Total Dose Hardness of TiN/HfO$_x$/TiN Resistive Random Access Memory

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Resistive random access memory based on TiN/HfOx/TiN has been fabricated, with the stoichiometry the HfO$_x$ layer altered through control of atomic layer deposition (ALD) temperature. Sweep and pulsed electrical characteristics were extracted before and after ^{60}Co gamma irradiation. Both stoichiometric HfO$_2$ and sub-oxides HfO$_{2-x}$ result in similar memory characteristics. All devices are shown to be radiation hard up to 10Mrad(Si), independent of stoichiometry .

***Index Terms*—Atomic Layer Deposition, Hafnium Oxide, Resistive RAM, Ionizing Radiation.**

I. INTRODUCTION

RESISTIVE random access memory (RRAM) is a potential new type of non-volatile memory which offers high density, low power and a simple device structure [1]. Although the physical mechanism of resistive switching is not fully understood, it is thought to be related to oxygen defects, such as oxygen vacancies in materials such as hafnium oxide [2]. Formation and breaking of an oxygen deficient filament creates a device that can switch between a high resistance state (HRS) and a low resistance state (LRS) [3]. Many metal oxides have been shown to exhibit memory characteristics. Hafnium oxide is one of the more promising materials with many reports showing successful switching [4-7].

Semiconductor memory has intrinsic limitation on radiation hardness capability [8]. RRAM can be considered a radiation hardened memory, by design, due to its simple Metal-Insulator-Metal and thin oxide layer structure. The radiation effects however must be fully investigated before RRAM is used as replacement in nuclear and space industries.

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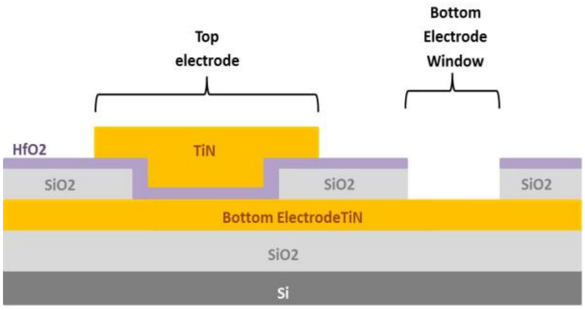

Fig. 1. Graphical representation of TiN/HfO$_x$/TiN resistive RAM device with device sizes varying from 5μm^2 to 20μm^2.

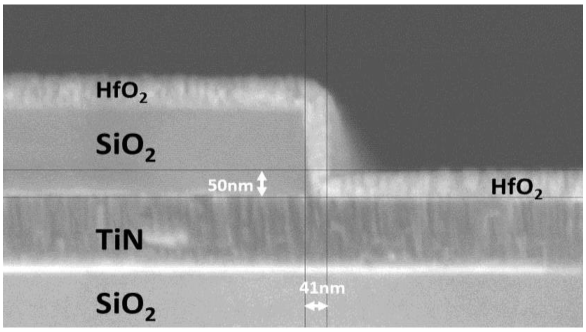

Fig. 2. SEM image of memory cell structure with hafnium oxide deposition temperature of 350^{o}C, resulting in a thickness of 50nm.

Radiation effects on hafnium oxide RRAM have been investigated, in terms of proton and heavy ion irradiation and very recently for gamma radiation [8-10]. TiN/HfOx/Pt devices were shown to be radiation hard up to 5.2Mrad(HfO2).

The irradiation of RRAM memory cells has been reported to result in additional oxygen ions and oxygen vacancies [11]. This increase in the concentration of O$_2^-$ anions is thought to lead to an increase in trapped holes at these sites, which can then result in the creation of a path for electron transport [12,13]. The oxygen concentration and movement within the oxide layer is thought to influence the switching and

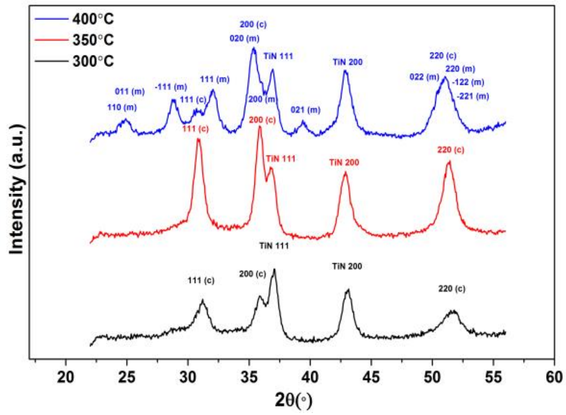

Fig. 3. XRD pattern for HfOx deposited at 300ºC, 350ºC and 400ºC. The peaks belonging to HfOx cubic structures are identified as (c) and monoclinic as (m). TiN peaks are also present due to the layer of TiN below.

