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The effect of top contact on ZnO write-once–read-many-times memory

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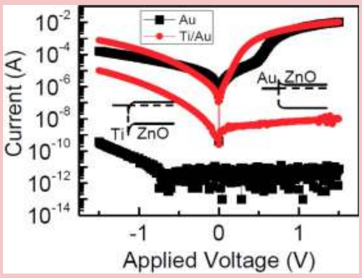
Write-once–read-many-times memory (WORM) devices were fabricated using Ti/Au and Au as top contacts on ZnO thin films on Si. Electrical characterization shows that both types of WORM devices have large resistance OFF/ON ratio (R ratio), small resistance distribution range, long retention and good endurance. WORM devices with Au top contact have better performance of higher R ratio because of a larger work function of Au compared to Ti.



1 Introduction Zinc oxide (ZnO) is a II–VI wide-band-gap compound semiconductor, which has promising applications in light-emitting diodes [1], field-effect transistors [2], laser diodes [3], solar cells [4], sensors [5], etc. 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]. Recently, ZnO materials have been utilized to fabricate resistive random access memory (RRAM) devices [8–12]. It was found that different metal contacts have significant effect on the performance of RRAM [13]. At the same time, write-once–read-many-times memory (WORM) devices, in which the data storage is permanent, as required for archival storage of video images and for non-editable databases, have attracted a great deal of interest [14, 15]. Previously, our group fabricated a WORM device with ZnO film [16]. The OFF/ON state resistance ratio for the ZnO WORM device 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. In this Letter, the effect of the top contact on WORM fabricated with ZnO is reported.

2 Experiments 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 (MBE) system. MgO is used here to form a tunnelling barrier between ZnO and Si to prevent the device from being totally reset, i.e. to obtain the WORM effect [16]. Ti(10 nm)/Au(90 nm) and Au(100 nm) square-shaped metal patterns of different areas, which act as top electrodes, were deposited on ZnO, respectively, by electron beam evaporation after photolithography, followed by standard lift-off process. Al was evaporated also by electron-beam evaporation as back contact onto p-Si (111). The electrical characteristics of the devices were measured by an Agilent 4155C semiconductor analyzer.

3 Results and discussion Figure 1 shows the typical *I–V* characteristics of WORM devices with Ti/Au and Au as top contacts, respectively, before (OFF state) and after (ON state) writing process under sweeping voltage from

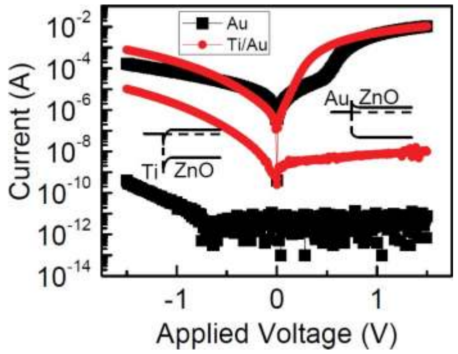


Figure 1 (online colour at: www.pss-rapid.com) Typical *I–V* characteristics for ON and OFF states of WORM devices with Ti/Au and Au as top contacts, respectively. Inset: energy-band diagrams of metal (left: Ti; right: Au) on ZnO.

0 to 10 V. The currents of the ON state are the same for both types of devices while the currents of OFF state for the Ti/Au-contacted device are almost three orders higher than those for Au-contacted devices, indicating that the WORM devices with Au as top contact have a higher resistive OFF/ON ratio (R ratio). The difference of OFF state current is caused by the different metal work function (W_m) of Ti (4.33 eV) and Au (5.1 eV) [17]. The work function of ZnO (W_s) is 4.5 eV [18]. As shown in the inset of Fig. 1, in the Ti case, $W_m < W_s$, the electron barrier between metal and ZnO can be ignored. Whereas in the Au case, $W_m > W_s$, the barrier plays an important role in the resistance of the device for OFF state. The same ON state current indicates that both types of WORM devices possess the same conduction mechanism, which is related to conducting filaments consisting of oxygen vacancies [16].

Figure 2(a) and (b) show the writing voltages and resistance for ON and OFF states of the two types of devices for different device area. 100 devices for each area were measured to obtain statistical results for both types of top contacts. As seen from Fig. 2(a), there is no obvious difference between the writing voltages of the two types of devices with Ti/Au and Au as top contacts, indicating that the conducting filaments are also responsible for the conduction mechanism of WORM devices with Au as top contact because the barrier between metal and ZnO should not affect the formation of conduction filaments. The resistance shown in Fig. 2(b) for WORM devices with Au as top contact for both ON and OFF states have the same trend as that with Ti/Au as top contact, which further proves that the conduction filaments are responsible for the conducting mechanism in Au-contacted WORM devices as well. The WORM devices with Au as top contact have higher R ratio for all six types of device area.

