

## Analysis of ZnO Film by Using Different Gas Flow Ratio and Annealing Temperatures During Sputtering

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*Abstract-This paper investigates the characteristics of zinc oxide films (ZnO) as RRAM using metal electrodes under various conditions. Various switching behavior and different conductive mechanism are involved. Effects of oxygen composition in ZnO films is also shown using different Ar/O<sub>2</sub> gas flow ratio, through this resistance ratio is improved that can be  $\sim 10^3$ , and the set and reset voltage is lower to 0.3V and 2.5V, respectively. This work further investigates the effect of Rapid annealing treatment on characteristics of ZnO films. The effect of annealing temperature on crystallinity and thus switching behavior is studied, adding it we will also see the leakage current behavior and conducting mechanism in low resistance state (LRS) and high resistance state (HRS) of ZnO RRAM. The RTA treated film reveals improvement in endurance up to  $10^3$  times. This exhibit reproducible resistive switching and good retention time, demonstrating their potential for low cost non volatile memory applications in the future.*

**Keywords:** Resistive switching, switching cycle, Rapid thermal annealing treatment, non-volatile memory, Zinc oxide (ZnO).

### I. INTRODUCTION

Resistive RAM has been considered as potential memory to replace the flash memory and has attracted immense amount of attention owing to its simplest structure, low power [1, 2], low cost, non-volatility and high speed. Resistance switching RAM has theoretically the smallest area  $4F^2$  ( $F$  is the feature size on a given process) [3]. Many researcher groups have investigated the RAM using various transition metal oxides (TMO) [4, 5] such as NiO, ZnO, TiO<sub>2</sub> etc. or rare earth materials. But Zinc oxide material is in use from recent years [6]. Zinc oxide material can be used as transparent conducting oxide (TCO) for solar cell applications as it has shown salient features such as high mobility, excellent environment stability and high transparency. And zinc oxide can be used for flexible electronics. For transparent and flexible electronics application zinc oxide is promising material for future application. Some researchers who have investigated the characteristics of ZnO RRAM used the expensive material as metal electrode, such as Pt, Ag and Au [7,8] come up with less switching cycles and unclear switching mechanisms drawbacks. In this work we investigate the effects of Rapid annealing treatment and different oxygen composition on resistive switching of

zinc oxide RRAM in addition, without RTA treated samples are fabricated to see difference.

### II. EXPERIMENTAL

Most of the RRAM cells have a simple capacitor-like 'MIM' structure, as shown in Fig.1, where 'M' denotes a kind of metal electrode as well as electro-conducting non-metals, and 'I' stands for an insulator or semiconductor layer sandwiched by two electrodes.

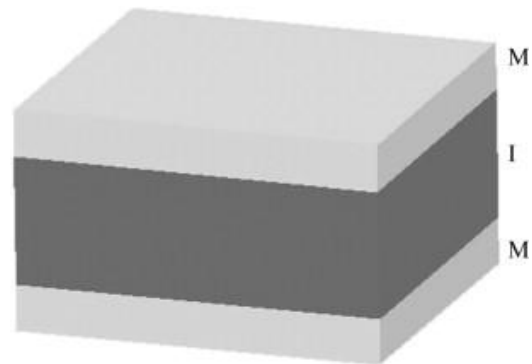
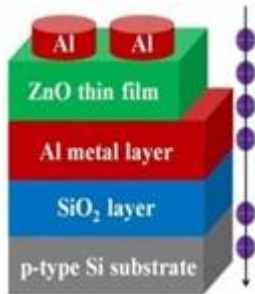


Fig.1 A Schematic Diagram Of Simple Capacitor-Like 'MIM' Structure Of A Single RRAM Cell.

