

# Resistive Switching Characteristics of Resistive Random Access Memory Devices after Furnace Annealing Processes

Chi-Yan Chu, Kai-Chi Chuang, Huang-Chung Cheng

**Abstract**—In this study, the RRAM devices with the TiN/Ti/HfO<sub>x</sub>/TiN structure were fabricated, then the electrical characteristics of the devices without annealing and after 400 °C and 500 °C of the furnace annealing (FA) temperature processes were compared. The RRAM devices after the FA's 400 °C showed the lower forming, set and reset voltages than the other devices without annealing. However, the RRAM devices after the FA's 500 °C did not show any electrical characteristics because the TiN/Ti/HfO<sub>x</sub>/TiN device was oxidized, as shown in the XPS analysis. From these results, the RRAM devices after the FA's 400 °C showed the best electrical characteristics.

**Keywords**—RRAM, furnace annealing, forming, set and reset voltages, XPS.

## I. INTRODUCTION

RECENTLY, many novel memory devices were proposed, including phase change memory (PCM) [1], magnetoresistive random access memory (MRAM) [2], ferroelectric random access memory (FeRAM) [3], and resistive random access memory (RRAM) [16]. RRAM was one of the most promising candidates of the next generation non-volatile memories because of its simple structures [7], [15], fast speed (<80 ns) [4], [6], [9], [11]-[13], [15], low power consumption [4], [6], [10], [13]-[15], high density [6], [7], [9], [10], [13]-[15], good endurance (~10<sup>6</sup> cycles) [6], [9]-[12], and reliable retention up to 10 years [13]. RRAM devices can be divided into two categories, which are metal-oxide RRAM [16] and conductive bridge RAM (CBRAM) [17]. The switching event of RRAM from high-resistance state (HRS) to low resistance state (LRS) was called set [8], while it was called reset when LRS turned to HRS. For the fresh RRAM device, a larger voltage than the set voltage is needed for the formation of conductive filament paths, which is called forming [5]. RRAM devices could be divided into two switching mode, which were unipolar and bipolar. When set and reset occur at the same voltage polarity, it was called unipolar, conversely which is called bipolar. RRAM devices usually had a current

compliance under the set processes to prevent hard breakdown, which could not have the switching phenomenon [16]. Transition metal oxides were usually used as the insulator layer for the RRAM devices. HfO<sub>2</sub>-based RRAM devices attract much attention because of the compatibility with silicon semiconductor technologies. [18]-[20]. The role of Ti was to attract the oxygen from the HfO<sub>x</sub> layer, which induced more oxygen vacancies, and so to lower the forming voltage [21]. However, inserting Ti layer was still not enough to improve the electrical characteristics of the device. Therefore, this problem needed to be solved.

In this study, the comparison of the TiN/Ti/HfO<sub>x</sub>/TiN RRAM device after different FA's temperature is investigated. It was found that the device after the FA's 400°C shows a better electrical characteristic than the device without annealing. The result showed that using FA could improve the electrical characteristics of the device. However, the device after FA's 500°C did not show any electrical characteristics. Therefore, it was important to choose an optimum annealing temperature.

## II. EXPERIMENTAL

Figs. 1 (a) and (b) are the structural and cross-section diagrams of the fabricated device. RRAM devices consisting of TiN/Ti/HfO<sub>x</sub>/TiN with the planar structure were fabricated. First, an oxidized silicon wafer with 1-μm-thick wet oxide was used as the substrate. Then a 150-nm-thick TiN layer was deposited by radio-frequency (RF) sputter as the bottom electrode. Then a 10-nm-thick HfO<sub>x</sub> layer was deposited by metal-organic chemical vapor deposition (MOCVD) as the dielectric layer. Finally, the 10-nm-thick Ti layer and the 100-nm-thick TiN layer were deposited by RF sputter on the dielectric layer as the top electrode. Then, the top electrode regions were defined by I-line stepper. After that, the devices were annealed by the FA method at 400 °C and 500 °C for 60 minutes. The X-ray photoelectron spectroscopy (XPS) analysis was also conducted to investigate the depth profile of all elements in TiN/Ti/HfO<sub>x</sub>/TiN RRAM devices. And it was clear to find that after post metal annealing (PMA) processes, the amount of oxygen vacancies was largely diffused toward the Ti interposing layer.

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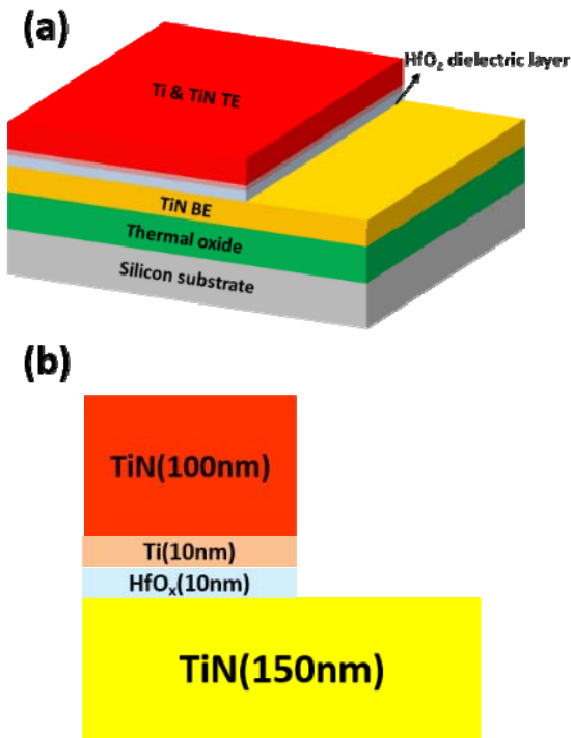


