TiN using MBE. RS of the oxygen deficient films occurs at drastically reduced forming voltages close to the operating voltage, which is interesting for low-power RRAM. Figure 2 (a) and (b) compares the Hf 4*f* signals. The stoichiometric sample was fitted with a single peak attributed to the $Hf^{4+}$ oxidation state. The deficient sample was fitted with three different peaks attributed to different oxidation states: $Hf^{4+}$, sub-oxide $Hf^{x+}$ and metallic hafnium $Hf^0$. Compared to the stoichiometric film, the FWHM of the $Hf^{4+}$ increases from 1.08 eV to 1.31 eV. This increase could be due to the presence of a higher degree of disorder in the deficient films or due to the coexistence of monoclinic and tetragonal phases with small differences in the binding energy. The valence band spectra are shown in Figure 2 (c) and (d). The measurements support the existence of oxygen vacancy states overlapping to a defect band close to the Fermi level in the oxygen deficient film.

**III- Engineered Ti/$HfO_2$ interface.** Interface engineering has been achieved by tuning $HfO_2$ morphology [7]. Figure 3 compares the Ti 2*p* spectra recorded at the buried interface for Ti/a-$HfO_2$ and Ti/poly-$HfO_2$ deposited by MBE. Clearly, Ti oxidized more for a-$HfO_2$. Complementary *ab-*

*initio* simulation supported that oxygen vacancies are stabilized in Ti/a-$HfO_2$. Hence, interface engineering is an interesting method to stabilize RS.

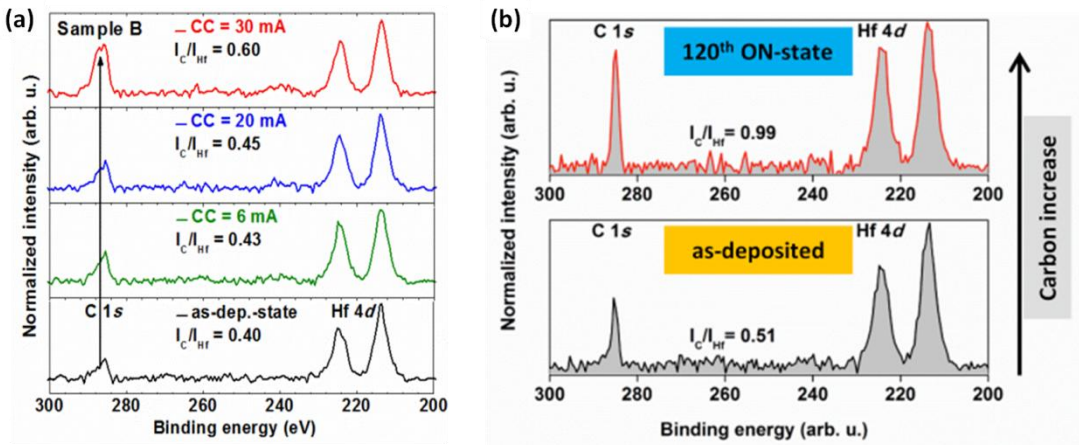


Figure 2: Normalized photoelectron spectra recorded at 8 keV at the Ti/$HfO_2$ interface: (a) as-deposited and three ON-states (CC = 6, 20 and 30 mA) ; (b) As-deposited and 120th ON-state (for CC 15 mA).

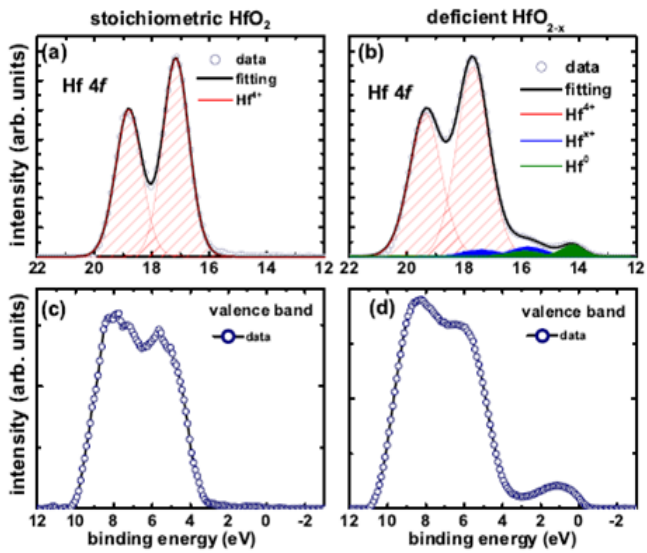


Figure 2: Hf 4*f* photoelectron spectra recorded at 8 keV for as-prepared hafnium oxide: (a) stoichiometric and (b) oxygen deficient conditions. In (c) and (d) the corresponding valence band spectra are plotted.

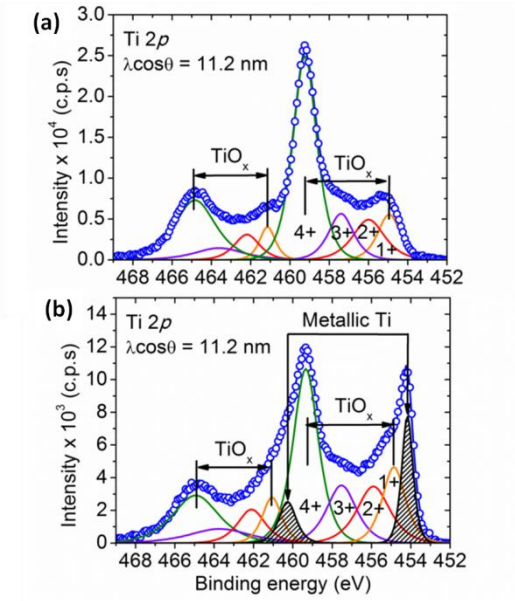


Figure 3: Ti 2*p* photoelectron spectra of Ti/$HfO_2$ for (a) a-$HfO_2$ and (b) poly-$HfO_2$.

**References**


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