Supplementary Information

Permanent charged domain walls under tip poling engineering

Wenping Geng [a,*], Xiaojun Qiao [a], Jinlong He [a], Linyu Mei [b], Kaixi Bi [a], Xiangjian Wang [c,d], Xiujian Chou [a]

a. Science and Technology on Electronic Test and Measurement Laboratory, North University of China, Taiyuan 030051, China

b. School of Mechanical Engineering, North University of China, Taiyuan 030051, China

c. School of Materials and Energy, Guangdong University of Technology, Guangzhou, 510006, China

d. Applied Physics, Luleå University of Technology, Luleå, SE-971 87, Sweden

Section S1: Ferroelectric domain reversal under external electric field

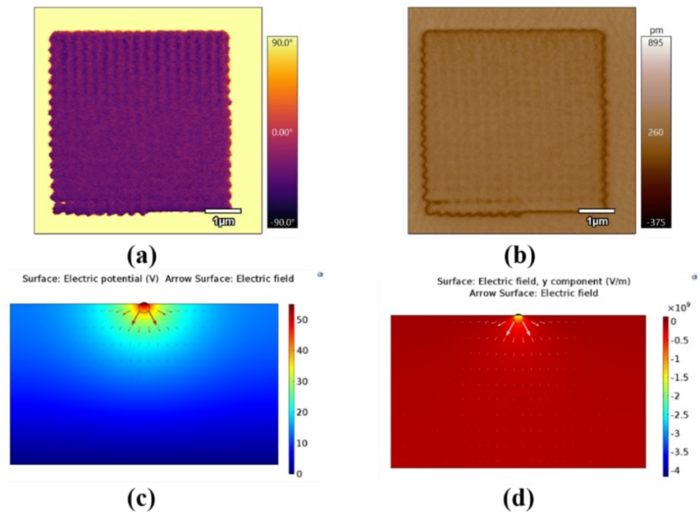

Fig. S1 Domain reversal in ferroelectric thin films with dense-points poling state: phase imagine (a), amplitude imagine (b), (c-d) refer to the simulation of electric field distribution under the tip bias; the tip radius is 20 nm and is modeled as a sphere.

Section S2: Domain manipulation and stability with self-defined pattern using electric fields poling beneath the tip

Tip voltage was biased along the direction of the z-axis, leading to an obvious polarization reversal. Following this strategy, individual dot domains can be prepared reproducibly, as shown in Fig. 1b. This method is advantageous because relatively high electric fields focus on the tiny contact area and do not need preparation of any complicated electrodes. The same domain reversal could also be obtained by routing the tip bias along the self-defined patterns shown in Fig. S2.

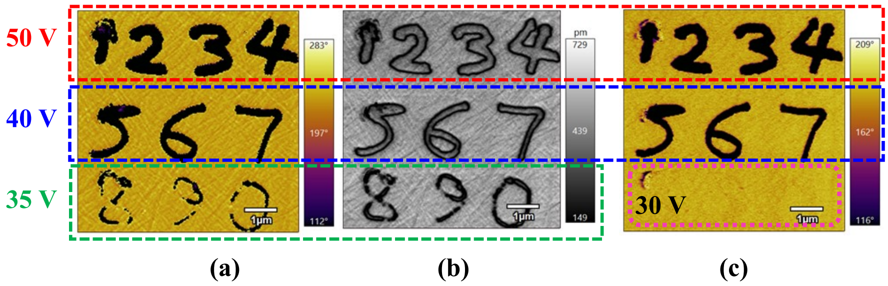

Fig. S2 Domain patterns using self-defined routes by tip bias.

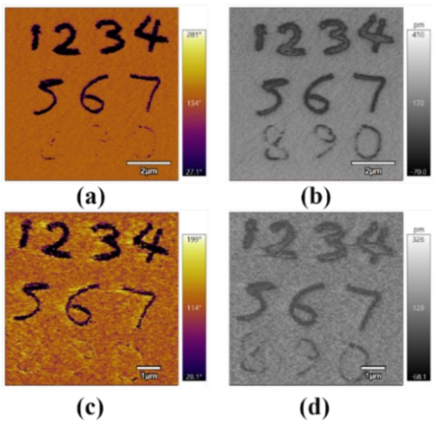

Fig. S3 (a–d) Retention property of the domain reversal, a and c refer to the retention of phase imagines after 28 days and 35 days, respectively, b and d refer to the corresponding amplitude imagines. Slight depolarization is observed under lower bias poling conditions.

