Supporting Information

Manipulating Ferroelectrics through Changes in Surface and Interface Properties

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1) X-ray diffraction before and after annealing

After annealing of the ferroelectric $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT) thin film, X-ray diffraction showed no change in lattice parameters (Fig. S1). Therefore, we conclude that the oxygen vacancies introduced through the annealing process result in surface-near changes in oxygen vacancy concentration only.

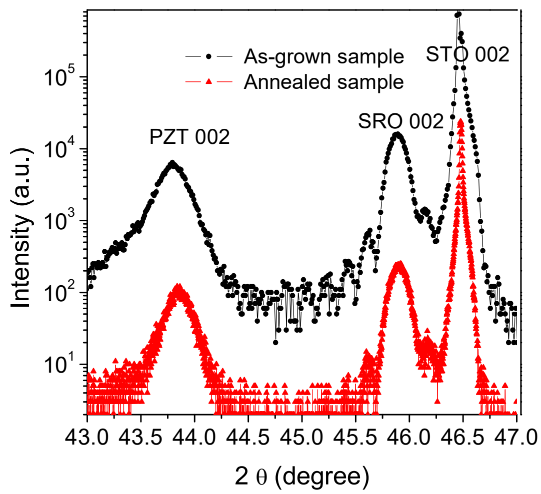

Figure S1. X-ray diffraction of as-grown PZT/SRO sample and sample after annealed at 10 mTorr and 380 ºC.

2) Procedure to investigate domain retention of differently oriented domains

The ferroelectric films grown on SRO or LSMO show a mono-domain state oriented along the so-called as-grown polarization orientation. Domains aligned in opposite direction can be easily studied by switching them locally with the tip within the as-grown domain matrix (bright domains in dark matrix in Fig. S2. However, if domains the as-grown polarization direction itself need to be studied, it was necessary to pole a bigger area to create a domain matrix of opposite direction. The nanodomains were then switched and studied in the middle of the poled area (dark domains in bright matrix in Fig. S2).

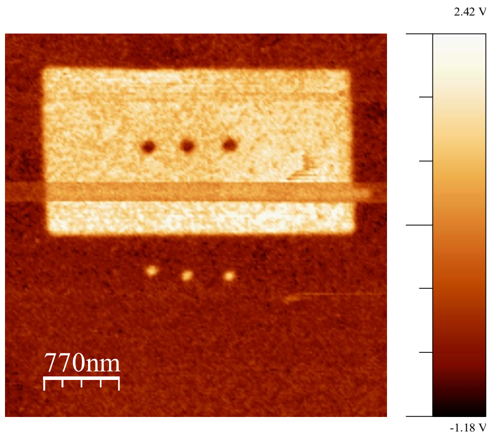

Figure S2. PFM phase image for PZT/SRO/STO explaining the procedure to study retention properties for differently oriented domains.

3) Temperature dependent retention properties of PZT/SRO

In the case of PZT grown on $SrRuO_3$ (SRO) as bottom electrode, the retention properties of ferroelectric domains pointing up and down do not show any temperature dependence as shown in Fig. S2.

