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Role of Ti and Pt electrodes on resistance switching variability of HfO₂-based RRAMs

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Abstract

This paper deals with the role of platinum or titanium-titanium nitride electrodes on variability of resistive switching characteristics and electrical performances of HfO₂-based memory elements. Capacitor-like Pt/HfO₂(10nm)/Pt and Ti/HfO₂(10nm)/TiN structures were fabricated on top of a tungsten pillar bottom electrode and integrated in-between two interconnect metal lines. First, quasi-static measurements were performed to apprehend the role of electrodes on *electroforming*, *set* and *reset* operations and their corresponding switching parameters. Memory elements with Pt as top and bottom electrodes exhibited a non-polar behavior with sharp decrease of current during *reset* operation while Ti/HfO₂/TiN capacitors showed a bipolar switching behavior, with a gradual *reset*. In a second step, statistical distributions of switching parameters (voltage and resistance) were extracted from data obtained on few hundreds of capacitors. Even if the resistance in low resistive state (LRS) and *reset* voltage were found to be comparable for both types of electrodes, the progressive *reset* operation observed on samples with Ti/TiN electrodes led to a lower variability of resistance in high resistive state (HRS) and concomitantly of *set* voltage. In addition Ti-TiN electrodes enabled gaining: (i) lower *forming* and *set* voltages with significantly narrower capacitor-to-capacitor distributions; (ii) a better data retention capability (10 years at 65°C instead of 10 years at 50°C for Pt electrodes); (iii) satisfactory dynamic performances with lower *set* and *reset* voltages for ramp speed ranging from 10⁻² to 10⁷ V/s. The significant improvement of switching behavior with Ti-TiN electrodes is mainly attributed to the formation of a native interface layer between HfO₂ oxide and Ti top electrode.

1. Introduction

Regardless their NAND (data memory – dense and cheap) or NOR (code memory – fast) architecture, Flash technology is still today the undisputed reference for the non-volatile memory market and related applications. However, as downscaling and cost reduction trend for conventional floating gate memories appear ever more complicated below the 20 nm technological node, opportunities are opened for alternative concepts. Among emerging technologies, Oxide Resistive Random Access Memory (OxRRAM) appears as one of the most promising solutions for the next non-volatile memory generation. Relying on a reversible voltage-controlled resistance change between high resistive state (HRS) and low resistive state (LRS), the simple capacitor-like Metal/Insulator/Metal (MIM) structure of OxRRAM offers suitable CMOS compatibility with possible integration between two metal interconnect lines into Back-End of Line (BEOL). Besides, this technology attracts an actual interest for very high-density storage and paves the way towards multilevel tri-dimensional architectures [1]. Excellent electrical performances were already demonstrated in terms of low voltage operations [2], high programming speed [3] and long retention [4]. However, OxRRAM concept is still in its infancy compared to other technologies and the device-to-device variability of switching parameters is still a key issue for future industrialization [5]. Regarding the switchable material, several metal oxides were reported to exhibit voltage-controlled resistance change [6] and recently a growing interest was turned towards hafnium oxide HfO_2 that undergoes a bipolar resistance switching. Beside the nature of switchable metal oxide, a particular attention must be paid to electrodes that may deeply modify the electrical behavior of MIM capacitors. In this context, this paper deals with the electrical characteristics of two sets of capacitor-like structures integrating either Pt or Ti-TiN electrodes and it brings to light the role of electrodes on the switching parameters and the intrinsic capacitor-to-capacitor variability.

2. Experimental

2.1. Fabrication of capacitor-like structures

Capacitor-like MIM structures were fabricated on top of a tungsten pillar bottom plug (600 nm in diameter) connecting metal lines M1 and M2 as shown in Fig. 1. MIM capacitors consisted in a 10 nm thick HfO₂ oxide layer grown by Atomic Layer Deposition (ALD) at 350°C and sandwiched between two sputtered metallic electrodes. To apprehend the influence of electrode materials on switching characteristics, two sets of devices were fabricated with either Pt (25 nm thick) as top and bottom electrodes (namely Pt/HfO₂/Pt structures) or Ti-TiN electrodes corresponding to Ti(10 nm)/HfO₂/TiN(25 nm) structures. Memory stacks were then etched to form MIM capacitors with a typical diameter of 1 μm. Finally a TiN-covering layer was deposited over the top electrode to connect the second metal line M2. It has to be mentioned that the device architecture is called "1R" (one Resistor), since it does not integrate an access metal-oxide-semiconductor transistor.