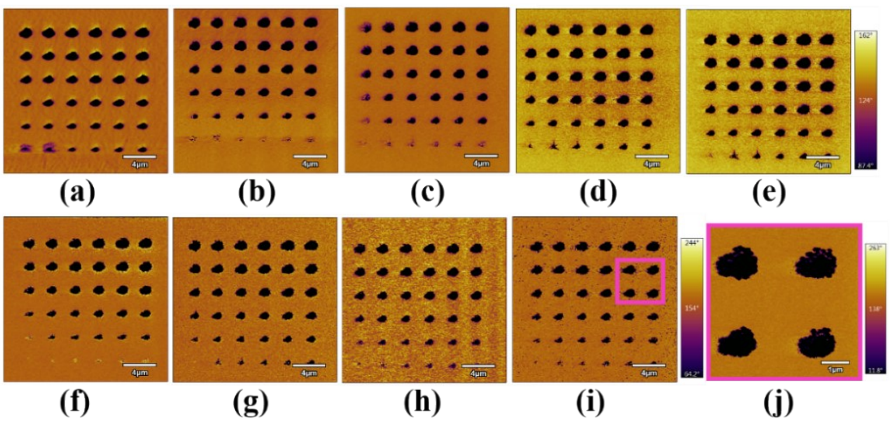

Fig. S4 Domain stability under various temperatures, (a-h) 27 °C, 47 °C, 67 °C, 87 °C, 97 °C 107 °C, 127 °C, and 147 °C, respectively, (i) refers to the domain pattern after cooling to room temperature again, and (j) refers to magnified area of room temperature (i), all of which show excellent temperature stability.

Section S3: Retention of dense poling in nearly square domain manipulation

Interestingly, when withdrawing the external DC bias, the out-of-plane phase contrast could still be observed within a time endurance of more than one month, which indicates the stability of domain reversal.

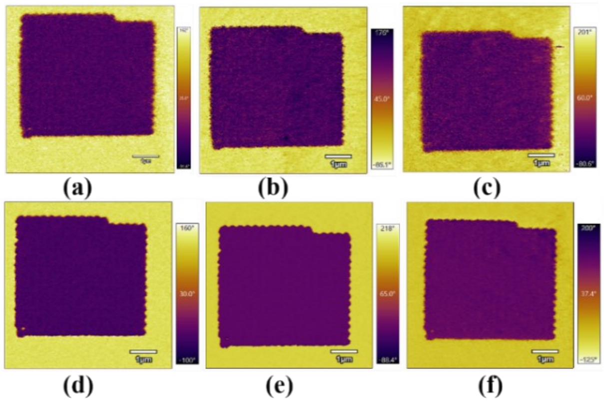

Fig. S5 Retention property of the domain reversal: (a-f) refer to the stable domain in various period of 40 h, 7 days, 15 days, 21 days, 30 days, and 34 days, respectively.

Section S4: Electric tunability of charged domain walls

Fig. S6 show the tunable conductivity of the DWs, leading to an increasing current with increasing voltage bias. In addition, CDWs are energetically unfavorable, and relaxation slowly into a less charged or uncharged state might be possible [1]. To determine if this phenomenon occurs in this specific DWs, c-AFM measurements were conducted directly without any other operation. The results are shown in Fig. 3, which exhibit stable conductivity along with a slight decrease in conductivity owing to the relaxation. The opposite charges might accumulate near the time endurance domain pattern to compensate for the domain boundary charge, leading to a decrease in the conductivity of the DWs [2].