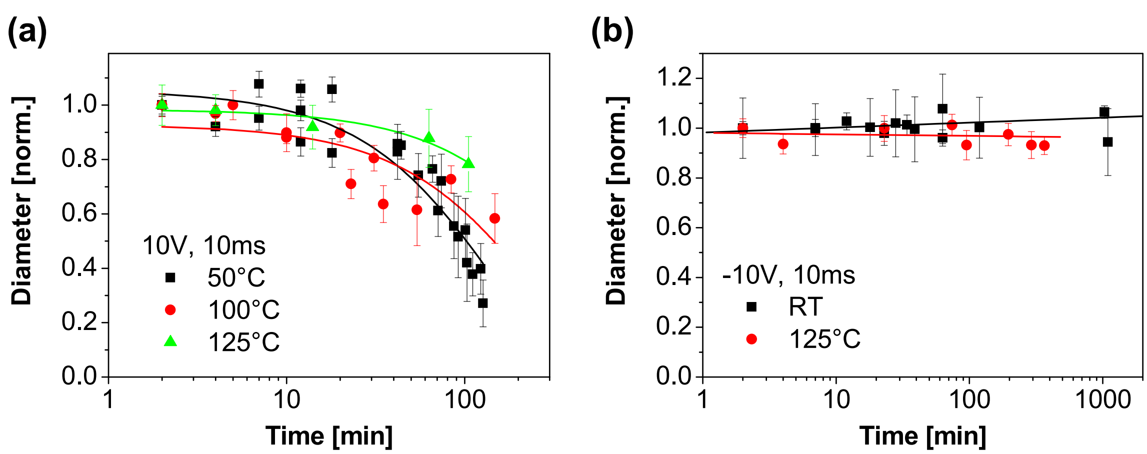

Figure S3. Temperature-dependence of domain size as function of time for PZT/SRO with domains switched to (a) downwards and (b) upwards from the opposite initial domain polarizations.

4) Temperature and size dependent retention properties of PZT/LSMO

In the manuscript it was shown, that the domain stability for domains switched in PZT/SRO depend strongly on the domain size (Fig. 4), whereas the stability of domains in PZT with $(La_{0.7}Sr_{0.3})MnO_3$ (LSMO) as bottom electrode is size independent (Fig. 5). This is not only true for measurements at room temperature but for also for the domain stabilities measured at higher temperatures up to 125ºC.

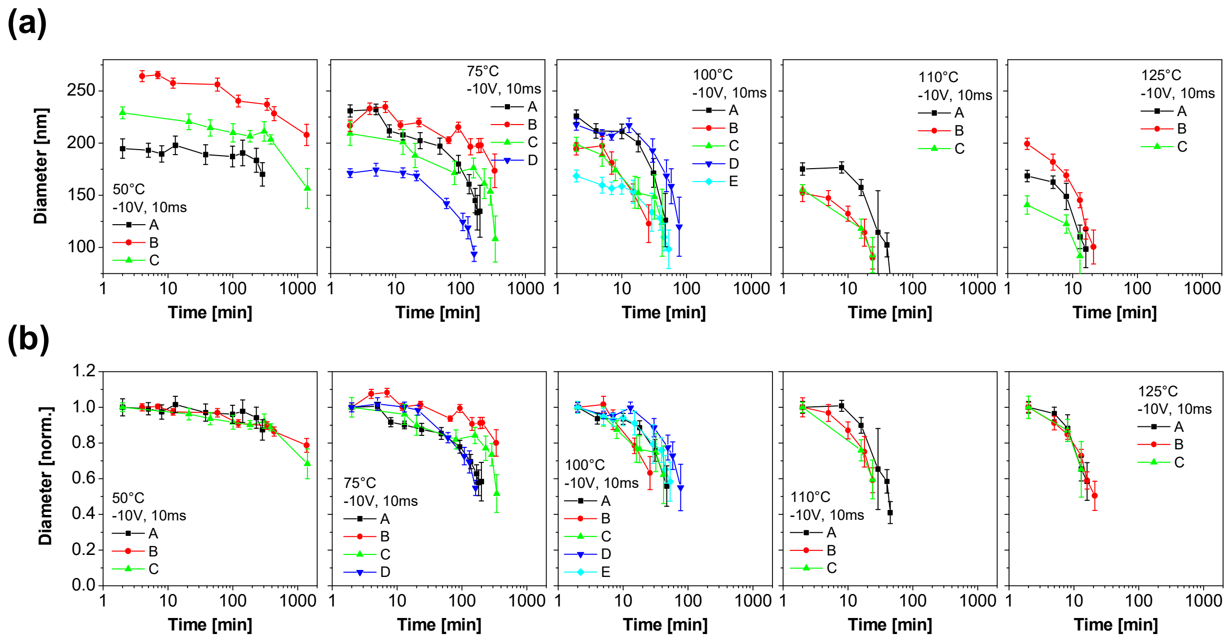

Figure S4. Temperature-dependence of domain size as function of time for PZT/6 nm LSMO/SRO after polarization switched to upwards with negative voltages. Each panel represents multiple repetitions of the same experiment. The measurement temperatures increase from left to right. (a) Displays the data on the x-axis nm whereas in (b) the domain sizes are normalized by the initial domain size after switching.