## **Support information**

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**Figure S1** and **S2** show the hysteresis loops of Pt/PZT/Pt with PZT layer prepared at 20 Pa oxygen pressure and Ag/PZT/Pt with PZT layer prepared at 30 Pa oxygen pressure. And the hysteresis loops prove that the resistive switching phenomena of the two devices are caused by Schottky barrier variations because of ferroelectric polarization. The Ag/PZT/Pt devices with PZT layers prepared at 20 Pa oxygen pressure and 10 oxygen pressure have no hysteresis loops, implying that the polarization is not the reason causing the resistive switching in the two devices. All the thickness of the PZT layers is about 30 nm. The hysteresis loop of Ag/PZT/Pt with PZT layer prepared at 30 Pa oxygen pressure is not good, it may be caused by the asymmetry electrodes.



Figure S1. Hysteresis loop of Pt/PZT/Pt with PZT layer prepared at 20 Pa oxygen pressure.



Figure S2. Hysteresis loop of Ag/PZT/Pt with PZT layer prepared at 30 Pa oxygen pressure.

In order to confirm that a lot of oxygen vacancies can forms at the interfaces between the PZT film and ZMO film because of  $Ag+O\rightarrow AgO_x$ , further investigations were taken. In the test, we investigated the current of the device with the PZT layer prepared at an oxygen pressure of 20 Pa at various temperatures, as shown below **Figure S3**. When the device is at LRS or at HRS, the temperature is ranging from  $30^{\circ}C\rightarrow 100^{\circ}C$ . 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  $90\sim 95^{\circ}C$ ,  $AgO_x \rightarrow Ag+O$ . 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.



Figure S3. Current of the device with the PZT layer prepared at an oxygen pressure of 20 Pa at

various temperatures

We can compare the initial oxygen vacancy concentrations by comparing the lattice constants of the PZT films prepared at different oxygen pressure. According to the XRD results (**Figure 2**), the calculated a-axis lattice constants of the PZT films fabricated under oxygen pressures of 10 Pa, 20 Pa and 30 Pa, respectively, are 4.0050, 3.9731 and 3.8082 Å, respectively. We attribute the modification of the lattice constants to the influence of the oxygen vacancies, naturally produced during the laser molecular beam epitaxy (LMBE) processes. <sup>[1-2]</sup> Ti and Zr ions vary from high to low valence states due to the existence of oxygen vacancies, thus leading to a larger manganese ionic radius and a larger lattice constant. <sup>[3]</sup> It is worth mentioning that similar phenomena of enlarged lattice constants induced by oxygen vacancies have also been observed in previous works. <sup>[3-5]</sup> In other words, a larger a-axis lattice constant corresponds to a larger number of oxygen vacancies, which could be induced by structural distortions in the thin films fabricated under a lower oxygen pressure.

## References

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