The starting materials for fabrication of Al/ZnO/Al were p-type, (100)-oriented silicon wafer with resistivity of 1-10  $\Omega$ -cm. First process is RCA cleaning. RCA cleaning is a standard set of wafer cleaning steps which are needed to be performed before high temperature processing steps of silicon wafer in semiconductor manufacturing. After a RCA cleaning, a 200-nm-thick SiO<sub>2</sub> layer was grown by furnace tube; after that 200-nm thick Al bottom electrode was deposited by dc magnetron sputtering (DC magnetron sputtering is method of physical vapor deposition of thin film of one material onto another material, sputtering occurs in a vacuum chamber. Magnetrons are used in the sputtering process to control the path of the displaced atoms that fly randomly around the vacuum chamber. The chamber is filled with a low-pressure gas, frequently argon, and several high-voltage magnetron cathodes are placed behind the coating material target. High voltage flows from the magnetrons across the gas and creates high-energy plasma that strikes the coating material target. The force generated by these plasma ion strikes

causes atoms to eject from the coating material and bond with the substrate). The 60-nm-thick ZnO film was deposited by reactive magnetron sputtering using Zn target in an Ar/O<sub>2</sub> gas mixture. After ZnO film deposition, the top electrode of Al is deposited, and patterned by circular shadow mask with diameter of 150 μm. The final structure is shown in Fig.2



1. RCA Clean
2. Grown SiO<sub>2</sub> film
3. Al deposition
4. ZnO thin film deposition
5. Top metal pattern
6. Al deposition

Fig.2 Schematic of Al/ZnO/Al (MIM) and Process Step of Sample Preparation

### III. SWITCHING BEHAVIOUR

RRAM switching characteristics depends on its two types of resistance states, i.e. High resistance state (HRS) and Low resistance state (LRS), which can be switched from one to another by an appropriate electric stimulus. For a general, the operation which changes the device from HRS to LRS is ‘SET’ process and while the reverse process is ‘RESET’. According to the relationship of electric polarity between ‘SET’ and ‘RESET’ process, the switching behavior is divided into unipolar and bipolar switching as shown by I-V characteristics in Fig.3. Devices which exhibits the unipolar I-V characteristics often (not always) have symmetric structure, which means the top electrode (TE) using the same material as bottom electrode (BE). In contrast to unipolar switching the switching direction of Bipolar RAM depends on polarity of the applied voltage. The polarity of V<sub>reset</sub> is opposite to that of V<sub>set</sub>, and LRS (HRS) is not affected by the electrical signal whose polarity is identical with that of V<sub>set</sub> (V<sub>reset</sub>). The device structure of bipolar switching is usually asymmetric. Here, Initially the Al/ZnO/Al device is in high resistance state (HRS), the voltage (electric stimulus) which brings about the change in state to low resistance state (LRS) is forming voltage (V<sub>forming</sub>), similarly switching from HRS to LRS occurs at set voltage (V<sub>set</sub>) and LRS to HRS at reset voltage. The characterization was carried out using a Semiconductor parameter Analyzer 4155C. The ratio of HRS(R<sub>off</sub>) to LRS(R<sub>on</sub>) is larger than 10<sup>2</sup> at reading voltage of

1V. Compliance current of 100mA was applied to prevent permanent breakdown of the device. The compliance current was only applied for set process.

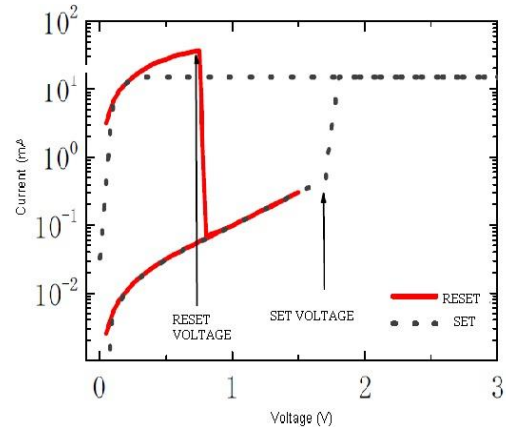


Fig.3 Set/Reset Switching Behavior

A. *Effect of different gas flow ratio on resistance ratio (HRS/LRS):* Here two Ar/O<sub>2</sub> gas mixtures were used to study the effect of oxygen composition on switching behavior of ZnO RRAM through change in Resistance ratio. One gas mixture of Ar/O<sub>2</sub> ratio is 2 (48 sccm/24 sccm) and ratio 3 (48 sccm/16 sccm) were taken. The TEM image of Al/ZnO/Al structure for both the gas flow ratio was observed, Fig 4. The thickness of ZnO film is around 71.4 nm, zinc oxide grain was observed. Same thickness was observed for ZnO RRAM with gas flow ratio 3. The surface morphology of ZnO RRAM with different gas flow ratio is shown in fig.5. Different gas flow ratio will affect the crystalline phase of ZnO film.

