Supporting information

Title: "Investigation of multilevel data memory using filament and polarization control"

Author(s): Pengfei Hou, Jinbin Wang and Xiangli Zhong

Thickness test using step profiler (AlphaStep D-120)

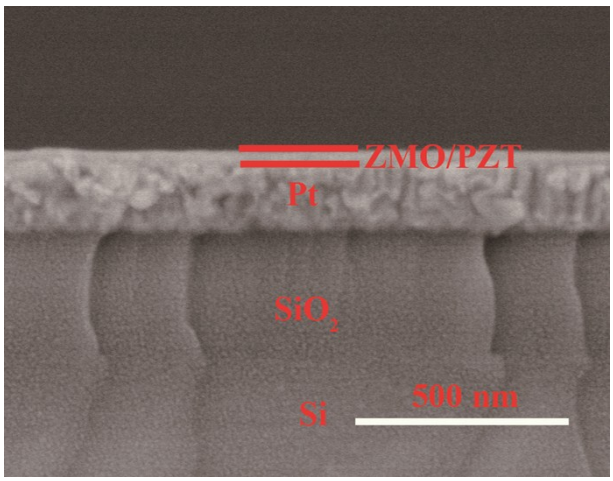

Figure S1. The cross section image of ZMO(ZnO:Mn2%)/PZT/Pt films measured by SEM.

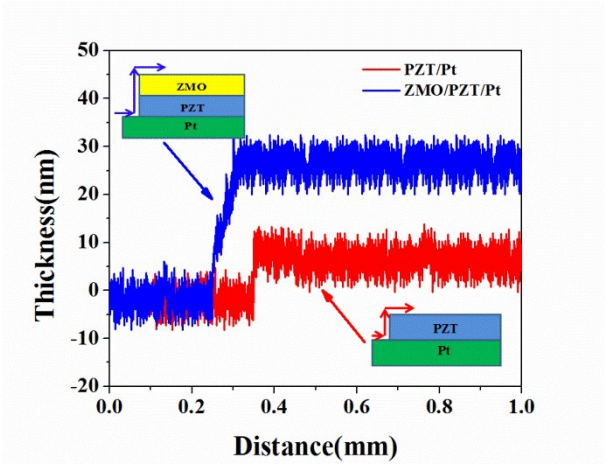

Figure S2. The step changes of PZT/Pt and ZMO/PZT/Pt films.

The cross section images measured by SEM are always an effective way to measure the film thickness, but the 8 nm thick PZT film and 20 nm thick ZMO film are too thin and can't be distinguished in the SEM images because of low resolution (as shown in Figure S1). So we measured the film thickness with step profiler and Filmetrics model F20-UV and F50-UV. According to the result of the test using step profiler, (as shown in Figure S2)) the thickness of the PZT and ZMO

films are almost the same to the result of the test using Filmetrics model F20-UV and F50-UV. The thickness of PZT film is about 8 nm, and the thickness of ZMO film is about 20 nm.

P-V curves of PZT films

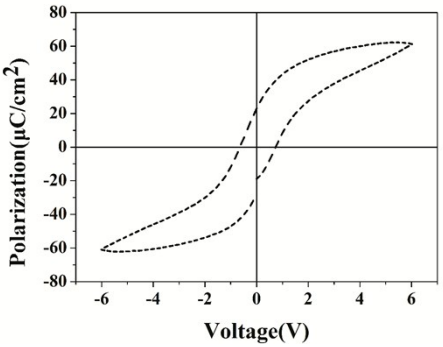

Figure S3. Hysteresis loops of Pt/PZT/Pt with 50 nm thick PZT film.

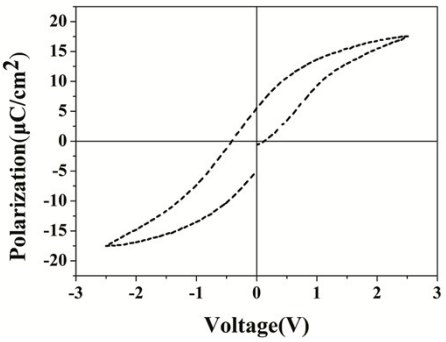

Figure S4. Hysteresis loops of Pt/PZT/Pt with 29 nm thick PZT film.

Controllable filamentary memory based on a PZT thin film

In this section we prove a controllable filamentary memory based on a 30 nm thick PZT thin film prepared at an oxygen pressure of 10 Pa in metal-ferroelectric-metal (MFM) structure, in order to prove that the oxygen vacancies filament can be formed with Ag electrode in the effect of electric field. The 30 nm thick PZT film with was grown by laser molecular beam epitaxy (LMBE) on Pt-coated silicon. During deposition of the PZT layer, substrate temperature was maintained at 625 °C with chamber oxygen pressure kept at 10 Pa. The samples were cooled down to room temperature at an oxygen atmosphere of 38 Pa.

