The Effect of Atomic Layer Deposition Temperature on Switching Properties of HfO_x Resistive RAM Devices

Katrina A. Morgan, Ruomeng Huang, Stuart Pearce, C. H. De Groot
Nano Research Group
Electronics and Computer Science, University of Southampton
Southampton, SO171BJ, UK
kam2g11@ecs.soton.ac.uk

Abstract—TiN/HfO_x/TiN resistive RAM (RRAM) devices have been fabricated where the hafnium oxide layer has been deposited at three different temperatures via atomic layer deposition (ALD). Material characterization shows the structure of the hafnium oxide is converted from cubic to monoclinic for 400 degrees C. Elemental analysis shows that the temperature affects the stoichiometric behavior of hafnium oxide, with a higher oxygen concentration at 350 degrees C and above. The switching behavior differs significantly for each device whereby the 400 degrees C device shows no successful switching, due to the change in structure to monoclinic. The two lower temperatures both show successful bipolar switching which set at negative voltages. The 300 degrees C device has a higher Roff/Ron of 13.9, with superior endurance. The 350 degrees C device has a lower Roff/Ron of 5.5 and shows deterioration in switching properties as the number of cycles are increased. At 300 degrees C, the oxygen hafnium ratio is at a minimum; hence the greatest amount of oxygen vacancies are present, which results in improved switching characteristics. This supports the theory that oxygen vacancies play a key role in the switching mechanism for metal oxide RRAM devices.

Keywords— oxygen concentration; Resistive RAM; hafnium oxide; switching mechanism

I. INTRODUCTION

Resistive RAM has the potential to become a new type of non-volatile memory, where its advantageous properties include high speed, high density memory with simple structures [1]. The switching mechanism behind this new type of memory however is still not fully understood although for metal oxide devices, oxygen vacancies are thought to play a key role [2].

Many papers have investigated the role of the electrode and insulator material types, where particular attention has been paid to the interfacial layers that form between these layers [3-5]. Other papers have also investigated the role of oxygen ions within the insulator materials, varying the amount of oxygen that is input into the chamber during deposition [6-8]. It has been seen that when oxygen vacancies are increased, the switching properties improve [5,9,10].

For HfO_x, atomic layer deposition (ALD) is often the tool of choice due to the self-limiting growth regime allowing a

uniform, stoichiometric and well controlled layer to be deposited [11-12]. When trying to alter the oxygen concentration however, an increase in oxygen flow rate does not necessarily result in an increase in oxygen due to the self-limiting growth reaction. Papers have instead reported the oxygen concentration is effected when the temperature of the sample holder is altered [13-14]. The purpose of these papers is to grow stoichiometric layers and does not include effects on device characteristics. This work will investigate how this temperature will affect the switching properties of the RRAM device. TiN/HfO_x/TiN devices have been fabricated where the table temperatures for ALD are 300°C, 350°C and 400°C. The fabrication of the devices is explained in section 2, followed by the material characterization in section 3. Section 4 discusses the I-V electrical characteristics of the RRAM devices. Finally, section 5 concludes this paper.

II. DEVICE FABRICATION

TiN/HfO_x/TiN devices were fabricated where the temperature of the HfO_x layer was varied. To fabricate the devices, silicon dioxide was reactively sputtered onto silicon wafers, providing electrical isolation between the device and wafer below, using a Leybold Optics Helios Pro XL. Following this, the bottom TiN electrode was reactively sputtered using a titanium target in nitrogen ambient. Silicon dioxide was again sputtered, followed by a photolithography and dry etching stage, creating the devices and access to the bottom electrode. Fig. 1 depicts the device structure, whereby the device area ranges from 1μm² to 100μm².

The hafnium oxide was then deposited via atomic layer deposition using an OIPT Flex ALD Tool DP03, with TEMAH and O₂ as the precursors. A dose time of 0.8s was used for 50 cycles. Three table deposition temperatures were selected; 300°C, 350°C and 400°C. After the material characterization, discussed in section 3, the top TiN electrode was deposited, followed by patterning with photolithography and dry etching.

