Supplementary information

Title: "Voltage pulse controlling multilevel data ferroelectric storage memory with nonepitaxial ultrathin film"

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AFM topography of 2 nm thick PZT film

The AFM topography of 2 nm thick PZT film is shown in **Figure S1**.

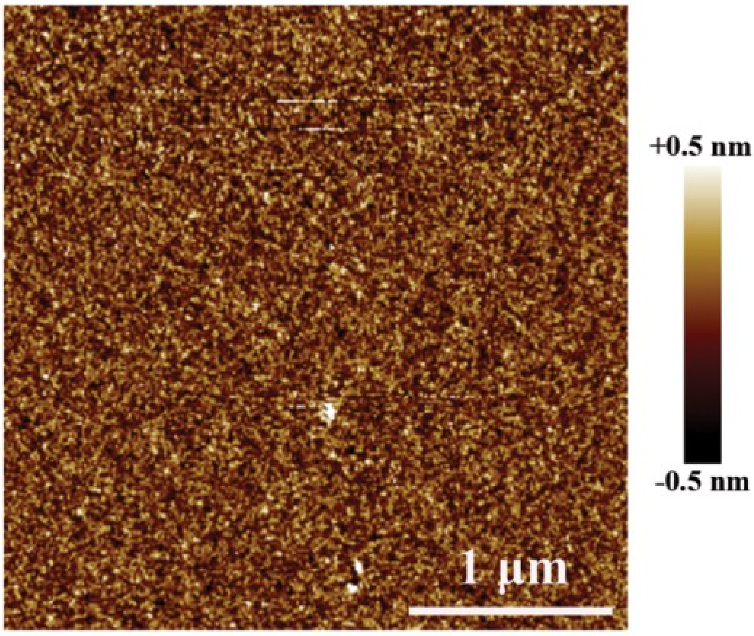

Figure S1. AFM topography of 2 nm thick PZT layer on As doped silicon wafer.

Investigation of oxygen vacancy migration

In this section, we prove a memory based on oxygen vacancy migration in Pt/$SrTiO_3$(STO)/SiO_x/Si device, in order to prove that the oxygen vacancies can migrate in the SiO_x layer and $SrTiO_3$ layer. During deposition of the STO layer substrate temperature was maintained at 625 °C with chamber oxygen pressure kept at 22 Pa. The samples were cooled down to room temperature in oxygen atmosphere at 22 Pa. Pt dot electrodes were fabricated by d.c. sputtering through a shadow mask about 100 μm in diameter at room temperature

The thickness of the STO film is about 3 nm after deposited 45 s using laser molecular beam epitaxy. A SiO_x layer was formed because of oxygen diffusion during the STO film deposition. The structure of the device with STO film is same to the structure of the device with PZT film.

In order to study the resistance states (RSs) that the devices can achieve, we test the sample as the processes which are used in the test of Pt/PZT/SiO_x/Si. SET (RESET) voltage pulse (+ 3 V or -3 V) is applied to get the largest RS or lowest RS of the STO thin film, then voltage sweeping of -0.8 V→0.8 V is applied to read the resistance, as shown in **Figure S2**. The two resistance states can be read clearly. After each write pulse, the current at V_{DC} = 0.8 V is recorded in increasing time intervals up to 100 s of total measurement time, as shown in **Figure S3**.

The STO layer in the device has no ferroelectricity, but the Pt/STO/SiO_x/Si device has the resistance switching phenomenon. The STO film is prepared at an oxygen pressure of 22 Pa, which is the same to the oxygen pressure of PZT film. Comparing with the former discussion, [1-3] it is a relatively high oxygen pressure in the preparation of STO film, it means that little oxygen vacancies are in the STO film. Considering the oxygen vacancies that formed in the SiO_x, the oxygen vacancy migration is the cause of the resistance switching. In the device of Pt/PZT/SiO_x/Si, the switch ratio is much high than the switch ratio of Pt/STO/SiO_x/Si, and the PZT layers have ferroelectricity, so the multilevel storage in Pt/PZT/SiO_x/Si devices is caused by ferroelectricity and oxygen vacancy migration together.

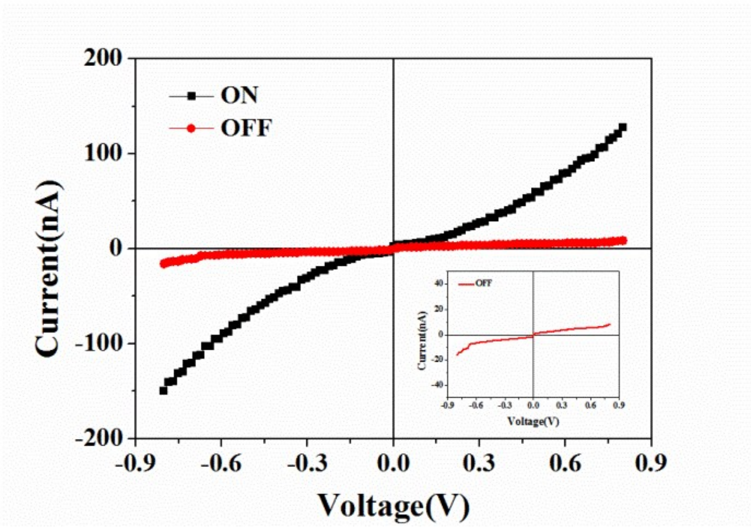

Figure S2. Current of Pt/STO/SiOx/Si with different resistance states at various applied voltage.

