HfO₂-based RRAM for Embedded Nonvolatile Memory: From Materials Science to Integrated 1T1R RRAM Arrays

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The Ti/HfO₂/TiN-based system is a very promising candidate for Resistance change Random Access Memory (RRAM). By combining material science studies and integration in a Si CMOS technology, we succeeded to give quantitative insight in the resistive switching mechanism and to process a 4 kbit array with 1T1R RRAM devices. In particular, *in-operando* hard X-ray photoelectron spectroscopy allows to describe the resistive switching mechanism by a push-pull model of oxygen vacancies as a function of voltage polarity. Moreover, the characterization of integrated 600×600 nm² TiN/Ti/HfO₂/TiN 1T1R devices in the pulse-induced mode and the recent realization of a 4 kbit memory array have demonstrated promising performance for embedded non-volatile memory applications.

Introduction

Low-cost embedded non-volatile memories (eNVM) with high density, high speed and low-power are attractive for applications oriented for consumers or automotive (1). Among all the alternative technologies currently investigated, Resistance change Random Access Memory (RRAM) is a very promising and worldwide studied candidate for eNVM because of the compatibility with silicon-based complementary metal-oxide-semiconductor technologies (Si CMOS) and a simple metal-insulator-metal (MIM) integration concept (2). Recently, Ti/HfO₂-based RRAM gained an increased interest and already demonstrated possibilities in terms of Si CMOS compatibility, low-power dissipation and memory block integration (3-5). However, reliability and an insufficient understanding of the resistive switching mechanism are the main challenges limiting RRAM technology development, as underlined by the International Technology Roadmap for Semiconductors (ITRS) (6). We have chosen HfO₂ as the dielectric in 2009 (7) and selected the Ti/HfO₂-based system (8,9), after the pioneer work of Lee *et al.* (10), in order to integrate a TiN/Ti/HfO₂/TiN (from top to bottom electrode) MIM stack with a transistor as the selector device for RRAM applications (5). Our work on RRAM covered an approach from materials science to system integration and focused in two directions: 1) to unveil the physics of the switching and 2) to integrate a complete memory module. Selected results on these two directions will be detailed in the following.

From materials science...

Two models of the RS mechanism are generally considered, both involving charged oxygen vacancies ($V_O^{\bullet\bullet}$) and locating the switching event at the metal-dielectric interface. The local growth and rupture of $V_O^{\bullet\bullet}$ -based nano-filaments between the bottom and top electrode (11-13) or the movement of oxygen vacancies at the metal/oxide interface induced by an electric field (14,15) can be considered as extreme cases of the same mechanism (16,17). Modern techniques are used to analyze the Ti/HfO₂ interface, suspected to be the localization of the switching event. For this purpose, non-destructive and *in-operando* hard X-ray photoelectron spectroscopy (HAXPES) investigations were recently performed on 10 nm Ti/ 14 nm HfO₂/ 112 nm TiN in order to highlight the chemical and electronic modifications induced by the resistive switching (18,19). *In-operando* HAXPES experiments were carried out at beam line P09 of the PETRA III storage ring at DESY (20). Photoelectrons were excited at 5.5 keV, 7 keV and 8 keV photon energy using a Si(311) double-crystal monochromator. More details of the sample preparation and the *modus operandi* can be found elsewhere (4,18,19). The electron inelastic mean free path at the corresponding kinetic energy of the electrons were calculated using the TPP-2M equation (21) and are equal to 8.6 nm, 10.6 nm and 11.3 nm for photoelectrons arising from the 2*p* core level metallic titanium, allowing to investigate the buried Ti/HfO₂ interface. HAXPES spectra were recorded for four different resistive states: virgin, electroformed, OFF and ON.

Figure 1. Ti 2*s* HAXPES spectra of the device in the virgin state (first two on the left) and in the electroformed state (last one on the right), recorded at excitation energies of 5.5 and 7 keV. A Shirley background and three different spectral components are shown (adapted from (18)).