X-ray diffraction patterns recorded on HfO₂ blanket film showed that the polycrystalline oxide layer crystallizes in a monoclinic symmetry when sandwiched with Pt electrodes while orthorhombic symmetry is favored by using Ti-TiN electrodes. Besides, composition profiles measured by either Energy Dispersive X-ray spectroscopy (EDX) [7] or X-ray Photoelectron Spectroscopy (XPS) [8] revealed the formation of an additional layer TiO_x/HfO_x at the interface Ti/HfO₂ due to oxygen-getter nature of titanium. This latter interface layer that was shown to be sub-stoichiometric in oxygen may subsequently enhance the defect-assisted conduction by acting as a reservoir of oxygen vacancies.

2.2. Electrical characterization

Quasi-static measurements were performed on capacitors to assess their electrical behavior and apprehend their switching characteristics at low voltage sweeps. Current-voltage (I-V)

characteristics were measured with a standard semiconductor parameter analyzer HP 4155 (Agilent Company) with a current compliance fixed at 1 mA for *forming* and *set* operations.

In complement, dynamic measurements were performed to evaluate the electrical performances of MIM structures submitted to voltage pulses. The dependence of switching parameters on pulse rise time was carefully studied for both *set* and *reset* operations with a pulse generator Agilent 81110A that enabled varying voltage sweeps from 10^{-2} up to 10^7 V/s.

3. Quasi-static measurements

3.1. Polarity assessment

Several *set* and *reset* cycles were applied to both sets of MIM structures to assess their electrical behavior, *i.e.* unipolar, bipolar or non-polar. Voltage was considered as positive when applied on top electrode. In agreement with results previously published by Goux *et al.* [9], the capacitors with Pt top and bottom electrodes showed a non-polar behavior: as shown on I-V characteristics in Fig. 2a, *set* operation (HRS-to-LRS) was achieved for both voltage polarities and *reset* (LRS-to-HRS) succeeded whatever the polarity (and independently of the polarity used in preceding *set* operation). In contrast, MIM capacitors with Ti-TiN electrodes systematically exhibited a bipolar behavior: as depicted in Fig. 2b, *set* operation was done only as a positive voltage was applied on top electrode and subsequent *reset* operation required the opposite polarity to switch back the memory element into a high resistance state.

Whatever the electrodes, *set* operation was achieved with a current of about 10 μ A. In contrast, non-polar and bipolar behaviors were clearly distinguished during the *reset* operation. Non-polar capacitors with Pt electrodes exhibited a *reset* with a sudden and sharp current drop towards a very high resistance state (average resistance of $4 \times 10^6 \Omega$), whereas bipolar capacitors with Ti-TiN electrodes showed a gradual *reset* with successive current jumps leading to smaller resistance in HRS ($4 \times 10^5 \Omega$). The abrupt *reset* transition for Pt electrodes is rather in favor of a thermal dissolution of conductive filaments proposed for non-

polar/unipolar devices [10-14] (requiring a high *reset* current I_{Reset} as shown in Table 1), while “multi-steps” *reset* for Ti-TiN electrodes is consistent with a field-driven migration of oxygen ions [15] with possibly a gradual variation of the local density of vacancy defects as proposed by Goux *et al.* [16]. This latter mechanism is surely strengthened by the oxygen vacancies reservoir existing within a native TiO_x/HfO_x interfacial layer [7,8] (or insert layer as shown in ref. [9]). This layer acts as respectable oxygen buffer layer during *electroforming* and exhibits low release energy of oxygen species required for *reset* operation. Note that a positive voltage applied on Ti top electrode is required to achieve *set* operation, in agreement with the field-driven movement of oxygen-vacancies ions towards TiN-Ti top ~~bottom~~ electrode that leads to the formation of conductive filaments of positively charged defects (*i.e.* oxygen vacancies) within HfO_2 layer [17,18]. A similar scenario was also proposed for Cr_2O_3 -based memories [19,20].

