Resistive switching properties of atomic layer deposited ZrO_2-HfO_2 thin films

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Abstract—**In this work we study the resistive switching properties of ZrO_2-HfO_2 based Metal-Insulator-Metal (MIM) devices. We observed different intermediate states and an overall good repetitiveness, expressed in terms of DC and AC parameters. Thin films consisting of mixtures of ZrO_2 and HfO_2 were grown by atomic layer deposition (ALD) on planar Si(100) and TiN substrates by alternately applying certain amounts of constituent binary oxide growth cycles. The experimental results revealed that zirconium oxide rich films provide better resistive switching behavior than pure zirconium oxide or hafnium oxide rich layers.**

Keywords—RRAM; electrical characterization; atomic layer deposition; resistive switching

I. INTRODUCTION

In the current state of the art memory devices (RRAMs) represent a very important topic these days. They may be considered as a probable future of Non-Volatile Memories, having into account the benefits they offer. These devices have the potential to eventually replace FLASH memories, offering shorter access times, smaller cell size, good reliability and compatibility with CMOS technology. Moreover, they can be applied to artificial intelligence tasks, by means of a completely physical network which can be called neuromorphic circuit [1]. These memories are based on a resistance change in a dielectric layer (metal oxide insulator) which can be modulated by means of electric pulses. From the physical point of view, the functioning is based on the creation, grow, and partial rupture of a conductive filament, usually composed by oxygen vacancies. The set of this filament in a closed path between both electrodes of the device and the subsequent disruption establish the different resistance values in a low resistance state (LRS) or in a high resistance state (HRS). As a result, this resistive switching enables multiple intermediate states in the device. Even though this technology has yet to take an enormous leap, it has been demonstrated that the advantages eclipse the deficiencies. In this situation, the materials which may be used as the intermediate dielectric film have a great impact on the behavior of the device, and here comes the main point of this work. Atomic layer deposited ZrO_2 and HfO_2 have been objects of interest due to their several potential applications, for example in microelectronics as a memory material [2-7]. In this paper, we compare different compositions of ZrO_2 and HfO_2 to optimize the fabrication method which could lead to efficient, stable and robust devices [8].

II. EXPERIMENTAL

A. Sample preparation

Films were grown on Si(100) cleansed and etched and highly-doped conductive Si substrates covered by 10 nm thick TiN film grown by chemical vapor deposition. The films, which were deposited on TiN substrates for electrical measurements, were also supplied with Ti/Al electrodes (area 0.204 mm2) electron-beam evaporated on top of the films, with ca. 30 nm thick Ti layer in direct contact to the films. The structure to conduct electrical measurements was, from top to bottom, Al/Ti/Functional layer/TiN/Si/Al. The functional layer films (dielectric) were deposited by alternating metal and oxygen precursors in sequential ALD cycles with certain cycle ratios. The proportions tested between Zr and Hf were 10:3 and 3:10. Both samples were then compared with another pair of monolayer devices, one of them constituted by only-Zr whilst the other was only-Hf.

TABLE I. LIST OF THE DIELECTRIC FILMS USED IN THIS WORK

Cycle ratio	Thickness, nm	Hafnia content Hf/(Zr+Hf)
ZrO_2 reference film	35	0
HfO_2:ZrO_2 3:10	10	0.46
HfO_2:ZrO_2 10:3	14	0.73

B. Electrical characterization procedure

Electrical measurements were carried out by means of a semiconductor analyzer (Keithley 4200SCS), with samples put on a probe station (Cascade Microtech with Leica microscope). The bias voltage was applied on the top electrode, while the bottom electrode remained grounded. For the admittance measurements there was used a 30 mV rms-ac signal at 100 KHz over the applied dc voltage. Some of the current-voltage and admittance experiments (Fig. 1, 3 and 4) were measured by applying voltage sweeps while the memory maps experiments [9] (Fig. 2, 5 and 6) were measured by applying incremental voltage pulses and after each pulse reading the current or admittance at 0.1V or 0V, respectively. The voltage pulses had a width of 1 s, subdivided into 1 s at 0V (setup stage) and 1 s at applied voltage (hold stage).

III. RESULTS AND DISCUSSION

These devices exhibited resistive switching, with notable repetitiveness and a clear distinction between HRS and LRS. The pure ZrO_2 sample offered a wider functional window on IV measurements (Fig. 1 and 2). Nevertheless, it consumed

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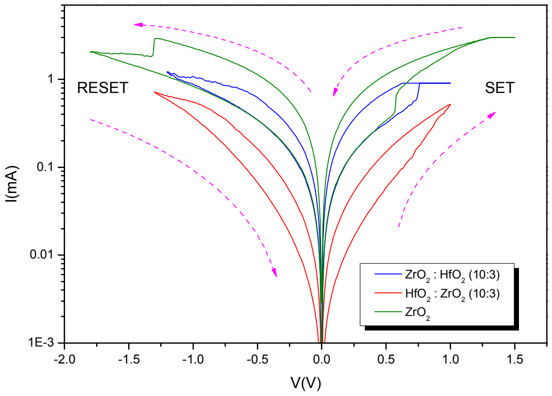

Fig. 1. Current-Voltage loops comparison of pure ZrO_2, ZrO_2:HfO_2 (10:3) and HfO_2:ZrO_2 (10:3) samples.

