Write-Once–Read-Many-Times Memory Based on ZnO on p-Si for Long-Time Archival Storage

Jing Qi, Qing Zhang, Jian Huang, Jingjian Ren, Mario Olmedo, and Jianlin Liu

***Abstract*—Write-once–read-many-times memory cells were fabricated using ZnO thin film on p-Si (111) substrate. The OFF- and ON-state resistance ratio is over 10^4 and can be well sustained for more than 100 years and perfectly endure reading cycles of 10^8. The conducting filaments consisting of oxygen vacancies are responsible for the switching mechanism.**

***Index Terms*—Conducting mechanism, write-once–read-many-times (WORM), ZnO.**

I. Introduction

WRITE-ONCE–READ-MANY-TIMES (WORM) memory devices, in which the data storage is permanent, as required for archival storage of video images and for noneditable database, have attracted a great deal of interest [1], [2]. Even though some studies regarding the formation and electrical properties of WORM memory devices using organic materials [3], [4], inorganic/organic nanocomposites [5], and inorganic/organic heterojunction [2] have been carried out, studies on WORM memory devices fabricated using ZnO film have not been reported yet. ZnO material is a promising candidate for WORM memory application primarily due to its environmental friendliness, abundant availability in nature, highly evolved growth technologies, compatibility with metal–oxide–semiconductor technology, and suitability for fabrication of small-size devices [6], [7]. This letter reports the switching characteristics and mechanism of WORM memory devices fabricated using ZnO on p-Si.

II. Experimental Procedure

ZnO (60 nm) was deposited on p-Si (111) substrate at 400 °C with a few atomic layers of MgO as buffer in a radio-frequency (RF) plasma-assisted molecular beam epitaxy system. An experiment on a reference sample with only MgO layer indicated that MgO is too thin to have similar memory performance (not shown here). The Si substrates were cleaned using standard RCA method to remove contamination and native oxide layer. High-purity Mg (6 N) and Zn (6 N) sources were evaporated from conventional low-temperature effusion cells. Atomic oxygen was provided by an RF plasma source. Ti (10 nm)/Au (90 nm) square-shaped metal patterns of different areas, which act as top electrodes, were deposited on ZnO by electron-beam evaporation after photolithography, followed by a standard lift-off process. Al was evaporated also by electron-beam evaporation as back contact onto p-Si (111). The electrical characteristics of the Au/Ti/ZnO/p-Si/Al structure were measured by an Agilent 4155 C semiconductor analyzer. Current maps for the surface of ZnO film were measured by a conductive atomic force microscope (C-AFM). A scanning electron microscope (SEM) was utilized to observe surface morphology change of top electrodes after electrical characterization.

III. Results and Discussion

Fig. 1(a) shows a typical current–voltage (I–V) curve of a memory cell [device structure with electrodes of different areas shown as the bottom right inset in Fig. 1(a)]. First, an external applied voltage (V_{ext}) was swept from -1.5 to 1.5 V to obtain the I–V curve for high-resistance state (OFF), as shown in Fig. 1(a) as black square curve. Then, as V_{ext} ($0 \rightarrow 20$ V) in sweeping mode increased to approximately the writing voltage (V_w) of 14 V, the current increased suddenly, which switched the memory cell to low-resistance state (ON), as shown in the right inset of Fig. 1(a). This phenomenon is similar to an electroforming process, which is a soft breakdown due to the protection of current compliance, in resistive random access memory (RRAM), where the sudden current increase is caused by the formation of the conducting filaments [8]. Finally, V_{ext} swept from -1.5 to 1.5 V again to obtain the I–V curve for ON state, as shown in Fig. 1(a) as red circle curve. Probability of resistance ratio (R-ratio, $R_{\text{OFF}}/R_{\text{ON}}$) obtained at a reading voltage of 1 V from 100 devices with an area of 30×30 μm^2 [left inset of Fig. 1(a)] shows that the R-ratio for most devices is between 10^5 and 10^6. Fig. 1(b) shows the dependence of R-ratio and writing power on the current compliance during the writing process. A WORM memory effect can still be clearly observed even if the writing power is lowered to be smaller than 1 mW. Furthermore, R-ratio decreases to 10^3 with the writing power lowered to 1 mW. This ratio is large enough to distinguish two different states.

