Supplementary materials for

"First-Order Reversal Curve Probing of Spatially Resolved Polarization Switching Dynamics in Ferroelectric Nanocapacitors"

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I. BEPS-Relaxation

The FORC measurements presented here collect the polarization switching information directly after applying the bias pulse. The slope of the saturated portions of the reversal curves is zero from which one can conclude that the there is no contribution from unstable polarization switching. Therefore, the present approach based on FORC-BEPS measurements allows exploring polarization switching dynamics without unstable hysterons.

In order to check the stability of the switched domains, a relaxation measurement after each step in individual hysteresis loops was collected using dynamic switching spectroscopy PFM (D-SSPFM) in the same scanned area as Figure 8.[1] Figure S1c, d present the piezoresponse hysteresis loops of the D-SSPFM response over a 300 ms delay time after the application of each bias pulse. The entire piezoresponse hysteresis loops are nearly identical to each other at both domain regions (no relaxation). This indicates that the present results are sufficiently stable during the BEPS measurements. To analyze further the relaxation behavior, the analysis was performed by fitting to an exponential function,[1,2]

$$A_r(t) = A_{r1}\exp(-\frac{t}{\tau}) + A_{r0} \qquad (S1)$$

where A_{r0} is the non-relaxing component, A_{r1} is relaxation amplitude, and τ is decay time. All the values in the spatial map of A_{r1} show nearly zero relaxation amplitude which also indicates very stable switched states. [Figure S1b]
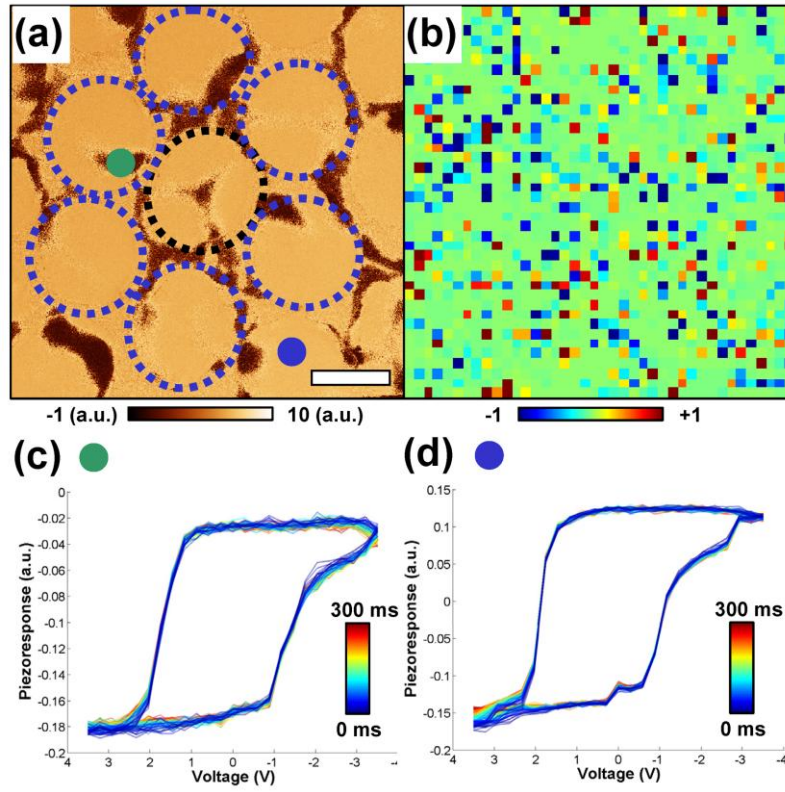
Figure S1. (a) PFM phase image of BFO nanocapacitors which is phase image of Figure 4b. (b) Spatial map of A_{r1} obtained by BEPS data fitted to eq S1. (c,d) D-SSPFM loops as a function of time delay illustrating relaxation dynamics at (c) green (upward domain region) and (d) blue (downward domain region) filled circles of figure a, respectively. Black and blue dashed lines mark the present capacitors. Scale bar represents 320 nm.

II. Adapted KAI model

The switchable polarization P_S map of Figure S2a was also similar to the work of switching A_S map of Figure 8d. The geometric dimension n of the domain wall motion was between 2 and 3. The activation voltage V_0 was in the range between 15 V and 20 V which can be rewritten as an actual activation electric field between 1.25 and 1.8×10^8 V/m. Even though the obtained values were very similar to those of Figure 8, overall images are rather noisier due to the single point data analysis of the switched polarization.
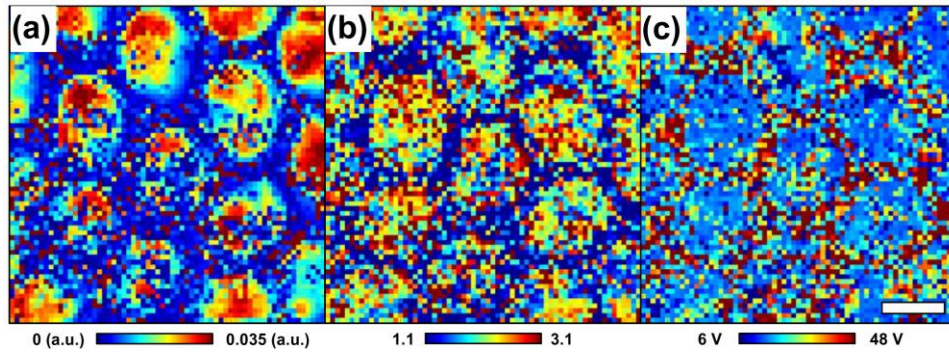

0 (a.u.)   0.035 (a.u.)   1.1   3.1   6 V   48 V

Figure S2. Spatial maps of KAI coefficients: (a) P_S, (b) n, and (c) V_0 of piezoresponse curve at local minimum voltage $V_{i,\min}$ which was obtained from switching polarization variation using eq 4. The distributions of the obtained values show similar features with those from eq 5 in Figure 8. Scale bar represents 320 nm.

REFERENCES

[1] Kumar, A.; Ovchinnikov, O. S.; Funakubo, H.; Jesse, S.; Kalinin, S. V. Real-Space Mapping of Dynamic Phenomena during Hysteresis Loop Measurements: Dynamic Switching Spectroscopy Piezoresponse Force Microscopy. *Appl. Phys. Lett.* **2011**, *98*, 202903.

[2] Rodriguez, B. J.; Jesse, S.; Kim, J.; Ducharme, S.; Kalinin, S. V. Local Probing of Relaxation Time Distributions in Ferroelectric Polymer Nanomesas: Time-Resolved Piezoresponse Force Spectroscopy and Spectroscopic Imaging. *Appl. Phys. Lett.* **2008**, *92*, 232903.