TABLE I
XPS RESULTS FOR ALL DEPOSITION TEMPERATURES

ALD Deposition Temperature (ºC)	300	350	400
Hf:O (x value of HfO$_x$)	1.78±0.05	1.99±0.05	1.95±0.05

radiation response of RRAM devices.

In our work, memory cells with different stoichiometry of hafnium oxide, controlled by the temperature of the atomic layer deposition (ALD), have been fabricated, enabling the oxygen concentration effects on radiation to be studied. Thick 50nm oxides were deposited in order to ensure even small radiation effects are measureable. The responses of these cells are investigated through voltage sweep and voltage pulse electrical measurements, before and after irradiation. The deposited oxides were fully characterized before device measurements.

II. Experimental Details

TiN/HfO$_x$/TiN memory cells have been fabricated on 6inch silicon wafers using three different deposition temperatures for the hafnium oxide layer via atomic layer deposition.

A. Device Structure

The device structure, shown in Figure 1, consists of a silicon dioxide layer, providing electrical isolation from the silicon wafer below, followed by a titanium nitride bottom electrode. Both of these layers are deposited via reactive sputtering, using a Leybold Optics Helios Pro XL. Following this, another layer of silicon dioxide is sputtered, patterned and etched to create the cell areas, using photolithography and reactive ion etching. The cell areas range from 5μm^2 to 20μm^2.

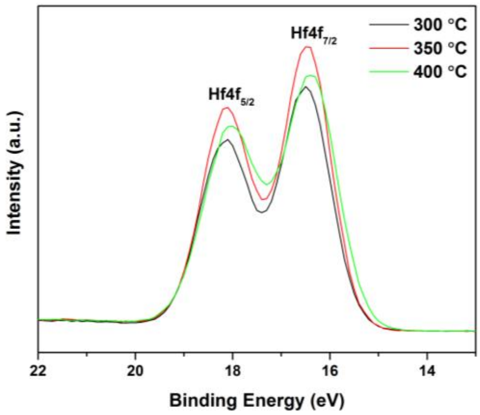

Fig. 4. XPS results showing core level spectra of Hf 4f for three different deposition temperatures of HfO$_x$

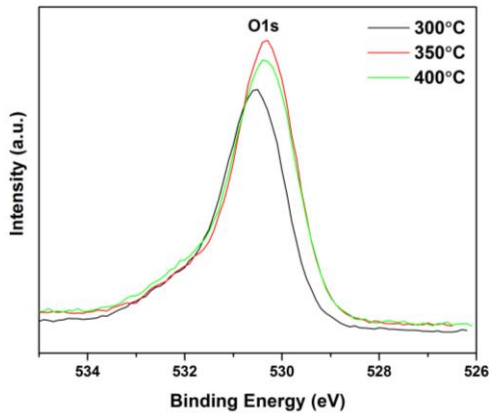

Fig. 5. XPS results showing core level spectra of O 1s for three different deposition temperatures of HfO$_x$

The hafnium oxide is deposited using an OIPT Flex ALD Tool DP03 with TEMAH and O_2 precursors. A dose time of 0.8s for 50 cycles was selected, at either 300ºC, 350ºC or 400ºC. After the hafnium oxide characterization, the top TiN electrode is reactively sputtered and patterned using reactive ion etching.

B. Material Characterization

The hafnium oxide layers are characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). These measurements were performed prior to the top electrode deposition. A SEM cross section can be seen in Figure 2 for the 350ºC cell, measured using a JEOL JSM 7500F FEGSEM. The thickness of the hafnium oxide layers is 48nm, 50nm and 63nm for the 300ºC, 350ºC and 400ºC cells, respectively.

