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Effect of Top Electrode Materials on Switching Characteristics and Endurance Properties of Zinc Oxide Based RRAM Device

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This work reports the effect of top electrode materials, i.e., Al, Ag, and Ti on the switching characteristics of resistive random access memory (RRAM) devices based on zinc oxide (ZnO) thin film. The RRAM devices with Si/Pt/Ti/ZnO/Top electrode (Al or Ag or Ti) structure were successfully fabricated, and their switching characteristics were measured. The structural properties of ZnO metal oxide thin film were studied using X-ray diffractometer (XRD), atomic force microscopy (AFM) and scanning electron microscope (SEM). The switching characteristics of the fabricated devices were measured with the help of *I-V* curves, which were measured using semiconductor parameter analyzer. It has been observed that the manufactured devices have exhibited bipolar properties. The Si/Pt/Ti/ZnO/Ag structure has shown the best endurance up to 10^3 cycles. Further, the measurement of retention properties at room temperature was also done for Si/Pt/Ti/ZnO/Ag structured device, which confirms the non-volatile properties of the obtained devices. The ratio of low resistance state (LRS) and high resistance state (HRS) was found maximum for Ag top electrode up to 10^2. It has been observed that LRS and HRS currents of the device do not degrade up to 10^4 s.

Keywords: RRAM, Switching characteristics, Top electrode, ZnO.

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1. INTRODUCTION

Due to the recent advancements in CMOS and other semiconductor devices, semiconductor memories are in huge demand. The memory occupies a significant portion in an IC, so it should be smaller in size, power efficient and stable. Due to the scaling in CMOS technology, the size of these conventional memories is reducing and now has reached a saturation point. The scaling has also increased the leakage power in CMOS circuits. To overcome the limitations of traditional memories and to bring advancement in new technologies like IoT and big data applications, the memories should be dense, power efficient and robust [1]. Existing non-volatile memory technologies like flash memories are charge storing memories and have now reached its physical limits [2]. Hence, nanoscale memories, which do not work on charge storing like FeRAM, MRAM, PCRAM, and RRAM, have drawn a significant interest of researchers for future non-volatile memories [3-6]. RRAM is a potential candidate for future memories due to its modest components, extraordinary compactness, low power, and exceptional scalability [7]. The device structure of RRAM is a capacitor like configuration with a metal-insulator-metal (M-I-M) structure. It is observed that the resistive switching occurring in the M-I-M structure can be changed by an electrical signal applied to it [8]. Recent reports on memory arrays are focused on the metal oxide-based RRAM due to the ease of the materials and exceptional compatibility with the fabrication procedure of CMOS.

The working principle of RRAM is established on the reversible resistive switching RS mechanism between two stable resistance states, which are low resistance state (LRS) and high resistance state (HRS). This reversible switching happens in transition metal oxides with the M-I-M configuration. There are two types of switching memories related to electrical polarity i.e. unipolar and bipolar [9]. The process, which brings variation in the resistance states of the device, i.e., from HRS to LRS is called SET process, while the variation from LRS to HRS is known as RESET process. An explicit resistive state (HRS or LRS) can be reserved after the cancellation of electric stress that specifies the non-volatile nature of RRAM. Generally, in the initial resistance state of a fresh sample, a higher voltage (more than the set voltage) is required to initiate the resistive switching behavior. This process is known as forming/electroforming process.

The mechanism of switching in the unipolar RRAM device is described as the formation of conductive filament when voltage is applied, which sets the device into a LRS. The Joule heating produced is responsible for rupture back to HRS. The polarity of the applied current does not affect the Joule heating effect, but its amplitude does. This type of devices shows unipolar switching behavior. Since switching direction is dependent on the applied voltage polarity in a bipolar RRAM, different polarity is used for erasing and writing the data. To circumvent the dielectric breakdown in every switching

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mode, we need to implement set compliance, which is being supplied by the semiconductor parameter analyzer or series resistor or memory cell transistor. A small voltage is required for data reading from the memory cell and it does not affect the memory cell to sense whether the cell is in LRS or HRS [5, 10, 11].

The mechanism of resistive RAM devices can be divided into two categories: (i) metal cation based and (ii) oxygen anion based. The top and bottom electrode materials are selected on the basis of their work function and chemical reactivity. In cation based devices, electrochemically active top electrode material such as Ag, Ti, Cu etc. [12, 13] are chosen, while electrochemically inert materials such as Pt, Au etc. [14, 15] are chosen as a bottom electrode material. In this paper, authors have reported the effect of top electrode material on the switching characteristics of designed ZnO based RRAM.