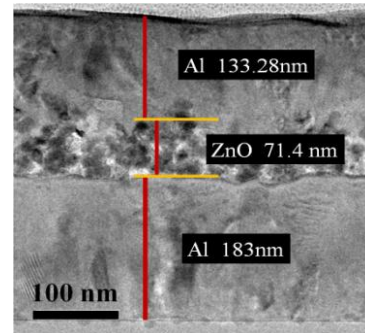


Fig 4 TEM Image for ZnO Film Deposited in Ar/O<sub>2</sub> Gas Ratio 2

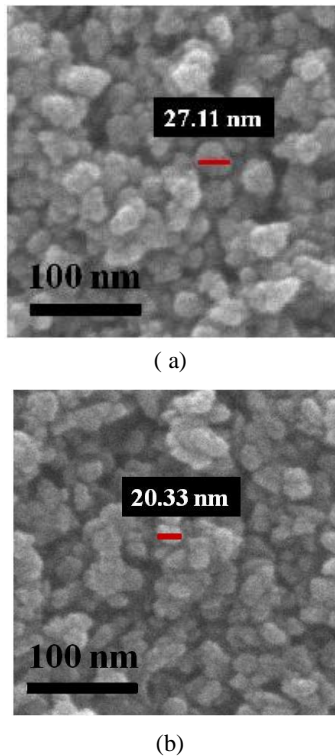


Fig 5-SEM Plane View Image for ZnO Film Deposited for Gas Flow Ratio of a) 2 and b) 3.

The current versus voltage characteristic of ZnO resistive RAM. The reset voltage with Ar/O<sub>2</sub> ratio of 2 is around 0.5V and the set voltage is around 2 and resistance ratio of HRS to LRS is up to 10<sup>6</sup> orders in fig-6. This is superior characteristics compared with other literatures [10, 11]. The larger Ar/O<sub>2</sub> results larger set and reset voltage and larger resistance ratio of HRS/LRS and lower leakage current as well.

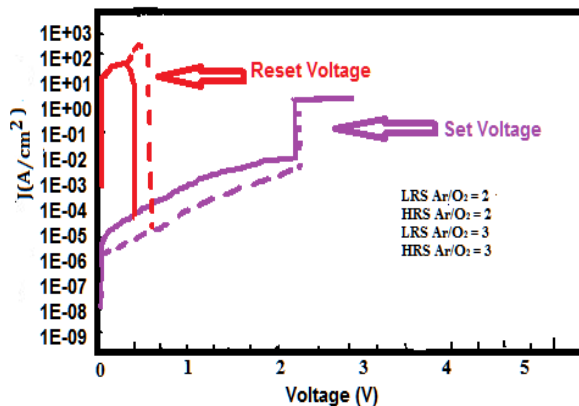


Fig:6 (J-V) Characteristics at Different Ar/O<sub>2</sub> Gas Flow Ratio.

On the other hand, the endurance of ZnO RRAM is 221 and 27 switching cycles for Ar/O<sub>2</sub> gas flow ratio of 2 and 3. Smaller Ar/O<sub>2</sub> gas flow ratio (larger oxygen composition) reveals better endurance. The resistance ratio of HRS/LRS is in the range 10<sup>2</sup> to 10<sup>10</sup>. The stability of LRD is better than that of HRS. Fig-7 shows the retention characteristic of ZnO RAM with 0.1V constant voltage stress. The retention of ZnO RRAM maintains superior performance up to 10<sup>4</sup> s.

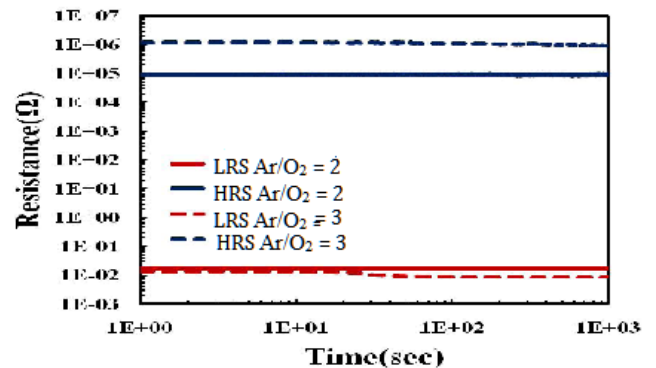


Fig-7 Retention Characteristic of HRS and LRS of Al/ZnO/Al RRAM in Reading Voltage 0.1V.