Fig. 1 The structural (a) and cross-section diagrams (b) of the TiN/Ti/HfO<sub>x</sub>/TiN RRAM device

### III. RESULTS AND DISCUSSION

In Fig. 2, the I-V curves of the TiN/Ti/HfO<sub>x</sub>/TiN devices without annealing process and after FA at 400 °C were shown. For these I-V tests, the TiN top electrode was biased while TiN bottom electrode was grounded, and the current compliances of the device without annealing and after FA at 400 °C are 300 μA and 750 μA, respectively, to prevent the hard breakdown of the device. From the results, the device showed a bipolar switching phenomenon. It also showed that the device after FA at 400 °C had a lower forming, set and reset voltages than the device without annealing. The reason was that under 400 °C annealed, more defects were formed in the HfO<sub>x</sub> layer, so Ti layer attracted more oxygen and formed a thicker TiO<sub>x</sub> layer than the device without annealing. Therefore, the filament paths in the HfO<sub>x</sub> could be easily formed. During the reset process, the thick TiO<sub>x</sub> could release more oxygen atoms back to HfO<sub>x</sub> to break the filament paths easily. Apart from this, it could be found that the initial resistance state of the forming process of the device after FA at 400 °C was lower than the one without annealing because a higher thermal budget was resulted and Ti would attract the oxygen in the HfO<sub>x</sub>, so more oxygen defects were formed and a thicker filament path was formed. Therefore, larger current could pass through and led to the lower initial resistance. As the total current of the device after FA at 400 °C was increased, a higher current compliance was needed in order to get a stable filament path and a stable resistive switching phenomenon could be obtained. However, TiN/Ti/HfO<sub>x</sub>/TiN device after FA at 500 °C for 60 minutes did not show any I-V switching phenomenon because the thermal budget was too

large so the oxygen in the surroundings dissolved into it. As a result, the RRAM device was oxidized. This will be proved by XRS analysis later.

In Fig. 3, the XPS of O1s was shown. By comparing Figs. 3 (a) and (b), it could be seen that between Ti and HfO<sub>x</sub> interface, the intensity of oxygen of (a) was higher than of (b). This proves that more defects in the HfO<sub>x</sub> were formed, so Ti could attract more oxygen, and a thicker TiO<sub>x</sub> layer was formed. Fig. 3 (c) shows almost unchanged through Ti, HfO<sub>x</sub> and TiN layers, so it means that TiN/Ti/HfO<sub>x</sub>/TiN is oxidized due to the high temperature and so cannot exhibit the switching phenomenon. Table I is summary of the three devices. It could be seen that the current compliance increased with the amounts of the oxygen vacancies. However, the relationship between the forming, set and reset voltages and the amounts of oxygen vacancies was inversely proportional.

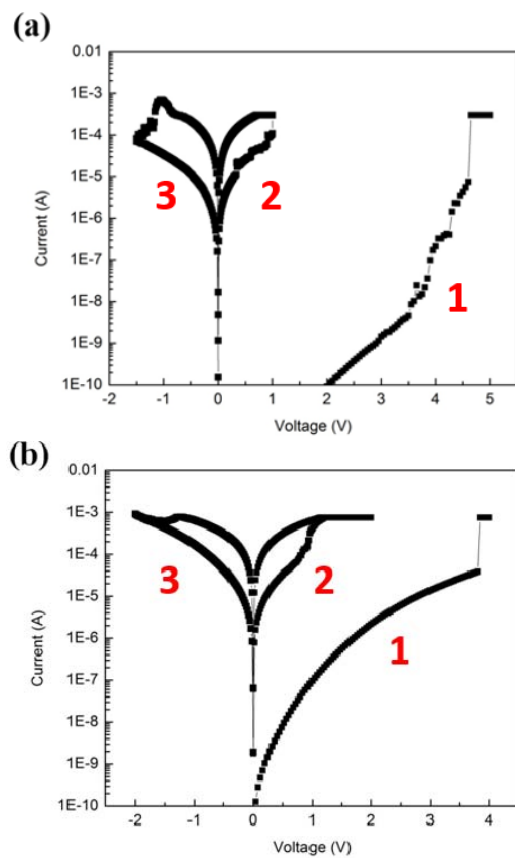


Fig. 2 TiN/Ti/HfO<sub>x</sub>/TiN device without annealing (a) and after the FA at 400 °C for 60 minutes (b). For (a) and (b), curves 1, 2, and 3 represent forming, set, and reset respectively. The forming, set, and reset voltages of (a) and (b) are 4.65 V, 1 V, and -1.28 V and 3.86, 0.89, and -1.12, respectively