2. EXPERIMENTAL DETAILS

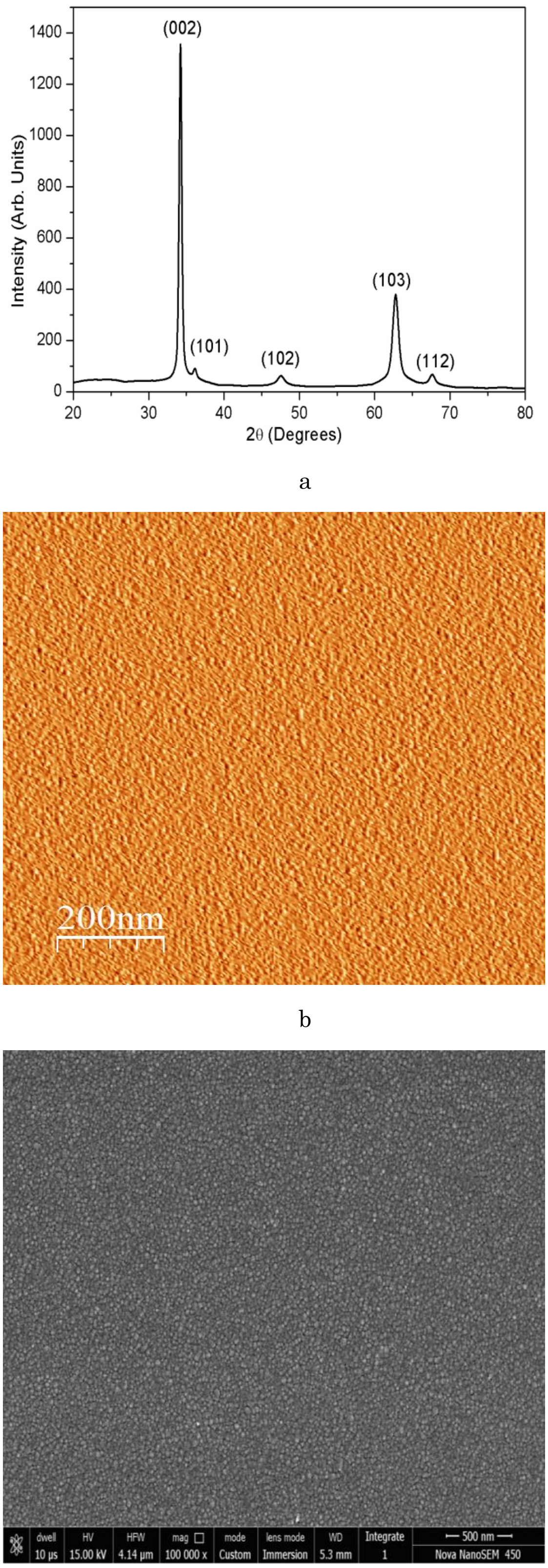
The standard RCA cleaning method was used to clean *p*-type Si (100) substrate for device fabrication. After cleaning of silicon wafers, wet oxidation was done to grow SiO_2 layer of 100 nm thickness on Si substrates to avoid the flow of the leakage current. Bottom contacts of Ti (50 nm) and Pt (20 nm), respectively, were deposited at room temperature using e-beam evaporation technique. The ZnO thin film with a thickness of 20 nm was also deposited at room temperature using an RF magnetron sputtering method. Finally, different top electrodes of Ag, Al, and Ti (20 nm) were deposited using e-beam evaporation method for different devices. The crystallographic and surface morphological properties of metal oxide ZnO thin films were measured using XRD (PANalytical X'Pert Pro- 18-kW Cu X-ray diffractometer with CuKα radiation ($\lambda = 1.542$ Å) and AFM (Multimode 8 SPM, Bruker) respectively. The switching characteristics of all the devices were studied using B1500A Agilent semiconductor parameter analyzer.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization

Fig. 1 shows the XRD pattern, atomic force microscopy image and scanning electron microscopy image of ZnO thin film deposited on bottom contact.