In the following, for clarity and for a better comparison of switching parameters, it was chosen to switch both sets of capacitors in a bipolar mode, *forming* and *set* operations being achieved with positive voltage on top electrode while *reset* state was reached by applying negative voltage.

3.2. Capacitor-to-capacitor variability for *set* and *reset* operations

Capacitor-to-capacitor variability was studied from a systematic analysis of more than 250 capacitors for each split of electrodes. Before being cycled (20 *set* and 20 *reset* operations), *electroforming* operation was done on pristine capacitors by applying a positive voltage sweep on top electrode with a current compliance fixed to 1 mA. Nevertheless, due to the very fast switching the current compliance does not avoid current overshoot occurring during *electroforming* stage. Tirano *et al.* [21] attributed this phenomenon to the discharge of a parasitic capacitance in parallel to the resistive device in this simple 1R architecture (one resistor without dedicated select device). These local transient voltage, current and

temperature [22,23] boost the motion of oxygen anions O^{2-} [24][25] and in turn favor the generation of oxygen-vacancy defects that subsequently form conductive filaments [7]. Table 1 summarizes *electroforming* voltages $V_{Forming}$ (and their error bars) measured on both sets of capacitors. The decrease of *forming* voltage for Ti/HfO₂/TiN capacitors (2 V instead of 4.3 V for Pt electrodes) was previously explained by the formation of an oxygen-vacancies-rich TiO_x/HfO_x interfacial layer at the top interface [7]. This oxygen sub-stoichiometric layer surely enhances the defect-assisted conduction and contributes to the decrease of the effective thickness of switchable oxide layer.

Beside *electroforming* stage, capacitor-to-capacitor variability was also studied for *set* and *reset* operations. A summary of corresponding switching parameters is given in Table 1. First, regarding LRS-to-HRS *reset* operations, Fig. 3a shows the cumulative capacitor-to-capacitor distribution functions of resistance in LRS (so-called *set* resistance R_{set}) for both sets of electrodes: a low variability was observed whatever the nature of electrodes. Nevertheless, capacitors with Ti-TiN electrodes exhibited a larger average resistance in *set* state of about 480 Ω instead of 120 Ω for Pt/HfO₂/Pt capacitors. This latter feature might be related to the current overshoot that occurred during *set* operation. Indeed, Ti/HfO₂/TiN capacitors exhibited a lower average *set* voltage (*cf.* Table 1) and consequently generated a lower current overshoot that led to a higher resistance in LRS [21]. In complement, Fig. 3b shows the variability of *reset* voltage V_{Reset} : unsurprisingly, since the average *set* resistances were found similar for both sets of MIM structures, *reset* voltages are subsequently close with a comparable variability as the one observed on R_{set} .

HRS-to-LRS *set* operations were also carefully analyzed. The cumulative distribution functions of *set* voltages V_{set} presented in Fig. 4a clearly show that Ti/HfO₂/TiN capacitors switched at a significantly lower voltage, typically 0.6 V instead of 2.5 V for Pt/HfO₂/Pt capacitors (*cf.* Table 1). Besides, it appears that the capacitor-to-capacitor variability was