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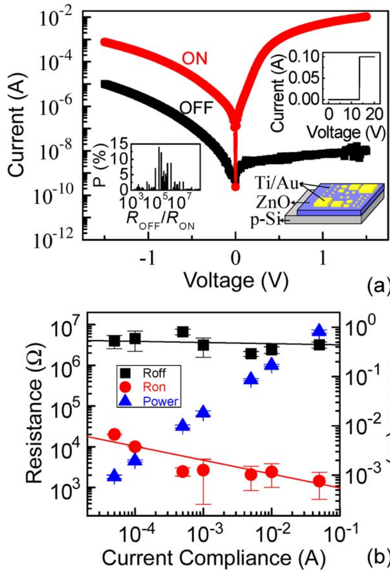

Fig. 1. (a) Switching characteristics of the WORM memory. (Black squares) Current–voltage (I–V) characteristic of the WORM memory before writing (OFF state). (Red circles) Data for the WORM memory after writing (ON state). (Bottom right inset) Device structure of the WORM memory. (Top right inset) I–V characteristic for the writing process. (Left inset) Probability of the resistance ratio between OFF and ON states for 100 devices of 30 μm × 30 μm. (b) Dependence of ON- and OFF-state resistances and writing power on current compliance during the writing process.

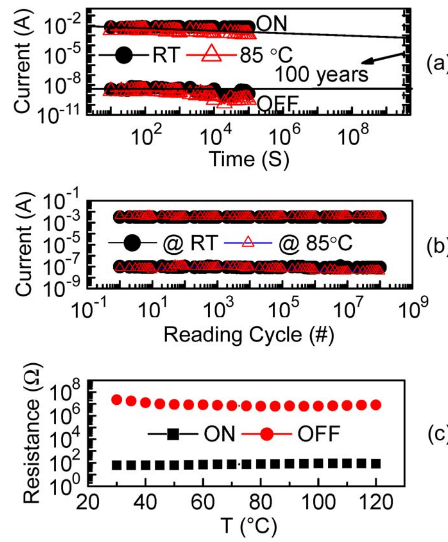

Fig. 2. (a) Retention and (b) endurance characteristics of the ZnO WORM memory device in the ON and OFF states at a read voltage of 1.0 V. (c) Dependence of resistance on measurement temperature.

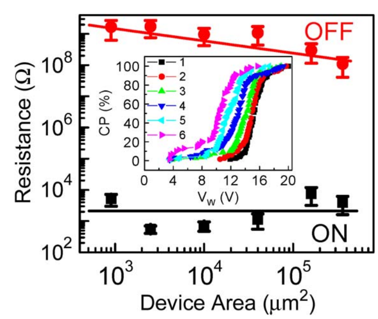

Fig. 3. Dependence of resistance for ON and OFF states on the area of the device. (Inset) Cumulative probability of writing voltage for different device areas [(noted as "1" in the inset) 30 × 30, (2) 50 × 50, (3) 100 × 100, (4) 200 × 200, (5) 400 × 400, and (6) 600 × 600 μm^2].

The typical retention and endurance performances of Au/Ti/ZnO/p-Si WORM memory measured at room temperature and higher temperature (85 °C) are shown in Fig. 2(a) and (b), respectively, in which the ON- and OFF-state resistances were measured at 1 V in sampling mode. The ON state exhibited little degradation after 1×10^5 s, while the OFF state showed no degradation. However, the two states can still be well distinguished by high OFF/ON resistance ratio of over 10^4, as the data trends are extrapolated to 100 years. It should be noted that the extrapolation method was extensively utilized by other researchers [9], [10]. This result indicates excellent retention. For endurance, as shown in Fig. 2(b), both ON and OFF states with a large resistance ratio of over 10^5 exhibited little degradation after reading cycles of 1×10^8. The relation between the resistances of both ON and OFF states and the measurement temperature is shown in Fig. 2(c). As the measurement temperature increases, the OFF-state resistance decreases slightly, while the ON-state resistance increases, which originates from the dependence of resistance on temperature for semiconductor/insulator and metal materials, respectively.