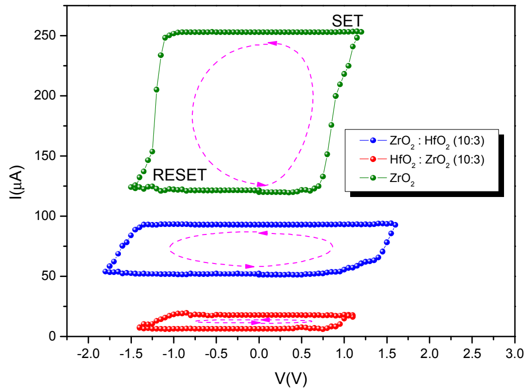

Fig. 2. IV memory map of pure ZrO_2, ZrO_2:HfO_2 (10:3) and HfO_2:ZrO_2 (10:3). These maps are obtained by reading the current at 0.1 V after applying a previous voltage V.

more power (more voltage, more current) than the doped samples. The general behavior that was confirmed on these experiments indicated a shorter window and less power consumption on the HfO_2:ZrO_2 sample grown with the cycle ratio of 10:3. This could be explained by the stabilizing effect of hafnium on the electrical response on the dielectric film. The presence of hafnium may allow a better control of the filament growth. At the same time, the ZrO_2:HfO_2 sample with the inverted cycle ratio of 10:3 increasing the effect of the zirconium, also presented similar set and reset voltages, but with an augmented current level.

Similar results were obtained when measuring the real, G, and imaginary, C, components of the admittance (Fig. 3 to 6): the functional window was clearly narrower on the hafnium-prevalent sample, while the zirconium-prevalent one occurred less stable (especially on the Reset process), although demonstrating wider distance between the HRS and LRS bands.

Regarding the results (Fig. 1), the pure zirconium sample showed a sharp reset process, with an immediate decreasing at approximately -1.3V. The other hafnium-doped samples behaved differently: they both had a progressive reset, with absence of drastic changes in the current level. Moreover, there was another difference attending to the set process in these two samples: the hafnium-prevalent one completed the set cycles in a smooth current curve, whilst the zirconium-prevalent one had a sharp increase at about +0.75V.

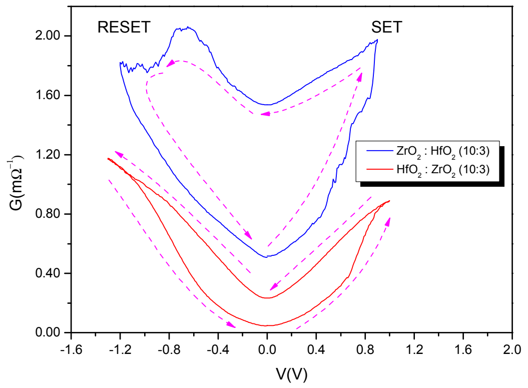

Fig. 3. Conductance vs voltage loops of ZrO_2:HfO_2 (10:3) and HfO_2:ZrO_2 (10:3) samples.

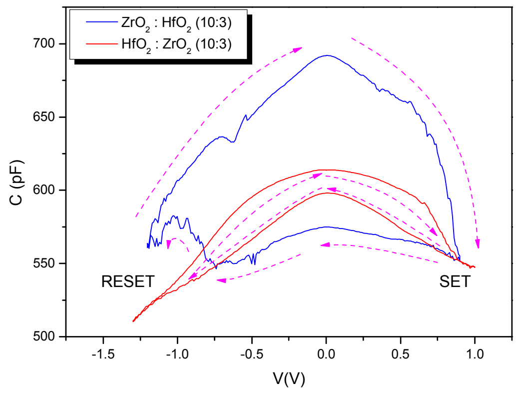

Fig. 4. Capacitance versus Voltage loops of ZrO_2:HfO_2 (10:3) and HfO_2:ZrO_2 (10:3) samples.

The presence of dopants inside the dielectric film could enable a more stable filament growing process as a result of the combination of oxygen vacancies with the impurities [7]. According to this, the filament formed by oxygen vacancies would tend to expand in a controlled path instead of spreading randomly.

There is a strange behavior in the admittance memory maps (Fig. 5 and 6): in the change from LRS to HRS, the conductance gets increased until the reset effect takes place. Correspondingly, the capacitance has the opposite behavior, also showing a reduction in its values just until the change to HRS. This could be related to the shape of the conductive filament in each state change.

The width of the HRS vs. LRS windows is clearly larger in the pure zirconium sample compared to the hafnium-doped samples (Fig. 2). As the band gap of the zirconium oxide is wider than the band gap of the hafnium oxide, this may explain this difference. In addition, (Fig.1) the width of the band gap could also give an explanation to the voltage required to change to HRS and LRS, which appears to be lower in the hafnium-doped samples with respect to the pure zirconium one.