I-V characteristics of the Ag/PZT/Pt memory cell were studied by dc voltage sweep measurements to evaluate the memory effects of the obtained devices, and the results are illustrated

in semilogarithmic (Figure S5) scales. During the measurements, a voltage of 2 V should be applied on the device first to set the resistance at high resistance state, because the original state of the device is low resistance state. Then the corresponding current is measured at dc voltage with *V* sweeping in a sequence of 0 V→-2 V→0 V→+2 V→0 V.

After the Ag/PZT/Pt device was set at HRS, the voltage was swept from 0 V to 0.2 V without current compliance. Then the voltage was swept from 0 V to 0.2 V without current compliance for 5 times to read the resistance states after the resistance states were written with voltage sweepings from 0 V to -2 V with current compliances of 10^{-6} A, 10^{-5} A, 10^{-4} A, 10^{-3} A and 10^{-2} A, respectively. As shown in Figure S6, we achieved 6 resistance states at last. In the Ag bridge system like Ag/ZMO/Pt,[1] the Ag bridge determines the resistance states. If the bridge is good, it will be LRS, when the bridge is broken, it will be HRS. Even more if the intermediate states may be stable between HRS and LRS, the current compliances of 10^{-5} A, 10^{-4} A, 10^{-3} A and 10^{-2} A are higher than the current at which the Ag bridge may form (about 10^{-9}~ 10^{-6}A in the sweeping of 0 V to -2 V in our case if it is existed). Even more the original state of our device is at low resistance state. Considering the oxygen vacancies forming by the interfaces of PZT and Ag layers, the oxygen vacancies may form the filament in the PZT film. [2] And in the preparation process, the Ag electrode can absorb the oxygen ions in the PZT layer, which will result the originally low resistance state of the device.

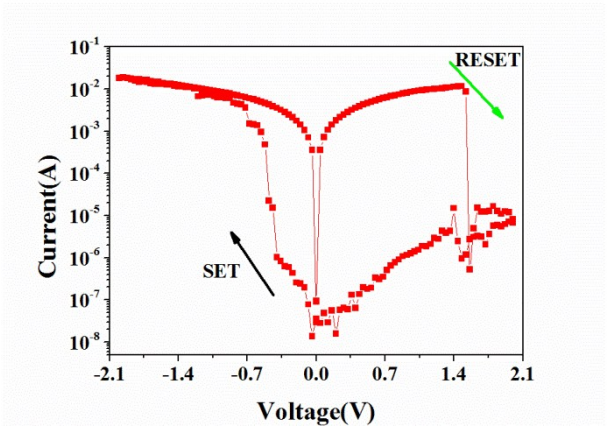

Figure S5. Current of Pt/PZT/Ag films at various applied voltage.

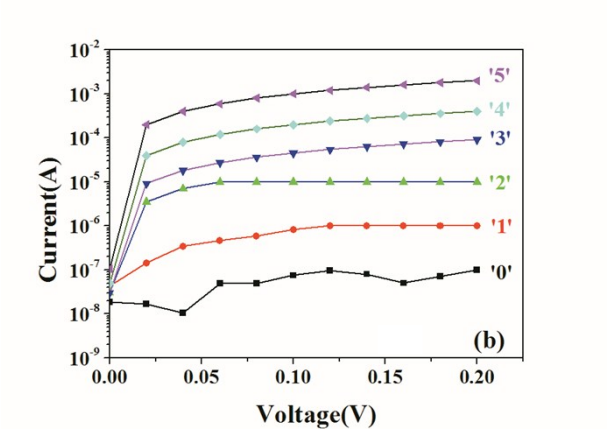

Figure S6. 6 states of the device after different write process. ′0′ was achieved after a 2 V voltage pulse process. ′1′, ′2′ , ′3′, ′4′ and ′5′were achieved after processes from 0 V to -2 V with current compliance of 10^{-6} A, 10^{-5} A, 10^{-4} A, 10^{-3} A and 10^{-2} A, respectively.

In order to confirm that a lot of oxygen vacancies can forms at the interfaces between the PZT film and Ag electrode because of Ag+O→AgO_x, further investigations were taken. In the test, we investigated the current of the device at various temperatures, as shown below Figure S7. When the device is at LRS or at HRS, the temperature is ranging from 30 ℃ → 100℃. It can be found that the HRS did not changed, while the LRS changed largely. It can be explained by the decomposition of AgO*x* because of the high temperature about 90~95℃, AgO_x →Ag+O. The oxygen ions merged with the oxygen vacancies, so the LRS turned to HRS. The phenomenon in our case is different with the Ag filament in reference [3].