XRD patterns were recorded in grazing incidence (ϴ1=3˚) using a Bruker D8 with GADDS diffractometer (Cu-Kα_1) for phase identification. Figure 3 shows the hafnium oxide to be cubic for the 300ºC and 350ºC deposition temperatures and monoclinic for 400ºC.

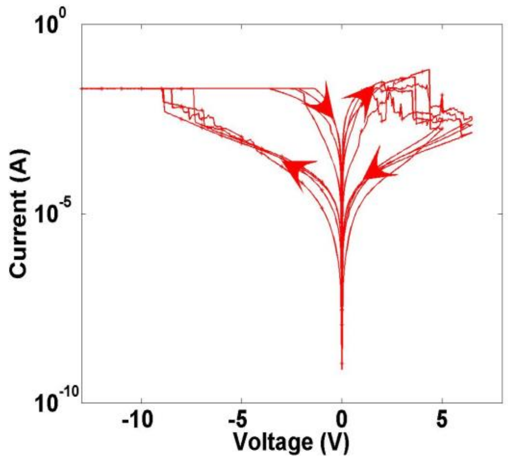

Fig. 6. IV measurement for 300°C memory cell showing reproducible voltage sweeps, before irradiation, with arrows showing direction of sweep.

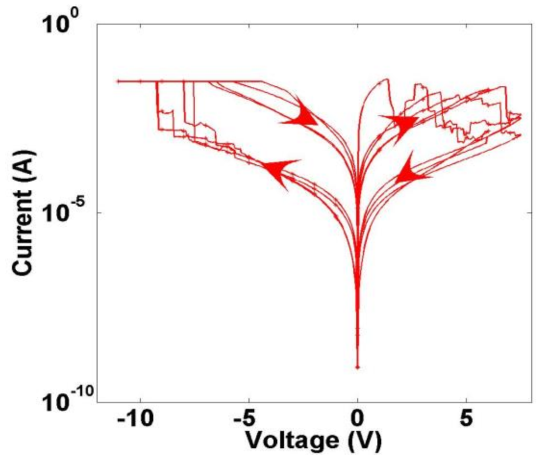

Fig. 7. IV measurement for 350°C memory cell showing bipolar switching, before irradiation, with arrows showing direction of sweep.

XPS was conducted on all hafnium oxide layers, allowing the stoichiometry of the layers to be measured, using a Thermo Scientific Theta Probe XPS system. Hf 4f, O 1s and C 1s peak energies were measured. Figure 4 shows the spectra for Hf 4f core level, whilst Figure 5 shows the spectra for the O 1s core level. It has been reported that a fully oxidized metal oxide has a lower binding energy than a sub-stoichiometric metal oxide [14,15]. Therefore, the shifting of the O1s peak towards higher binding energies, as seen for the 300ºC in Figure 5, indicates a lower oxygen concentration. The peaks were fitted using Thermo Avantage software. The ratio of hafnium to oxygen is presented in Table I, confirming the 300ºC layer is oxygen deficient.

III. Electrical Measurements Pre-Irradiation

Two types of IV measurements were used to electrically test the TiN/HfO_x/TiN memory cells before irradiation to ensure successful switching is achieved and to measure the response difference of the different stochoimetries; voltage sweep and voltage pulse. The voltage sweep results are presented first, followed by the pulse results. For each type of device, different memory sizes were measured, but as the results are very similar, only the cell size of 20µm^2 is reported here.

TABLE II
VOLTAGE SWEEP RESULTS SHOWING SWITCHING PARAMETERS - PRE IRRADIATION

ALD Deposition Temperature (ºC)	300	350
Average Vset (V)	-8.4	-8.5
Average Vreset (V)	+3.5	+5.1
Average Roff (Ω)	1.8×10^4	7.7×10^4
Average Ron (Ω)	3.5×10^2	1.5×10^3
Average Roff/Ron	50	52

A. *Voltage Sweep Measurements*

Voltage sweep measurements were conducted using a B1500A Agilent semiconductor analyzer. The cell with an atomic layer deposition temperature of 400ºC did not switch. This could be attributed to the structural change from cubic to monoclinic at this deposition temperature. The other memory cells with atomic layer deposition temperatures of 300ºC and 350ºC did switch. A current compliance of 20mA and 30mA was used for 300ºC and 350ºC cells, respectively. The forming voltage is -18V for 300ºC cell, and -17V for the 350ºC cell. Typical memory cell characteristics of two different resistance states are seen in Figure 6 and Figure 7 for the 300ºC and 350º memory cells respectively. The Roff and Ron values are shown in Table II for the presented cells, along with the Roff/Ron values. Both the on and off resistance values are similar for different sized cells. Most remarkably, the memory characteristics are similar even though one cell is sub-stoichiometric.