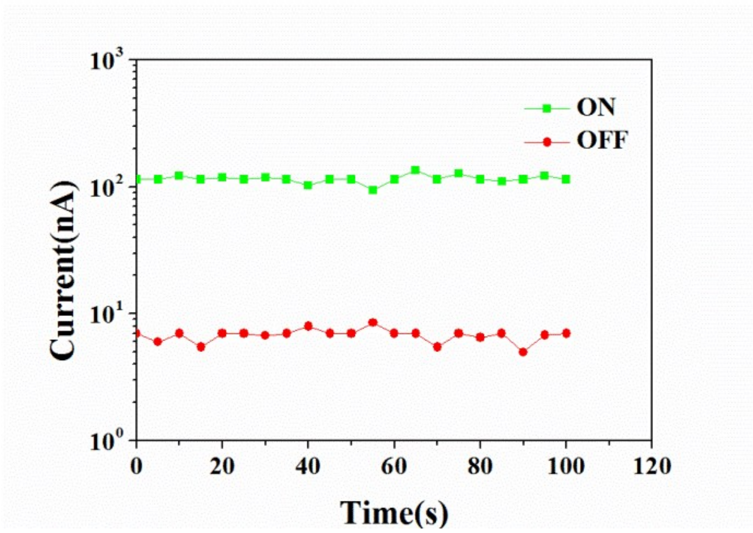

Figure S3. The retention of the Pt/STO/SiOx/Si device.

Piezoresponse phase image of the 2 nm thick PZT film

In this section, we provide PFM image for each stage in figure 9, to verify the polarization direction and confirm the validity of the mechanism proposed, as shown in **Figure S4**. Although the contrast of the images is not very large, these images still show the polarizations switching. [4, 5] The results are fit the hysteresis loops of 2 nm thick PZT layer. According to the *P-V* curves of figure 3a, the large voltage may get the large polarization. But the results of figure 7 show that the oxygen vacancies affect the leakage current largely. So the mechanism proposed in figure 10 is reasonable, and the barrier height really affects the leakage current.

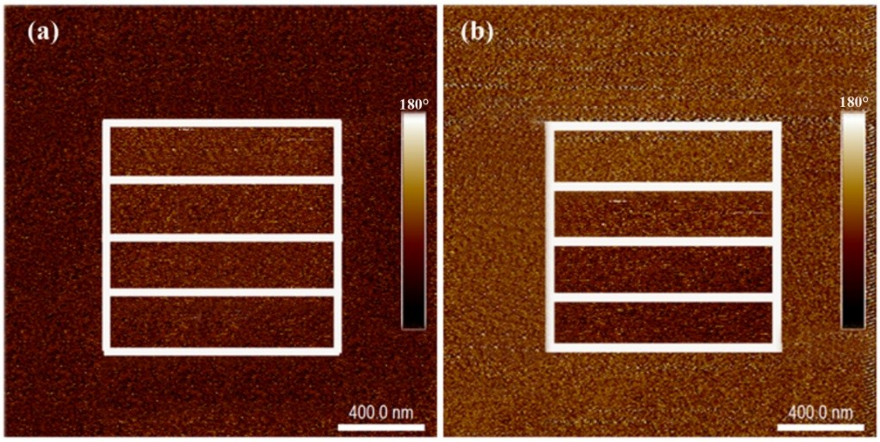

Figure S4. PFM images of the 2 nm thick PZT film. (a) After the film is first polarized by 5 V pointing to in-plane, the film is polarized by 5 V ('7'), 4.5 V ('6'), 4 V ('4') and 2 V ('2') pointing to out-of-plane from top to bottom. (b) After the film is first polarized by 5 V pointing to out-of-plane, then the film is polarized by -2 V ('5'), -3 V ('3'), -3.5 V ('1') and -5 V ('0') pointing to in-plane from top to bottom.

References

[1] Appl. Phys. Lett. 2012,100, 223503.

[2] Phys. Rev. Lett. 2007, 98, 196802.

[3] Phys. Lett. 2009, 467, 313.

[4] J. Mater. Chem. C, 2013, 1, 418.

[5] RSC Adv. 2013, 3, 24362.