XRD pattern reveals the polycrystalline nature of ZnO with dominant *c*-axis (002) plane observed at 34.44°. Additional low-intensity peaks observed at 36.24°, 47.69°, 62.96°, 68.08° correspond to (101), (102) (103) and (112) planes respectively. The lattice parameters along (002) plane were found to be $a = b = 3.004$ Å and $c = 5.203$ Å respectively, which are in agreement with JCPDS data (36-1451) for ZnO [16]. The crystallite size along (002) plane was obtained using Scherrer's formula [17] and was found to be around 36 nm. Fig. 1b shows two-dimensional AFM image of deposited ZnO thin film for an area of 1×1 μm². The RMS roughness for the deposited ZnO film was found at 2.45 nm.



a

b

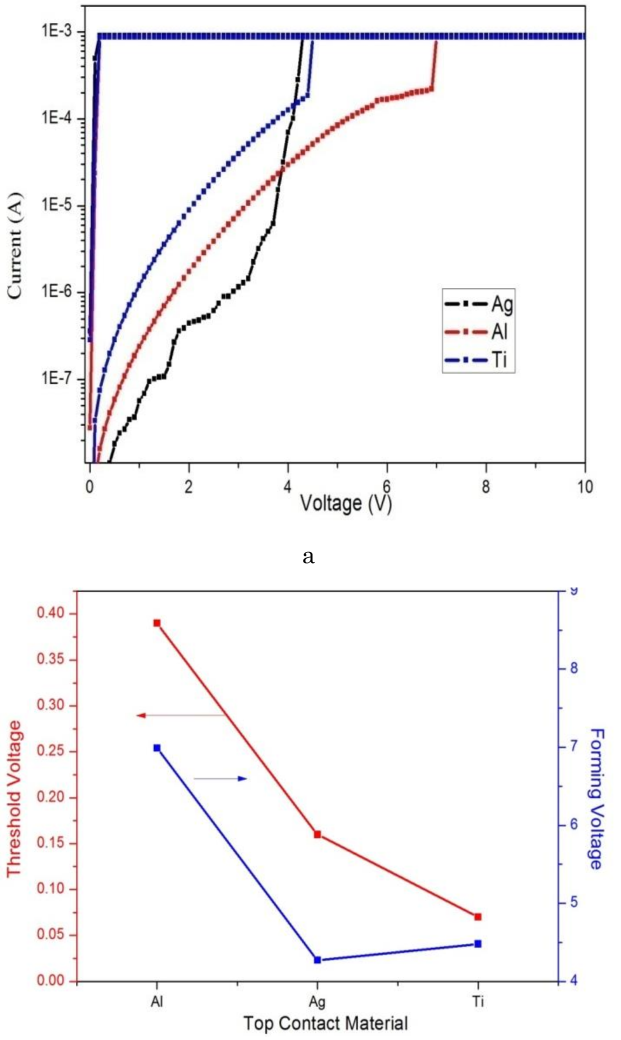
c

Fig. 1 – XRD pattern of ZnO thin film (a), surface roughness of ZnO thin film using AFM (b), surface morphology of ZnO thin film using FESEM (c)

Fig. 1c shows the FESEM image of ZnO thin film with 100-kX magnification. It is clearly depicted from FESEM image that the surface of the deposited ZnO thin film is uniform, smooth, and crack free.

3.2 Switching Characteristics

The *I-V* characteristic curves of the designed RRAM devices are shown in Fig. 2a.



a

b

Fig. 2 – The *I-V* characteristic curves of the designed RRAM devices with different top electrode material (a), the variation of forming voltage and threshold voltage with top electrode material (b)

The compliance current was taken as 5 mA for all the measurements. It has been observed that all the devices with different top electrode materials have exhibited bipolar switching characteristics. A sudden increase in current is known as the forming process and it is the main characteristic of the device. Fig. 2b shows the variation of forming voltage with a top electrode material, which is justified with its work function values. It is clearly seen from Fig. 3b that the forming voltage and threshold voltage vary with the change of the top contact material. It also confirms that the top electrode material plays an important role in device performance. If the device has a higher forming voltage that means it will require higher power to get ready for working mode. From this point of view, Al contact is better as compared to other materials studied here.

Fig. 3 illustrates the characteristic bipolar switching process of the devices with different top electrode materials.