B. *Voltage Pulse Measurements*

Voltage pulse measurements were carried out on the cells, using a pulse width of 50ms and a current compliance of 50mA. The 300ºC and 350ºC memory cells showed successful switching with two clear resistance states, Roff and Ron, as seen in Figure 8 and Figure 9 respectively. The switching regime for the 300ºC

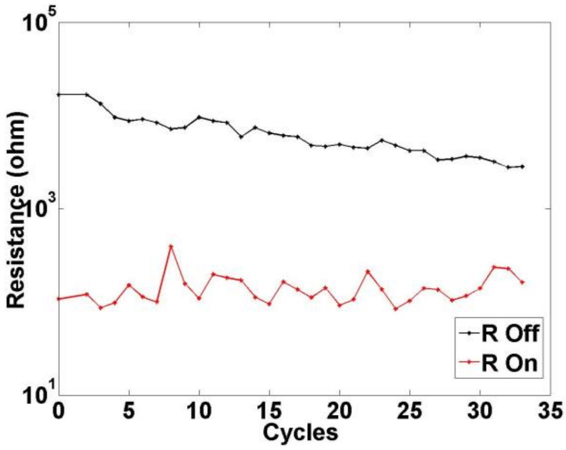

Fig 8. IV pulsed measurements for 300°C cell, before irradiation, showing up to 40 switches. Average Roff=6.5x10^{3}Ω and average Ron=1.4x10^{2}Ω.

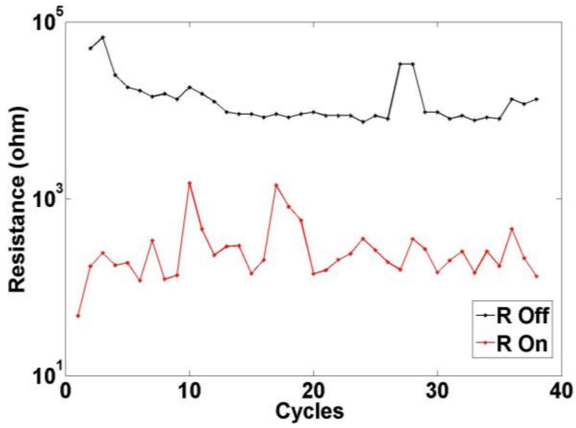

Fig 9. IV pulsed measurements for 350°C cell, before irradiation, showing up to 40 switches. Average Roff=1.5x10^{4}Ω and average Ron=3.2x10^{2}Ω.

TABLE III
PULSED SWEEP RESULTS SHOWING SWITCHING PARAMETERS – PRE IRRADIATION

ALD Deposition Temperature (ºC)	300	350
Average Roff (Ω)	6.5x10^3	1.5x10^4
Average Ron (Ω)	1.4x10^2	3.2x10^2
Average Roff/Ron	46	47

memory cell was: +2V, +4V, +6V for the reset and -10V for the set. A maximum reset voltage of 7V was used for the 350ºC with a set voltage of -12V. The resistance states were read using a +1V read. The Roff and Ron values are shown in Table III, along with the Roff/Ron ratio. Both the pulsed and sweep measurements show little difference in Roff/Ron between the 300ºC and the 350ºC cells. The insensitivity of the memory cell characteristics to the stoichiometry could be beneficial for future fabrication through the removal of stoichiometric constraints.