substantially narrower for capacitors with Ti-TiN electrodes. This latter characteristic may be linked to the capacitor-to-capacitor variability observed on R_{Reset} resistance in HRS (Fig. 4b). Indeed, one can observe a clear narrowing of variability for Ti/HfO₂/TiN capacitors while Pt electrodes evidently led to a higher *reset* resistance with a significantly broader distribution. This feature matches well the two types of *reset* operations observed for either non-polar/unipolar or bipolar capacitors. As previously mentioned in section 3.1, non-polar Pt/HfO₂/Pt capacitors exhibited a very sharp current drop during *reset* operation leading to a very high resistance state. In contrast, bipolar Ti/HfO₂/TiN capacitors showed a softer and gradual *reset* operation with several current jumps (*cf.* Fig. 2b) and a resulting lower resistance in HRS. Moreover, the lower variability of R_{Reset} evidently demonstrated a better repeatability of *set* operations. Nevertheless, it should be noted that the lower resistance in HRS led to a closing of the programming window (*i.e.* R_{Reset}/R_{Set} ratio), decreasing from 8×10^5 to 7×10^2 for Pt and Ti-TiN electrodes, respectively.

To summarize, bipolar asymmetric Ti/HfO₂/TiN capacitors evidently exhibited a better repeatability revealed by a narrower capacitor-to-capacitor variability of lower *set* voltages V_{Set} and lower *reset* resistances R_{Reset} . In contrast, in agreement with previous published data [9], non-polar Pt/HfO₂/Pt capacitors showed a worse reliability evidenced by significantly broader capacitor-to-capacitor distribution functions of larger *set* voltages and higher *reset* resistances. As suggested by Goux *et al.* [9], the permeability of Pt electrode to oxygen certainly limits the switching yield and explains why asymmetric Ti/HfO₂/Ti stack exhibits better reliability performances as compared to Pt/HfO₂/Pt stack.

3.3. Data retention

Data retention was estimated by measuring the time-to-failure from either LRS or HRS state at different temperatures. Whatever the electrodes and in agreement with results published by Huang *et al.* [18], HRS state was found to be highly stable in time since no failure was

observed after 10 hours at 300°C. In contrast, LRS appeared unstable with failures detected at high temperature. To give a better insight on LRS retention capability, the time-to-failure was measured as MIM capacitors were heated at different temperatures. First successive *electroforming*, *reset* and *set* operations were performed at the testing temperature to check the capacitors functionality. Capacitors were then programmed in LRS state and their resistance was subsequently measured in time. As shown in inset of Fig. 5, the time-to-failure was determined when resistance reached 10 times the initial LRS resistance. Results for different testing temperatures are displayed in the form of an Arrhenius plot shown in Fig. 5. This latter plot is in good agreement with behavior generally observed on OxRRAM memory elements [26] and clearly demonstrates better retention capabilities for Ti/HfO₂/TiN capacitors. The extrapolation to 10 years enabled estimating 65°C as retention temperature for Ti-TiN electrodes against 50°C for Pt electrodes. Hence, Ti and TiN electrodes sandwiching HfO₂ oxide layer enable improving data retention capabilities. This improved characteristic may be related to a higher *set* resistance for Ti/HfO₂/TiN capacitors and to a smaller ~~larger~~ amount of oxygen vacancy defects that decelerates the time-dependent dissolution of conductive filaments.

4. Pulsed measurements

As shown in inset of Fig. 6a, the experimental setup associated a load resistance in series with the device under test. Applied voltage V_{Appl} and voltage across capacitor V_{Cell} were monitored during *set* and *reset* operations to determine the switching voltages V_{Set} and V_{Reset} in pulsed mode. Fig. 6a presents *set* operation achieved as Ti/HfO₂/TiN capacitor was submitted to a triangular voltage pulse. Switching was detected as a sudden variation of V_{Cell} induced by the resistance change that modifies the ratio of the voltage divider formed by load resistance and capacitor resistance.

Ramp speed dependence of *set* and *reset* voltages was measured on both sets of MIM structures (Fig. 6b). In agreement with quasi-static measurements previously described, *set* and *reset* voltages and their associated variability were shown to be significantly lower for Ti/HfO₂/TiN capacitors, with V_{Set} and $|V_{Reset}|$ below 1 V even at 10⁷ V/s (*i.e.* 0.7 V at 8×10⁶ V/s). In contrast, Pt/HfO₂/Pt capacitors exhibited higher voltages with significantly larger dispersions. Consequently, Ti-TiN electrodes incontestably enabled improving dynamic performances with *set* and *reset* operations achieved below 1 V (in absolute values). Once again, the existence of TiO_x/HfO_x interface layer may be invoked to explain the better dynamic electrical characteristics since this layer may represent an optimized trade-off between efficient oxygen confinement and low energy of oxygen release.