**B. Effect of Rapid thermal annealing on switching characteristics:** During sample preparation, after ZnO film deposition, the samples were introduced into a rapid thermal annealing in nitrogen ambient at 450°C for 2 min. After RTA treatment, the top electrode Al is deposited by dc magnetron sputtering as explained above. The thickness of ZnO thin film in Al/ZnO/Al structure of RRAM was observed by TEM image. The thickness of ZnO thin film is same with and without thermal annealing treatment but the grain size of ZnO film with 450°C is larger than that without thermal annealing treatment (grain size is about 30nm vs. 27nm). The RTA annealing will affect the crystalline phase of ZnO film, the reset voltage is around 0.5 and set voltage is around 2V. Fig 8 shows the current vs. voltage characteristic of ZnO RRAM. For ZnO RRAM without RTA treatment, the reset voltage is around 0.5V and the set voltage is around 2.5V. For RRAM in negative bias operation, the I-V characteristic reveals similar behavior (not shown). The resistance ratio of HRS to LRS is up to 10<sup>6</sup> orders. For annealed films it results in larger set voltage (2.6V) and smaller reset voltage (0.3V) and higher resistance ratio of 10<sup>9</sup> orders approx. and lower leakage current. The RTA treatment improves the film properties as well as the distribution of the oxygen vacancies in ZnO film. More crystalline phases are beneficial to improve the HRS/LRS

ratio. The grain size which is inversely proportional to degree of crystalline ordering becomes larger as annealing temperature increases. The HRS current can be explained by Poole-Frenkel emissions or by hopping conduction [10]. In both theories oxygen vacancies are a dominant factor of the current transport mechanism in the HRS. Oxygen vacancies act as electron traps according to Poole-Frenkel or as electron hopping site according to hopping conduction theory. In addition, the filament model suggest that filaments are composed of defects such as oxygen vacancies or metal ions [11,12]. When oxygen vacancies are formed and accumulated around the grain boundaries, the conductive filament follow the grain boundaries and then make conductive paths. As there are fewer grain boundaries that can potentially become conductive paths in film with the higher degree of crystallinity, the current paths can be reduced in the HRS with the increase in annealing temperature. In this only  $R_{off}$  (HRS) was significantly affected by the annealing temperature  $R_{off}$  increases as anneal temperature increases but  $R_{on}$ ,  $V_{set}$  and  $V_{reset}$  did not change with changes in anneal temperature.

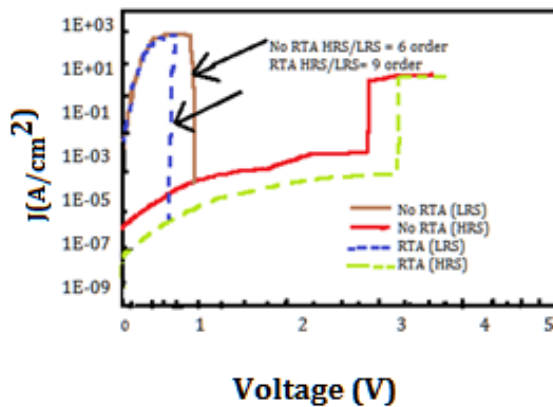


Fig 8 : ZnO Analysis With and Without RTA Treatment

#### IV. CONCLUSION

To conclude, For the characteristics of different oxygen composition in ZnO RRAM, the gas flow ratio 2 is better than that of 3, and switching cycles is up to 220 times, the investigation results in higher resistance ration and low set reset voltage with inexpensive metal electrode. In  $N_2$  RTA treatment the resistance ratio was also studied for the ZnO film, the resistance ratio is increased to  $10^9$ , even more in specific ambient conditions and set, reset voltage lower down to 0.3V and 2.4V respectively, further the  $N_2$

RTA treatment improves the switching cycle up to thousand times.

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