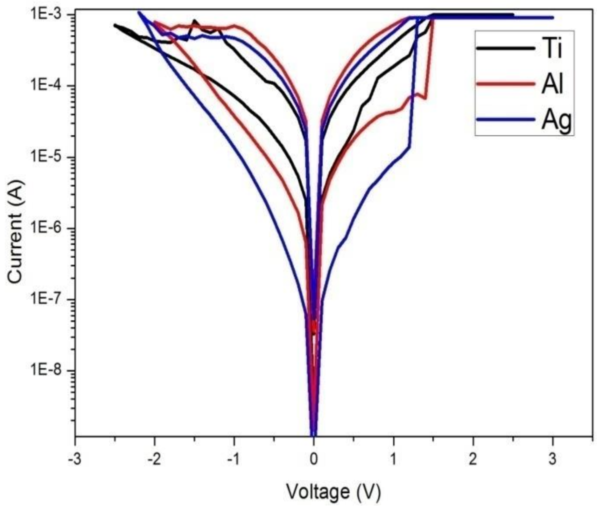


Fig. 3 – The typical bipolar resistive switching process of the devices with different top electrode materials

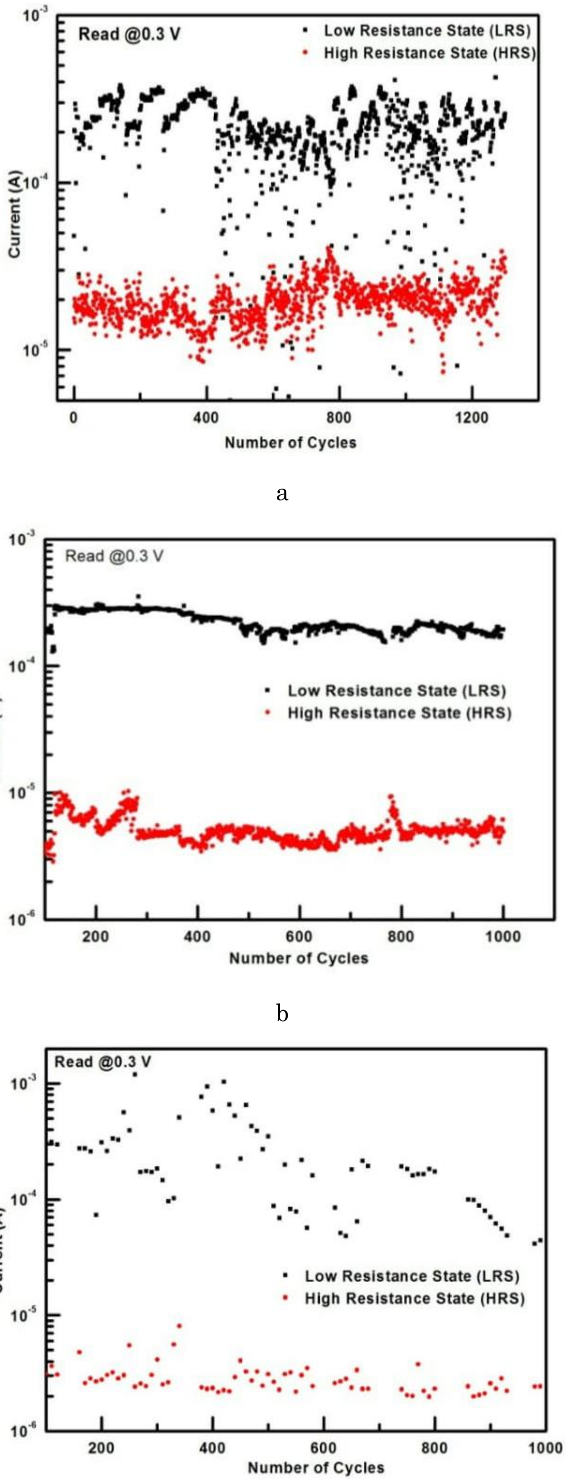
As we increase the forward voltage, the devices show the LRS, which is called ON state/SET state. As we apply the reverse bias voltage, the device switches to HRS, which is called OFF state/RESET state. In addition to this, for the measurement of conduction and switching mechanism between LRS and HRS of the devices, the *I-V* characteristic curves in log-log scale were plotted. The curves were fitted for the positive region, and it has been observed that LRS is dominated by ohmic conduction mechanism. On the other hand, HRS is dominated by space charge limited conduction mechanism (SCLC). Fig. 4 demonstrates the effect of the read/write cycle on LRS and HRS.