Figure 3 shows the resistance distribution of WORM devices with Au and Ti/Au as top contacts for ON and OFF states. For the ON state both types of devices have the same distribution range between $2 \times 10^2\ \Omega$ and $5 \times 10^4\ \Omega$ while for the OFF state, devices with Au as top contact have a smaller resistance range than that with Ti/Au as top contact, which are from $6 \times 10^{10}\ \Omega$ to $3 \times 10^{12}\ \Omega$ and from $4 \times 10^6\ \Omega$ to $6 \times 10^9\ \Omega$, respectively. In addition to the contact between the top electrodes, rectification of the n-ZnO/p-Si interface also plays an important role in the high resistance of OFF states for both types of devices according to the shape of *I–V* curves [16].

Figure 4(a) and (b) show the retention and endurance characteristics of the two types of devices. Retention was measured at a bias of +1 V while endurance was obtained at reading pulses with an amplitude of +1 V and a period of 2 µs with 50/50 duty cycle. Both retention and endurance of WORM device with Au as top contact are as good as those with Ti as top contact. Both ON and OFF states

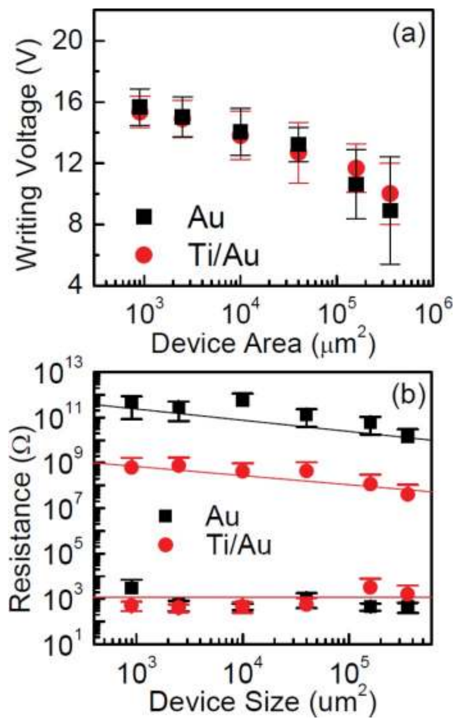


Figure 2 (online colour at: www.pss-rapid.com) Dependence of (a) writing voltage and (b) resistance for ON and OFF state on the area of the two devices with Ti/Au and Au top contacts.

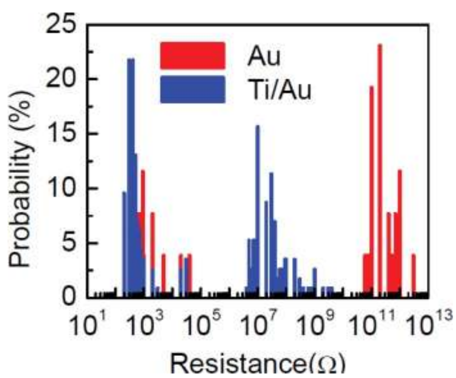


Figure 3 (online colour at: www.pss-rapid.com) Probability of the resistance of both types of devices for ON and OFF states.

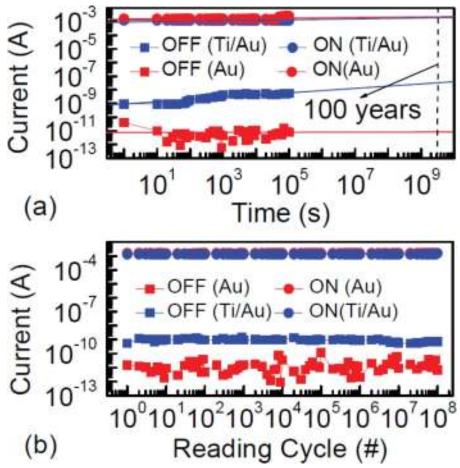


Figure 4 (online colour at: www.pss-rapid.com) (a) Retention and (b) endurance characteristics of the ZnO WORM memory device in the ON and OFF states at a read voltage of 1.0 V.

show little degradation after 1×10^5 s. As the data trends are extrapolated to 100 years, the two states can still be well distinguished by high OFF/ON resistance ratios of over 10^5 and 10^8 for devices with Ti and Au as top contact, respectively, which indicate excellent retention for both types of devices. For endurance, as shown in Fig. 4(b), both ON and OFF state with a large resistance ratio of around 10^6 and 10^8 for the two types of devices, respectively, exhibit no degradation after reading cycles of 1×10^8.

4 Conclusion Both Ti and Au can be utilized as top contacts for WORM devices fabricated with ZnO. WORM devices with Au as top contact have a higher R ratio and a smaller resistance range than those with Ti as top contact while their retention and endurance are comparable. The different R ratio can be explained by different energy barrier between different metals and ZnO.

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