IV. RADIATION SETUP

The memory cells with atomic layer deposition temperatures of 300ºC and 350ºC were irradiated with a ^{60}Co source, with a dose rate of 500krad(Si)/hr. The experiment was conducted at the military defense academy in Shrivenham, UK. Both cells were subjected to 4 different doses by varying the time within the chamber; 100krad(Si), 500krad(Si), 5Mrad(Si), 10Mrad(Si). When RRAM devices are used for memory applications, the devices will spend a majority of the time in the unbiased state, retaining the Roff or Ron value. The time taken to switch, i.e. the time the device is biased, is minimal compared to the unbiased state. For this reason, the irradiation was undertaken with the memory cells in the unbiased state.

V. ELECTRICAL MEASUREMENTS POST IRRADIATION

Both voltage sweep and voltage pulsed measurements were conducted before and after the irradiation. The voltage sweep results are presented first, followed by the pulsed measurements.

A. Voltage Sweep Measurements Post Irradiation

Voltage sweep measurements were carried out before and after irradiation. For each size, the memory cell was left in three states before the irradiation; virgin, in high resistance state (HRS), and in low resistance state (LRS). After irradiation, each memory cell was measured again using up to 6 more voltage sweeps i.e. set, reset x3. At all radiation doses up to the maximum of 10Mrad(Si), no change was observed in the set voltage, reset voltage, or Roff and Ron values for any of the cells, within the margin of error. Figure 10 shows a typical 300ºC memory cell before and after irradiation using the voltage sweep technique, whilst Figure 11 shows this for a typical 350ºC memory cell. The pre and post irradiation switching parameters for the two devices can be seen in Table IV. No correlation was seen between the HRS, LRS or virgin states or cell area, before or after irradiation. The radiation hardness is the same for the 300ºC and 350ºC memory cells, independent of the different stoichiometries.

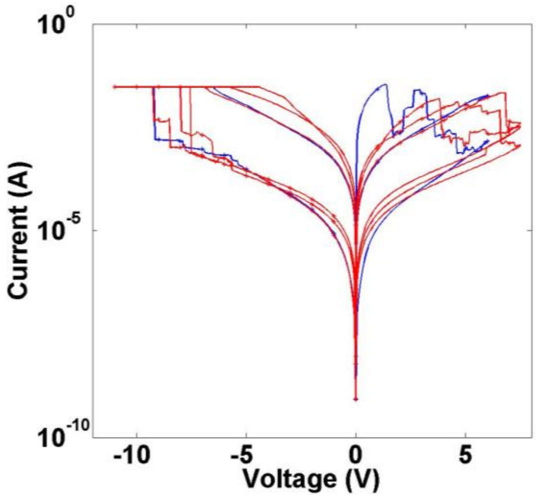

Fig. 10. Pre and post irradiation IV measurement for 300^{o}C - blue showing pre irradiation measurements, and red showing post irradiation after 10Mrad(Si).

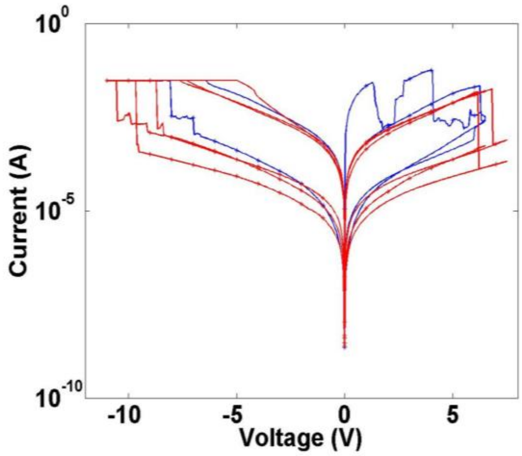

Fig. 11. Pre and post irradiation IV measurement for 350^{o}C - blue showing pre irradiation measurements, and red showing post irradiation after 10Mrad(Si).