The measurements indicate both chemical changes (underlined with the different Ti oxidation states) and electronic changes (with peak shifts towards higher binding energy in the order $BE^{\text{virgin}} < BE^{\text{OFF}} < BE^{\text{ON}}$ which come from modifications of the band diagram structure). We present in Fig. 1 the fitting results of the Ti 2*s* HAXPES spectra of the device in the virgin and electroformed states, at two different excitation energies. From the two spectra of the virgin-state, obtained at two different energies, one can see an increase of the TiO_x components and a decrease of the metallic Ti. This is the proof of the presence of a TiO_x interface layer between the Ti and the HfO₂, consequence of an oxygen-gettering activity of the Ti. A detailed analysis of the peak fitting shows that the electroforming process induces an increase of the Ti/HfO₂ interface oxidation (namely of

the TiO_x interface layer) by a movement of oxygen atoms towards the Ti under the positive voltage applied at the top electrode. This process creates at the same time oxygen vacancies in the HfO_2 layer. The accumulation of these n -type defects at the interface induces then an increase of the downward band bending at the Ti/ HfO_2 interface, responsible for the observed peak shifts and increasing the conduction (18). By comparing the OFF- and ON-states, the results point out the possibility to describe the resistive switching event in our Ti/ HfO_2 /TiN-based system by a push-pull model of oxygen vacancies as a function of the voltage polarity (17,19). As sketched in Fig. 2 in the middle, a positive voltage applied to the top electrode (Reset process) repels the positively charged vacancies from the interface which reduces the band bending and brings the device to the OFF-state. At the reversed polarity (Set process), oxygen vacancies are attracted which increase the band bending and brings the device to the ON-state (Fig. 2 on the right).

Figure 2. Band diagrams presenting the proposed electronic changes during the resistive switching of Ti/ HfO_2 /TiN-based RRAM devices. The used symbols are defined as: Φ_b – the conduction band offset, Φ_m – the metal work function, BE – the binding energy, E_g – the gap energy, E_F – the Fermi level, CB – the conduction band, VB – the valence band, χ – the electron affinity (adapted from (19)).

These results give an important insight in the understanding of the resistive switching mechanism, using the *in-operando* experiments. Here, non-destructive HAXPES has enabled to correlate the material properties and the electrical state of the Ti/ HfO_2 /TiN-based RRAM system.

... to integrated 1T1R RRAM arrays

Based on the model system analyzed previously, we successfully integrated $1 \times 1 \mu\text{m}^2$ and $0.6 \times 0.6 \mu\text{m}^2$ 1R (1-resistor) (4) and 1T1R (1-transistor/1-resistor) devices (5). Several electrical measurements were performed, from temperature dependence in the DC sweep mode (4) to the impact of the pulse width and amplitude in the pulsed-induced mode (5) in order to obtain reliable, fast and low-power resistive switching characteristics. Recently, a 4 kbit memory array module with the complete circuitry was processed in

IHP's Si CMOS technology. As shown in Fig. 3, the memory module is built in the following architecture: a 4 kbit memory array (based on TiN/Ti/HfO₂/TiN-based 1T1R devices), a word address decoder (connected to the gate of the select transistor), a bit address decoder (connected to the top electrode of the MIM device).

Figure 3. Photograph of the 4 kbit memory module with control circuits realized in IHP's Si CMOS technology platform.

This test structure allows us to investigate statistically the resistive switching in TiN/Ti/HfO₂/TiN-based RRAM cells. Indeed, we have recently performed better resistive switching characteristics (i.e. electroforming, reset and set) on more than 100 cells integrated in this complete memory array (22). The electroforming process, required to initiate the resistive switching behavior in the MIM cells, was prevented to pass to hard breakdown by using the intrinsic current limitation of the transistor in the 1T1R architecture. Then, as shown in Fig. 4, the resistive switching characteristics were studied by DC sweep measurements.

Figure 4. I-V characteristics of the typical reset (left) and set (right) process of 1T1R RRAM cells integrated in a 4 kbit array architecture.

Fig. 4 on the left (Fig. 4 on the right) shows the typical reset (set) curves obtained for 100 devices. The devices exhibit a good statistics that is promising for future integration of RRAM memory modules.

Summary

We have presented an innovative experiment by performing *in-operando* HAXPES studies of resistive switching memory cells. *In-operando* electrical switching experiments allow to investigate one and the same RRAM sample in different resistive states in order to correlate the material properties with the electrical state of the device. Using the Ti/HfO₂/TiN-based RRAM system, this material science study gave physical insights of the resistive switching mechanism in order to optimize the 1T1R memory point and the 4 kbit memory module.

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