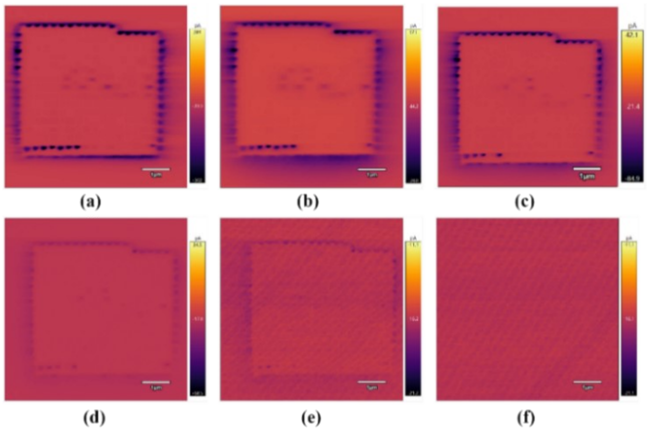

Fig. S6 Voltage dependence of current mapping: (a–f) refer to selected area under sample voltages of -9.5 V, -7.5 V, -5 V, -3 V, -1.5 V, and 1 V, respectively.

Section S5: Repeatability of formation of charged domain walls

To exclude the accidental influence on domain manipulation, we conducted repeated experiments and obvious conductive behavior was still observed, which reveals the reproducibility of the tip-poling method.

It should be noted that no accidental switching behavior was observed. There are spatial, point-to-point variations in the local conductivity, as shown in Fig. S7, which could be due to but not limited to the following facts: (a) the surface topographic features (contaminations) that affect the tip-sample contact resistance, (b) remanent domains left after poling or local polarization switching induced during c-AFM imaging, and (c) local variations in polarization magnitude due to defect structure as observed from the local hysteresis loops [3]. However, the variation is much smaller in principle compared with the difference in conductivity between the domains and DWs.

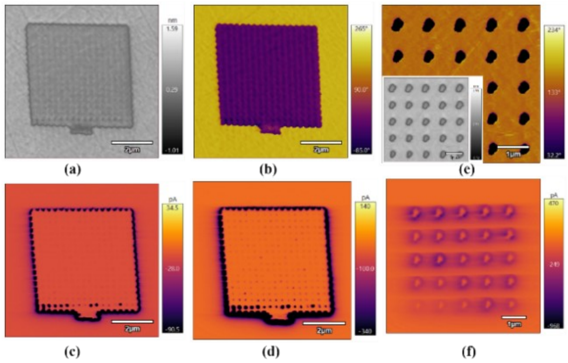

Fig. S7 Repeated poling utilizing tip-poling method: (a-b) amplitude contrast and phase images, (c-d) current image mapped at different sample bias of -5 V and -9.5 V, respectively. Dot arrays of phase images in the single-crystal film polarized by a tip bias of 50 V and duration of 0.1 s with an increasing step of 0.1 s (e); inset in (e) is the corresponding amplitude images, and (f) shows the current maps under a bias of -5 V.

Section S6: Erasing domain reversal

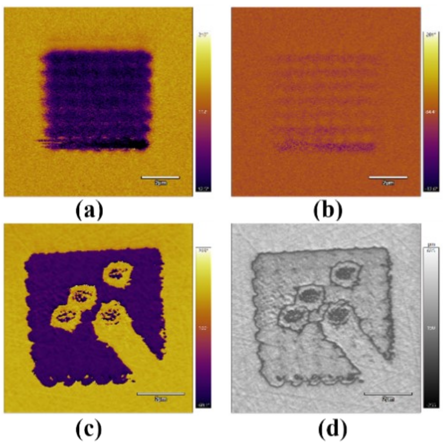

Fig. S8 Domain patterns under opposite poling bias: phase imagine of the as-write state in the switched state (a) and erasing with an opposite bias of -20 V (b), domain reversal of single-point poling with a triangle-square wave: phase contrast of (c) and corresponding amplitude image (d).

References

1. Godau C, Kämpfe T, Thiessen A, Eng LM, Haußmann A. Enhancing the Domain Wall Conductivity in Lithium Niobate Single Crystals. ACS nano. 2017;11(5):4816-24.

2. Jiang AQ, Zhang Y. Next-generation ferroelectric domain-wall memories: principle and architecture. NPG Asia Materials. 2019;11(1).

3. Rana A, Lu H, Bogle K, Zhang Q, Vasudevan R, Thakare V, et al. Scaling Behavior of Resistive Switching in Epitaxial Bismuth Ferrite Heterostructures. Advanced Functional Materials. 2014;24(25):3962-9.