It has been observed that the fabricated devices perform well without any degradation up to $1.5 \cdot 10^3$ cycles. Also, the device with Ag top gives better discrimination in LRS and HRS, which will give the better accuracy of reading and writing data. So, for further study of the device we have taken only Ag as top electrode material. The non-volatile nature of data storage for Si/Pt/Ti/ZnO/Ag device is verified by the measurement of retention test at room temperature. From Fig. 5 it has been seen that both HRS and LRS do not show any degradation up to 10^4 s. Hence, the device may be used more than 10^4 s without any degradation. To investigate the current transport mechanism of the Si/Ti/Pt/ZnO/Ag device structure, temperature dependent electrical conductivity (from 300 K to 450 K) was measured as shown in Fig. 6.

It is evident that LRS current is constant throughout the temperature range, and consequently shows a metallic ohmic behavior of LRS. Conversely, the HRS current strongly depends on temperature and the current increases with the increment in temperature, which concludes a semiconductor like behavior.

The switching mechanism of ZnO based resistive random access memory is explained in Fig. 7.

The fresh sample is in initial resistance state, i.e., very less density of oxygen vacancies (V_0) is present in the ZnO layer. To make the device operational, a high electric field of the order of > 10 MV/cm was applied.



a

b

c

Fig. 4 – The endurance measurement of LRS and HRS of the designed device with Al (a), Ag (b), Ti (c) top contact material

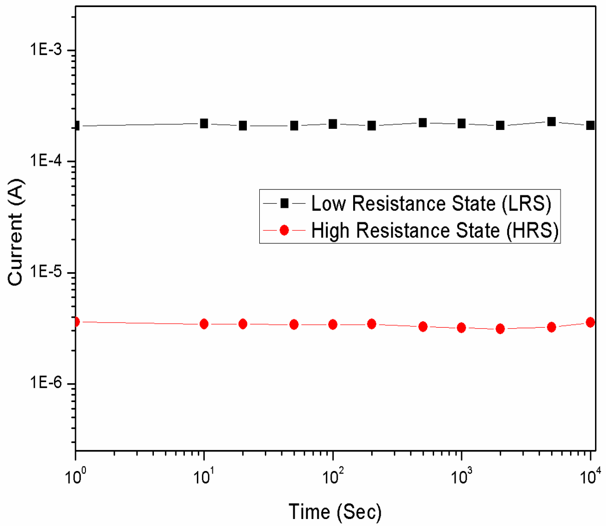


Fig. 5 – The retention measurement of LRS and HRS of a designed device with Ag top contact material

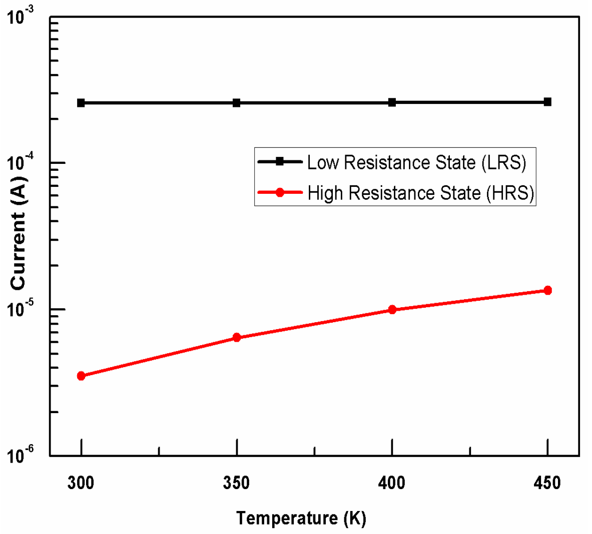
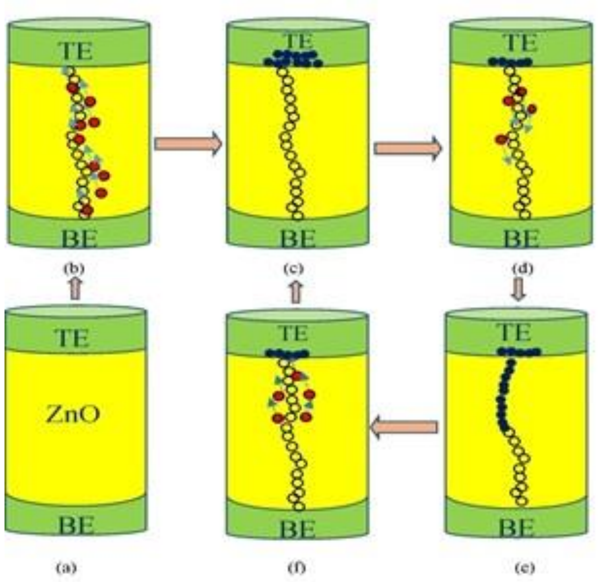