III. MATERIAL CHARACTERISATION

The material characterization for the HfO_x layer was conducted using X-ray diffraction (XRD), scanning electron

Fig. 1. Graphical representation of TiN/HfO_x/TiN device structure where area of devices range from 1μm² to 100μm².

Fig. 2. SEM image of device structure prior to top electrode deposition, where HfO_x is deposited at 400°C. Thickness of hafnium oxide layer on device bottom is 64nm, where sidewall coverage is 37nm.

microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

A. SEM images showing thickness variation of HfO_x films

In order to measure the thickness of the hafnium oxide layer deposited, each device's cross section was measured using an SEM, before the top electrode was deposited. Fig. 2 shows a cross section of the device whose HfO_x was deposited at 400°C. The layers of each material can be seen clearly, along with the thickness of the hafnium oxide layer. Please note the HfO_x sidewall is thinner than the bottom; however this is the same for all the devices and will have little impact. It was noted that the thickness of the HfO_x layers varied with deposition temperature, where Table I shows the thickness of the HfO_x on the bottom of the device opening.

The variation in thickness can be attributed to the temperature variation, whereby ALD results in a self-limited chemical reaction which is heavily effected by many parameters, including temperature. This complex reaction will alter for each parameter change, resulting in variations in thickness, atomic concentration and structure.

Fig. 3. XRD pattern for three deposition temperatures of HfO_x whereby 400°C device (top) is shown to be monoclinic and the remaining devices are cubic

TABLE I. HfO_x THICKNESSES FOR VARIED DEPOSITION TEMPERATURES

ALD Deposition Temperature (°C)	300	350	400
Thickness at bottom electrode (nm)	48	55	63

B. XRD of HfO_x films

The crystal structure of each device was measured using XRD where patterns were collected in grazing incidence (Θ₁=3°) using a Bruker D8 with GADDS diffractometer (Cu-Kα₁) for phase identification purposes. The XRD patterns for each device are shown in Fig. 3 where the peaks have been identified as cubic HfO_x, labeled as (c), monoclinic HfO_x labeled as (m) or TiN. The TiN is present due to the HfO_x being situated on top of the bottom electrode. The 300°C and 350°C devices have a similar cubic HfO_x structure. A clear structural change is evident for the 400°C device where monoclinic HfO_x peaks are identified.

C. XPS of HfO_x films

XPS was conducted on all three devices, before the top electrode was deposited allowing the HfO_x to be analyzed, using a Thermo Scientific Theta Probe XPS system. Hf4f, O1s and C1s peak energies were measured eight times, where an argon etch was performed between the measurements, allowing for surface contamination to be reduced. The results are shown in Fig. 4 whereby the dashed lines show the atomic concentration of the oxygen and the solid lines show hafnium. Please note the carbon detected was negligible and therefore disregarded in atomic concentration calculations by the

Fig. 4. XPS results showing atomic concentration of hafnium and oxygen found in three HfO_x layers, deposited varied temperatures. 300°C can be seen to have a lower oxygen concentration when compared to higher temperatures

TABLE II. X RATIO VALUES FOR HfO_x AT VARIED DEPOSITION TEMPERATURES

ALD Deposition Temperature ($^\circ\text{C}$)	300	350	400
Hf:O – (x value of HfO_x)	1.68	1.85	1.92

TABLE III. SWITCHING PROPERTIES FOR 300 AND 350°C HfO_x DEVICES

ALD Deposition Temperature ($^\circ\text{C}$)	300	350
AVERAGE R_{ON} (Ω)	2.1k	3.5k
AVERAGE R_{OFF} (Ω)	27.0k	14.7k
AVERAGE $R_{\text{OFF}} / R_{\text{ON}}$	13.9	5.5

Avantage software. The results show that all devices are sub-stoichiometric. The 300°C can be seen to have the lowest oxygen concentration which is displayed in Table II, where the ratio of the hafnium to oxide concentration values can be seen.

IV. ELECTRICAL CHARACTERISATION

Preliminary characterization was performed on each device after the top electrode was deposited. I-V sweeps were conducted using an Agilent B1500 semiconductor analyzer system on a prober bench. All devices were found to be bipolar, where forming and set steps occurred in negative voltages and reset steps occurred when positive voltage was applied to the top electrode. Table III shows the resistance values for the on and off state along with the ratio for the 300°C and 350°C devices. Please note these values are average values taken from at least eight IV sweeps per device, over at least three devices for each temperature.