In order to determine which combination of dopants offer the best properties to function, we made a comparison among the normalized values of conductance and current for the hafnium-doped samples. Therefore, we were looking for

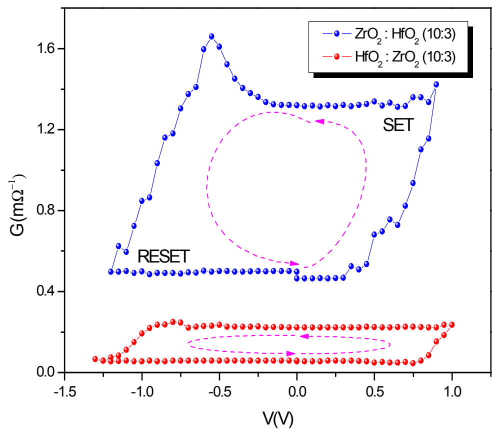

Fig. 5. GV memory maps of ZrO$_2$:HfO$_2$ (10:3) and HfO$_2$:ZrO$_2$ (10:3) samples. These maps are obtained by reading the conductance at 0 V after applying a previous voltage V.

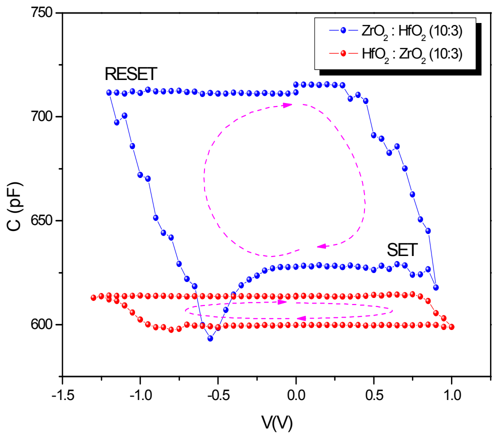

Fig. 6. CV memory map of ZrO$_2$:HfO$_2$ (10:3) and HfO$_2$:ZrO$_2$ (10:3) samples. These maps are obtained by reading the capacitance at 0 V after applying a previous voltage V.

ratio differences instead of absolute differences to assess the advantages of the dielectric with more hafnia than zirconia. As we stated before, the hafnium rich sample offered reduced power consumption by a combination of lower voltages to switch and lower currents between HRS and LRS. Also, it was much more stable than the other pair of samples. And regarding the normalized comparison (Fig. 7 and 8) we demonstrated that the "normalized window" is wider than the one corresponding to the zirconium rich sample. This is a very important difference because it implies that the power consumption is low in both reads and writes and there is no resolution loss, because the ratio between HRS and LRS is bigger than in the zirconia prevalent sample.

The zirconium oxide has been used in ReRAM researching since some years ago, because of its good stability and robustness in resistive switching computation. For this reason, an improvement in the dielectric properties using zirconium and hafnium (which is another widely used component in ReRAM layouts) could help to drive the research on these two species, given that they are perfectly suitable for its integration.

IV. CONCLUSIONS

In this work we demonstrated that the resistive switching properties of ZrO$_2$-HfO$_2$ films grown by atomic layer deposition (ALD) are noticeably influenced by the film composition. It is interesting to remark the "smoothing effect" which was the likely result of a moderate amount of hafnium added to these zirconium oxide based samples. Better results were obtained for hafnium oxide rich films compared to those for pure zirconium oxide layers or zirconium rich mixed layers.

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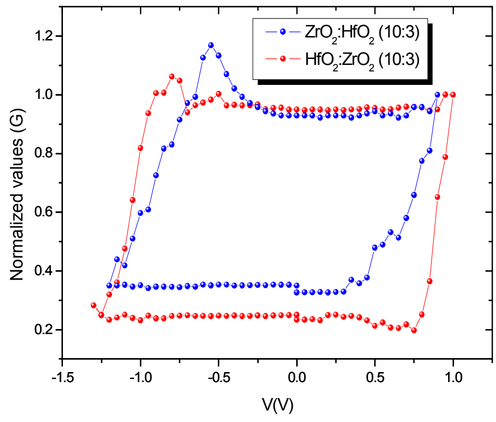

Fig. 7. Normalized values of conductance vs. voltage. There are compared the hafnium-doped samples. The conductance at ON state is considered as 1.0.

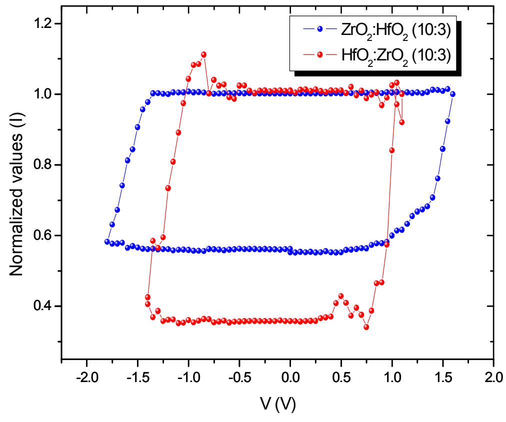

Fig. 8. Normalized values of current vs. voltage. There are compared the hafnium-doped samples. The current at ON state is considered as 1.0.

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