B. Pulsed Measurements

Pulsed measurements were conducted before and after irradiation whereby the memory cells were pulsed 20 times before irradiation, followed by 20 times after irradiation. The 20 pulsed measurements before irradiation ensured that the

TABLE IV
VOLTAGE SWEEP RESULTS SHOWING SWITCHING PARAMETERS – PRE AND POST IRRADIATION 10MRAD(SI)

ALD Deposition Temperature (ºC)	300		350	
	PRE	POST	PRE	POST
Average Vset (V)	-7.7	-8.2	-8.0	-9.6
Average Vreset (V)	+3.8	+5.2	+5.2	+6.6
Average Roff (Ω)	$5.2x10^4$	$3.1x10^4$	$5.1x10^4$	$5.9x10^4$
Average Ron (Ω)	$2.4x10^3$	$2.3x10^3$	$1.4x10^3$	$1.8x10^3$
Average Roff/Ron	22	14	36	33

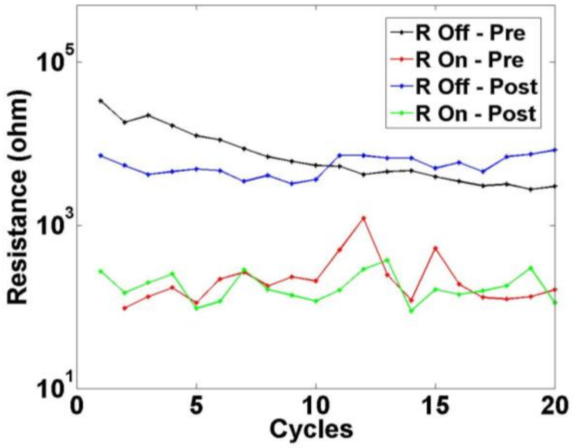

Fig. 12. Pre and post irradiation for pulsed IV measurement for 300^{o}C - after 10Mrad(Si).

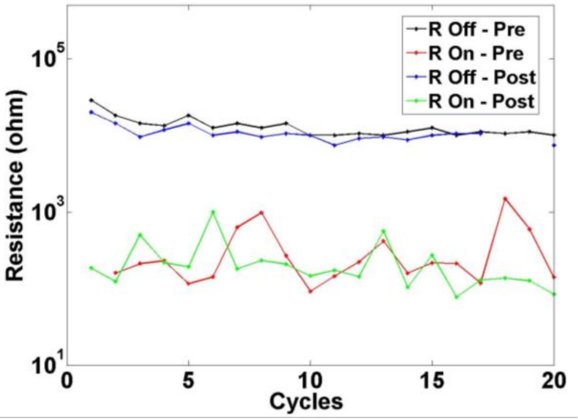

Fig. 13. Pre and post irradiation for pulsed IV measurement for 350^{o}C - after 10Mrad(Si).

effects of degradation of the OFF state were eliminated. The memory cells were left in LRS, HRS and virgin states during irradiation. Figure 12 and Figure 13 show the results for memory cells with atomic layer deposition temperatures of 300ºC and 350ºC respectively, which were irradiated to 10Mrad(Si). These cells show no change in switching parameters within the typical cycle to cycle variation. This is repeatable for all cell sizes, for all states of memory cell, with no correlation seen between areas or states. As with voltage sweep measurements, the radiation response was the same for both stoichiometries of HfO_x.

VI. CONCLUSION

TiN/HfO_x/TiN memory cells have been shown to have a high degree of hardness to gamma radiation up to 10Mrad(Si), in line with recent results of [8] on TiN/HfO_x/Pt. No radiation shift

TABLE V
VOLTAGE PULSED RESULTS SHOWING SWITCHING PARAMETERS – PRE AND POST IRRADIATION 10MRAD(SI)

ALD Deposition Temperature (ºC)	300		350	
	PRE	POST	PRE	POST
Average Roff (Ω)	$7.7x10^3$	$5.5x10^3$	$1.1x10^4$	$8.0x10^3$
Average Ron (Ω)	$2.6x10^2$	$1.8x10^2$	$3.4x10^2$	$2.2x10^2$
Average Roff/Ron	30	30	32	36

is discernible for our memory cells also, even with thicker oxides, with thick oxides being more sensitive to radiation damage. Memory cells with atomic layer deposition temperatures of 300ºC and 350ºC show similar switching characteristics pre-irradiation, with no change in post-irradiation characteristics. This shows that the hafnium oxide RRAM devices have the potential to be used in harsh radiation environments. This work has also shown that hafnium oxide resistive memories with different stoichiometries result in similar memory characteristics, which could be beneficial for repeatable memory characteristics, despite the difference in oxygen concentration, allowing for easier fabrication.

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