5. Conclusions

This paper compared switching characteristics and capacitor-to-capacitor variability of MIM structures relying on HfO₂ oxide layer sandwiched by either platinum or titanium-titanium nitride electrodes. Capacitor-like structures were deposited on top of a tungsten pillar and integrated in-between two interconnect metal lines. While Pt/HfO₂/Pt capacitors exhibited a non-polar behavior, Ti/HfO₂/TiN capacitors unambiguously showed bipolar switching. Quasi-static and dynamic measurements clearly demonstrated better performances for Ti/HfO₂/TiN capacitors: (i) lower *electroforming* and *set* voltages with significantly narrower capacitor-to-capacitor distribution functions; (ii) a improved data retention (10 years at 65°C, instead of 50°C for Pt electrodes); (iii) better dynamic electrical characteristics with lower *set* and *reset* voltages for ramp speed up to 10⁷ V/s.

The better performances of Ti/HfO₂/TiN capacitors are surely related to switching mechanisms dominated by thermal-driven oxygen movement during *electroforming/set* operations and electrochemical re-oxidation during *reset* operation. The native TiO_x/HfO_x interface layer certainly plays a predominant role in the switching mechanism by providing a

reservoir of oxygen vacancies. It acts as an oxygen buffer layer during *electroforming/set* operations and exhibits low release energy of oxygen species required for *reset* operation.

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Figure captions

Fig. 1. Schematic representation of HfO₂-based memory elements in the form of capacitor-like MIM structures integrated between two interconnect metal lines noted M1 and M2. Memory stack is deposited on top of a tungsten pillar bottom electrode.

Fig. 2. Depending on the chemical nature of electrodes sandwiching HfO₂ layer, the switching behavior is either non-polar with Pt top and bottom electrodes (a) or bipolar with Ti-TiN electrodes.

Fig. 3. Cumulative capacitor-to-capacitor distribution functions for resistance in *set* state (a) and *reset* voltage (in absolute value) (b). Distributions are given for MIM capacitors integrating either Pt (blue) or Ti-TiN (red) electrodes.

Fig. 4. Cumulative capacitor-to-capacitor distribution functions for *set* voltage (a) and resulting resistance in *reset* state (b). Distributions are given for MIM capacitors integrating either Pt (blue) or Ti-TiN (red) electrodes.

Fig. 5. Temperature-dependent Arrhenius plot of time-to-failure of LRS state for both sets of electrodes. Extrapolation to 10 years enables extracting the retention temperature (10 years retention at 65°C for MIM capacitors with Ti-TiN electrodes). Inset shows time dependent evolution of resistance that enables determining the time-to-failure corresponding to LRS-to-HRS switching.

Fig. 6. (a) Triangular waveform of applied voltage pulse V_{Appl} for dynamically measuring *set* voltage V_{Set} across Ti/HfO₂/TiN capacitor. Experimental setup is shown in inset. (b) Ramp speed dependence of *set* and *reset* voltages for the two sets of capacitors integrating either Pt electrodes (blue) or Ti-TiN electrodes (red).

Table

Table 1. Summary of switching parameters extracted on the two sets of capacitors (operations achieved in bipolar mode).

Capacitors	$V_{Forming}$	V_{Set}	V_{Reset}	R_{Set}	R_{Reset}	I_{Reset}
	[V]	[V]	[V]	[Ω]	[Ω]	[mA]
Pt/HfO ₂ /Pt	4.3 ± 0.6	2.5 ± 0.9	-0.38 ± 0.09	120	$\sim 4 \times 10^6$	4.2
Ti/HfO ₂ /TiN	2.0 ± 0.7	0.6 ± 0.4	-0.42 ± 0.06	480	$\sim 4 \times 10^5$	1.2