TABLE I  
SUMMARY OF THE ELECTRICAL CHARACTERISTICS OF THREE DEVICES

	Current compliance ( $\mu\text{A}$ )	Forming voltage (V)	Set voltage (V)	Reset voltage (V)
RT (without annealing)	300	4.65	1	-1.28
FA at 400°C for 60 minutes	750	3.86	0.89	-1.12
FA at 500°C for 60 minutes				

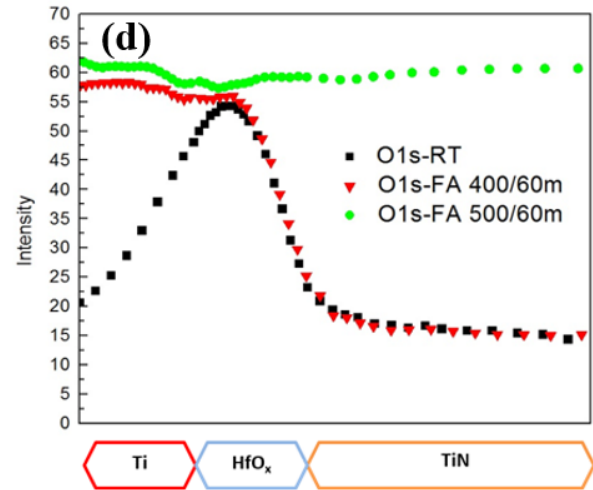
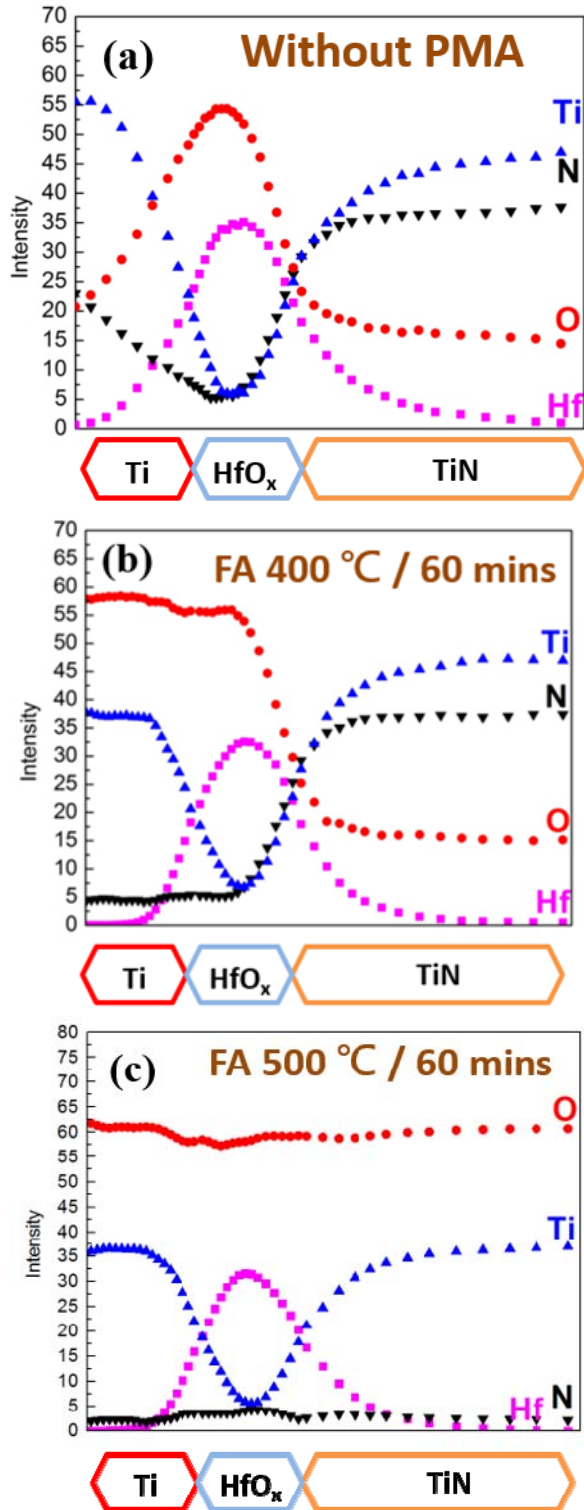


Fig. 3 XPS analysis of O1s for RT (room temperature): (a), FA at 400 °C for 60 minutes (b), 500 °C for 60 minutes (c) and the comparison of the O1s of three different RRAM devices (d)

#### IV. CONCLUSION

In summary, TiN/Ti/HfO<sub>x</sub>/TiN RRAM devices after FA at 400 °C and 500 °C temperatures for 60 minutes were reported. The devices after FA at 400 °C for 60 minutes exhibit the best performance due to the increased thermal budget in the HfO<sub>x</sub>, so more oxygen vacancies were formed. Therefore, Ti layer could attract more oxygen and formed a thicker TiO<sub>x</sub> layer. As a result, a conductive filament was easily formed and led to the result of the low forming, set and reset voltages.

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