

The memory effect induced by oxygen vacancies in HfO₂ based MOS stacks

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The dominating technology of present non-volatile memories is based on floating gate devices. However, to meet the requirements for lower power consumption the development of new concepts is needed. In this work, the new concept of non-volatile memory based on the charge distribution in high-k dielectrics is proposed. The mechanism utilizes changes of the flatband voltage in a metal-oxide-semiconductor (MOS) stack resulting from the spatial redistribution of electrical charges in a dielectric upon an applied bias voltage to write/erase information. The use of a high work function metal electrode in contact with a transition metal oxide based high-k dielectric (particularly, HfO₂) is shown to facilitate the formation of positively charged oxygen vacancies by transferring electric charge across the interface (Fig.1, a). The built up electric dipole layer drives the metal Fermi level up, thus decreasing its effective work function and setting the flatband condition. When a positive bias voltage is applied to the MOS stack, especially at elevated temperatures, the electric field drives charged oxygen vacancies from the upper interface to the bulk of the dielectric and the redistribution of electric charges ultimately determines the value of the flatband voltage [1] (Fig.1,b). Thereby, a memory effect is obtained when the bias voltage is applied to the moderately heated MOS stack containing charged oxygen vacancies at the metal/dielectric interface. The proposed mechanism is different from non-polar resistive switching effects in a dielectric which is observed upon biasing of metal-insulator-metal structures [2] since the latter suggests the formation of paths for the electric current which is carefully avoided in our experiments.

To test the proposed memory mechanism, ALD grown HfO₂(10 nm) based MOS structures were prepared. Al and Au, having different work functions, were used as gate electrodes to investigate the effect of initial band alignment (electric dipole) on the memory effect discussed above.

To enable heating up to T=300°C under a voltage bias, special adjustments were made to the C-V setup. The memory effect was monitored by shifts of the C-V curves. No effect was observed for Al-gated stacks as expected for a low WF metal which does not facilitate the formation of charged vacancies. However, the same treatment applied to Au/HfO₂/p-Si structures (U= ± 2 V, T=300°C) clearly results in cyclic shifts of $\Delta V_{FB} \approx 0.5$ eV.

To prove that the observed shifts in the flatband voltage are related to the redistribution of electric charge initially formed at the metal/dielectric interface, high resolution X-ray photoelectron spectroscopy was used [3]. Au(6 nm)/HfO₂(10 nm)/p-Si samples with a round Au gate electrode of 3 mm diameter, electrically split into two separated parts, were prepared (Fig.2), and only one part of the Au electrode was subjected to a (positive) bias during the heat treatment. The electronic conditions at the interfaces were analyzed utilizing the hard X-ray photoelectron spectroscopy (HAXPES) instrument at the DORIS III storage ring which enables to probe deep (10-20 nm) layers and thus provides an opportunity to directly observe changes in the charge distribution across the MOS stack with a continuous metal layer. The observed splitting of the Au 4f doublet with a separation as large as $\Delta E=1$ eV originates from the two parts of the Au electrode (biased vs. unbiased) being simultaneously illuminated by the X-ray beam (Fig.2). This result unambiguously indicates a charge redistribution from the upper interface to the bulk of the dielectric upon biasing of the Au/HfO₂/p-Si stack at elevated temperatures.

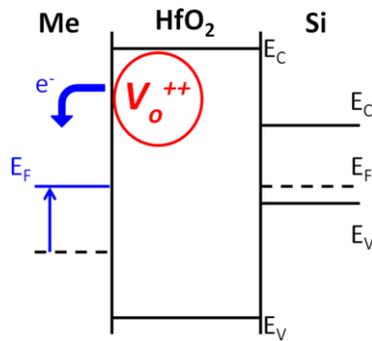


Figure 1: a) Formation of charged oxygen vacancies V_o^{++} at the Me/dielectric interface; b) schematic of flatband voltage changes due to charge redistribution upon biasing U at elevated temperatures T .

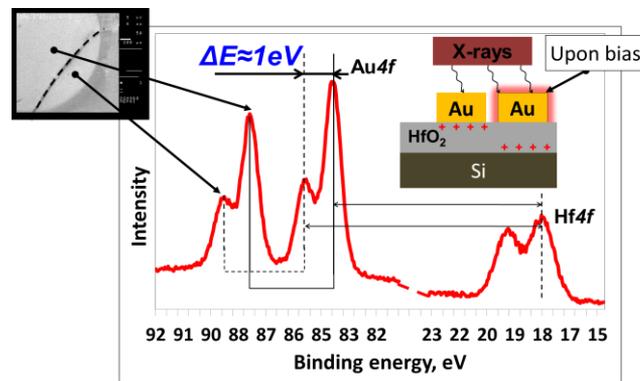


Figure 2: HAXPES at $E=4.5$ keV probing the bi-electrode Au/HfO₂/Si stack: the observed split of Au 4f doublet illustrates the redistribution of electric charge in HfO₂ from the upper to the lower interface upon ex situ biasing in combination with moderate heating.

References

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