I–V characteristics were measured on 100 devices for all six different metal contact areas to obtain the statistic information for this kind of memory. As shown in the inset of Fig. 3, when the area of the device decreases from 600 × 600 μm^2 to 30 × 30 μm^2, V_w increases to the range of 12–20 V. The writing voltage of over 12 V ensures reliability of the memory states. The dependence of average resistance for both ON and OFF states on the device area is shown in Fig. 3. The OFF-state resistance increases linearly with the decrease of the area. However, there is no obvious relationship between ON-state resistance and device area, similar to the reported results in RRAM [11], where resistive switching was caused by formation/rupture of conducting filaments. In this conducting filament model, the effective cell area is attributed to the conducting filament density and diameter rather than to the geometrical size of the electrode [12]. Voltage sweeping of larger range ($-5 \sim 5$ V) was performed at different current compliance. Typical results are shown in Fig. 4, which shows that the memory cell can be reset slightly at negative bias. The I–V curves for the RESET process are not linear in the low-voltage region, indicating the formation of tunneling barrier at the MgO–Si interface during the SET process due to the existence of a few MgO monolayers. The formation of this barrier prevents the device from being totally reset [13]. These larger range voltage sweeping results mean that WORM memory and RRAM can coexist in one memory cell and the switching mechanism is controlled by the conducting filament. In the ZnO WORM memory case, the formed conducting filaments cannot be totally ruptured. For OFF state, the device is a heterojunction diode consisting of ZnO and Si substrate, which leads to diodelike I–V characteristics. After the formation of the conducting filaments in ZnO, the device becomes a metal/semiconductor contact, in which the top electrode and conducting filaments act as metal while the Si substrate is a semiconductor part of the device. This

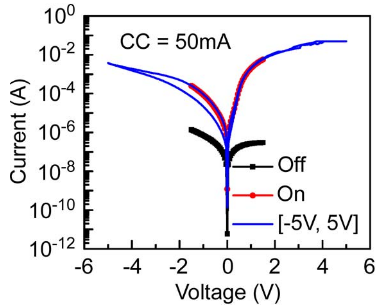

Fig. 4. Coexistence of WORM memory and RRAM in one cell.

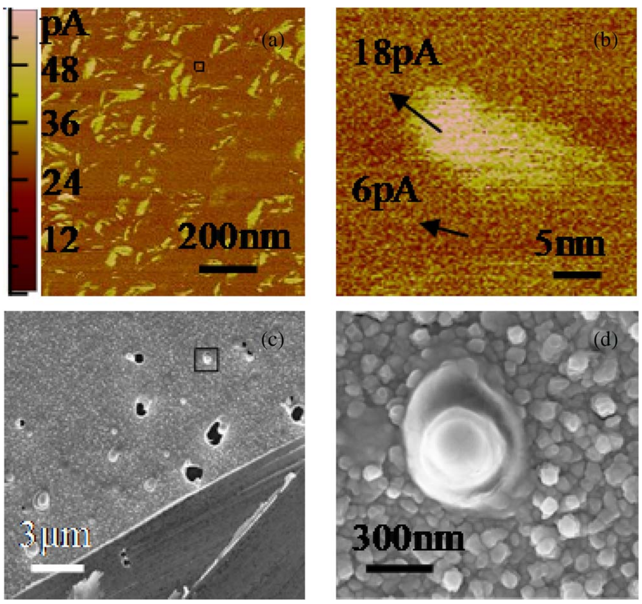

Fig. 5. (a) C-AFM image of the surface of ZnO thin film. (b) Spot of 5 nm corresponding to the black square area in (a). (c) Typical SEM images of blown-off and bubble areas on top of contact for ON-state WORM memory. (d) Magnified images of the bubble in the rectangular area of (c).

results in much higher current for ON state than that of OFF state at a positive external applied voltage. The error bars plotted in Fig. 3 are indicative of the variability of OFF- and ON-state resistances from one memory element to the other.

Fig. 5 shows the C-AFM current map for the surface of ZnO thin film and typical SEM images for ON-state devices. The current maps shown in Fig. 5(a) and (b) suggest that conducting filaments are responsible for the switching mechanism and the diameter of the filaments can be as small as 5 nm, indicating good potential of scaling down. Some blown-off and bubble areas are observed on the surface of the top contacts, as shown in the SEM images [Fig. 5(c) and (d)]. These areas were caused by the production of oxygen gas because of the oxidation reaction that happened during the writing process, corresponding to the positions with the strongest filaments. Similar bubble phenomenon caused by redox reaction during the filament-forming process was also reported by Szot *et al.* [14]. These results again indicate that conducting filaments consisting of oxygen vacancies are responsible for the switching behavior.

IV. Conclusion

WORM memories fabricated using a ZnO epitaxial thin film have shown excellent performance of suitable writing voltage (12–20 V), high resistance ratio of OFF and ON states (mainly in the range of 10^5-10^6), good retention (100 years), and excellent endurance ($> 10^8$ cycles). The characteristics of writing process, the dependence of ON- and OFF-state resistances on the device area, current maps for the surface of ZnO thin film, and morphology change of the contact area for ON-state devices show that conducting filaments consisting of oxygen vacancies are responsible for the conduction mechanism.

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