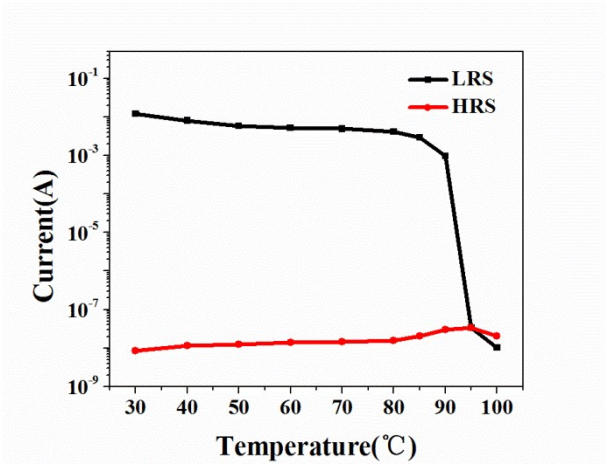

Figure S7. Current of the device with the PZT layer at various temperatures

Based on the investigations, it is reasonable that the controllable filamentary memory based on a 30 nm thick PZT thin film is caused by oxygen vacancies. And it can be used to prove that the oxygen vacancy filament can be achieved in the device of Ag/ZMO/PZT/Pt. Because the Ag/ZMO/PZT/Pt device is written by voltage sweepings, so the Ag migration may also happen. And the Ag migration may help the formation of oxygen vacancy filament as shown in reference [4].

I-V curves of PZT and ZMO films with Ag electrodes

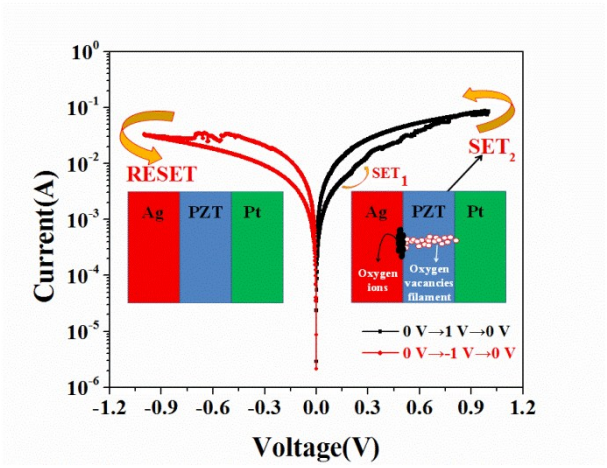

Figure S8. I-V curves of Ag/PZT/Pt device with 8 nm thick PZT layer.

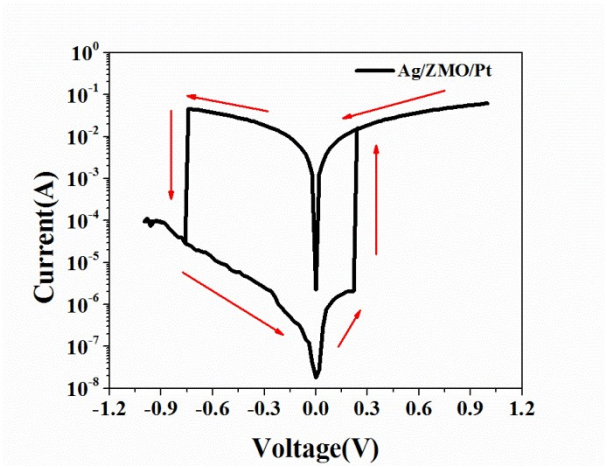

Figure S9. I-V curves of Ag/ZMO/Pt device with 20 nm thick ZMO layer.

Endurance test of Ag/ZMO/PZT/Pt device

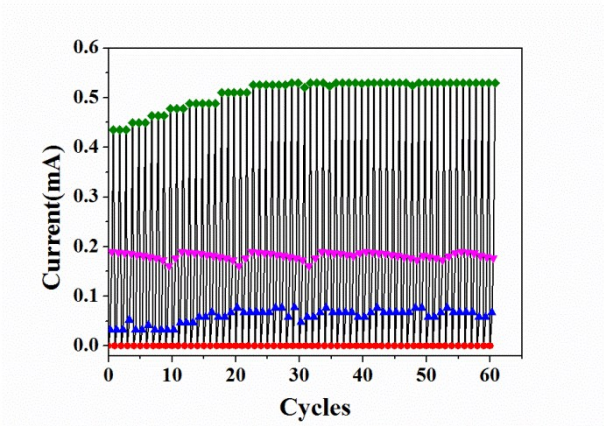

Figure S10. The endurance test of Ag/ZMO/PZT/Pt device.

References

[1] Yang, Y. C., Pan, F., Liu, Q., Liu, M. & Zeng, F. Fully room-temperature-fabricated nonvolatile resistive memory for ultrafast and high-density memory application. *Nano Letters* **9**, 1636 (2009).

[2] Hou, P., Wang, J., Zhong, X. and Wu, Y. RSC Advances, 2016, DOI: 10.1039/C6RA08257B.

[3] Tsunoda, K., Fukuzumi, Y., Jameson, J. R., Wang, Z., Griffin, P. B. and Nishi, Y. Bipolar resistive switching in polycrystalline TiO2 films. Appl. Phys. Lett. 90, 113501 (2007).

[4] Wang, Z. Q., et al. Performance improvement of resistive switching memory achieved by enhancing local-electric-field near electromigrated Ag-nanoclusters. *Nanoscale* **5**, 4490-4494 (2013).