A. HfO_x deposition at 300°C

Fig. 5 Shows the I-V sweeps for an $8\mu\text{m}^2$ sized device where the HfO_x was deposited at 300°C . The I-V graphs show repeated sweeps, whereby the direction of sweep is shown with black arrows. The order of the sweeps is shown in the legend

Fig. 5. IV sweeps of an $8\mu\text{m}^2$ HfO_x device at 300°C where average switching parameters are: forming voltage = -18V , reset voltage = 4V , set voltage = -10V , $R_{\text{on}}=3.2\text{k}\Omega$, $R_{\text{off}}=39.4\text{k}\Omega$, $R_{\text{off}}/R_{\text{on}}=12.4$

Fig. 6. IV sweeps of a $6\mu\text{m}^2$ HfO_x device at 350°C where average switching parameters are: forming voltage = -17V , reset voltage = 4V , $R_{\text{on}}=2.3\text{k}\Omega$, $R_{\text{off}}=9.4\text{k}\Omega$, $R_{\text{off}}/R_{\text{on}}=4.1$

where the first sweep is labeled as number 1, followed by the second sweep labeled as 2 etc. The repeatability of the switching enabled a stable average $R_{\text{off}}/R_{\text{on}}$ ratio of 13.9 to be obtained for +10 cycles (one cycle is set followed by reset). The successful repeatable switching with the large $R_{\text{off}}/R_{\text{on}}$ ratio indicates the sub-stoichiometric HfO_x layer with lower oxygen concentration produces reliable RRAM devices.

B. HfO_x deposition at 350°C

Fig. 6 Shows the I-V sweeps for a $6\mu\text{m}^2$ sized device where the HfO_x was deposited at 350°C . The direction of the sweeps is labeled with individual arrows, where the colored arrows respond to certain sweeps as shown by the legend. The repeatability of the switching is reduced, compared to the 300°C device, in terms of set voltage stability, off resistance and $R_{\text{off}}/R_{\text{on}}$ ratio. The set voltage for this device was found to decrease as measurements continued which then resulted in a reduction in off resistance, and therefore $R_{\text{off}}/R_{\text{on}}$ ratio. The $R_{\text{off}}/R_{\text{on}}$ ratio of this device reduces as the number of cycles increased, resulting in a lower average $R_{\text{off}}/R_{\text{on}}$ value of 4.1, when compared to the 300°C devices. This reduction in ratio was also seen in $8\mu\text{m}^2$ sized 350°C devices, removing the

possibility that the switching alterations could be due to size. The material characterization showed the 350°C HfO_x layer had the same crystal structure as the 300°C device, but with an increased oxygen concentration. This implies that the increase in deposition temperature, and therefore the increase in oxygen concentration in the HfO_x layer, has reduced the switching reliability of the RRAM device.

C. HfO_x deposition at 400°C

No switching was observed for the device whose HfO_x was deposited at 400°C. The material characterization showed the oxygen concentration of the 350°C and the 400°C HfO_x layer were the same and therefore switching would be expected. However the XRD results show the crystal structure has altered from cubic to monoclinic HfO_x and therefore it can be concluded that this structural change has caused the device switching to fail.

V. CONCLUSION

This work shows how the deposition temperature used for ALD of HfO_x can affect the switching properties of TiN/HfO_x/TiN RRAM devices. It is shown that when the temperature of deposition is at 400°C, the crystal structure altered from cubic to monoclinic resulting in the inability to exhibit switching behavior. The lower temperatures show successful bipolar switching where the 300 °C HfO_x device exhibits Roff/Ron=13.9 with superior repeatability of I-V switching compared to the 350°C device. The material characterization showed that the 300°C HfO_x has lower oxygen concentration i.e. higher concentration of oxygen vacancies; this verifies the current understanding of the switching mechanism seen in metal oxides which is thought to be related to oxygen vacancies and redox-based reactions.

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