Fig. 6 – The temperature dependence of the electrical conductivity of the designed device with Ag top contact material

Under the influence of the high electric field, the pair of oxygen ions and oxygen vacancies will be created $(\mathbf{O} + \mathbf{2e^-} = \mathbf{O_2^-} + \mathbf{V_0})$ as shown in Fig. 7b. The oxygen ions drift towards the top electrode. At a particular voltage, a conduction filament of oxygen vacancies will be created as shown in Fig. 7c, which results in LRS or ON state. As we apply reverse polarity on the top electrode, oxygen ions start to migrate towards the ZnO layer, which results in the recombination of oxygen ions and oxygen vacancies. Due to this, conduction filament starts to break and HRS builds up. This stage is known as RESET state and shown in Fig. 7d. When conduction filaments break, this state is known as HRS, and only leakage current flows during this state, which is very less. Further, when the polarity of the top electrode changes again, the generation of oxygen ions and oxygen vacancies starts and conduction filament is formed, which results in LRS. This mechanism is demonstrated in Fig. 7.



IRS: initial resistance state, BE: bottom electrode, TE: top electrode,

○: oxygen vacancy, ●: oxygen ion, ● oxygen atom

Fig. 7 – Switching mechanism of the RRAM devices: fresh sample (IRS) (a), forming process (b), conduction filament (LRS) (c), RESET (d), bulk leakage conduction (e), SET (f)

4. CONCLUSIONS

This work investigates the effect of different top electrode materials (Ag, Al, Ti) on the switching characteristics of ZnO metal oxide based RRAM. The XRD pattern of ZnO oxide layer reveals the polycrystalline nature of ZnO with dominant *c*-axis (002) plane. FESEM and images show that the surface of the deposited ZnO thin film is uniform, smooth, crack free and with very less roughness. It has been observed that the use of different top electrode material, e.g. (Ag, Ti, Al) plays an important role in bipolar resistive switching characteristics. It was observed that resistive switching properties of Si/Ti/Pt/ZnO/Ag device are better than those of Si/Ti/Pt/ZnO/Ti and Si/Ti/Pt/ZnO/Al. Series of positive and negative bias, the set and reset process of Si/Ti/Pt/ZnO/Ag device have very low working voltage, good endurance and high on-off ratio due to the formation of rupture, Ag bridge and shapeless oxygen vacancies. Read and write operations for Si/Ti/Pt/ZnO/Ag device can perform up to $1.5 \cdot 10^3$ cycles without any degradation. The switching mechanisms of the RRAM devices were explained on the basis of formation and dissolution of conductive filament.

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Вплив матеріалів верхнього електрода на комутаційні характеристики та властивості витривалості пристрою RRAM на основі оксиду цинку

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У роботі повідомляється про вплив матеріалів верхнього електрода, тобто Al, Ag та Ti, на комутаційні характеристики резистивних пристроїв пам'яті з випадковим доступом (RRAM) на основі тонкої плівки оксиду цинку (ZnO). Пристрої RRAM зі структурою електрода Si/Pt/Ti/ZnO/Top (Al або Ag або Ti) були успішно виготовлені, і були виміряні їх комутаційні характеристики. Структурні властивості тонкої плівки оксиду металу ZnO вивчалися з використанням рентгенівського дифрактометра (XRD), атомно-силової мікроскопії (AFM) та скануючого електронного мікроскопа (SEM). Комутаційні характеристики виготовлених пристроїв визначали за допомогою кривих *I-V*, які отримували за допомогою напівпровідникового аналізатора параметрів. Було помічено, що виготовлені пристрої виявляли біполярні властивості. Структура Si/Pt/Ti/ZnO/Ag показала найкращу витривалість до 10^3 циклів. Крім того, вимірювання утримуючих властивостей при кімнатній температурі проводилося також для структурованого пристрою Si/Pt/Ti/ZnO/Ag, що підтверджує енергонезалежні властивості вироблених пристроїв. Співвідношення станів низького опору (LRS) та високого опору (HRS) було встановлено максимальним для верхнього електрода Ag до 10^2. Помічено, що струми LRS та HRS пристрою не погіршуються до 10^4 с.

Ключові слова: RRAM, Комутаційні характеристики, Верхній електрод, ZnO.