Supporting Information

Improved ferroelectric switching endurance of La-doped $Hf_{0.5}Zr_{0.5}O_2$ thin films

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S1. Calculation of the coercive fields for two domain groups in HZLO and HZO films after RTP at 450 °C

As it was mentioned in the main text, the observed current response showed that multiple components were involved for the HZLO film, even in the awakened state (after 10^5 switching cycles), which could be attributed to the presence two groups of ferroelectric domains with different built-in biases. Similar phenomenon was reported for La:HfO_2 film previously[1]. The current responses of the HZLO and HZO thin films were presented in Fig. S1. It can be seen that the measured current response for the HZLO film could be fitted according to this assumption. As a result, two well-distinguishable peaks were present in both the positive and negative electric field regions. There were small additional current peaks, which may be associated with the presence of the AFE phase. The first group of ferroelectric domains can be characterized by two peaks maxima: the switching field (E_{s1}) and back-switching field (E_{bs1}), and the second one can be characterized by the switching field (E_{s2}) and back-switching field (E_{bs2}). The main criteria of the proposed fit were the conservation of the total charge in each domain group (the area under the peak corresponds to the switched charge). Interestingly, the E_{bs1} and E_{bs2} of the HZO film were almost identical. When the switching (E_{s1} and E_{s2}) and back-switching (E_{bs1} and E_{bs2}) fields for both domain groups were known, coercive fields (E_{c1} and E_{c2}) for each domain group could be calculated according to the formula:

$$E_{c1} = \frac{E_{s1} - E_{bs1}}{2}; \qquad E_{c2} = \frac{E_{s2} - E_{bs2}}{2} \qquad \text{(S1)}$$

The estimated E_s and E_{bs} values of the two domain groups of the HZLO and HZO films annealed at 450 °C in the awakened state (after 10^5 switches) and the calculated coercive fields E_{c1} and E_{c2} were presented in Table S1. $E_{bs1} = E_{bs2}$ was assumed for the case of HZO.

It should be noted that such procedure aimed to justify the hypothesis of built-in bias fields, approximately estimate the coercive field for both domain groups, and compare the coercive fields between HZLO and HZO films. A deeper analysis of switching domains evolution during wake-up process within the framework of the Preisach model was presented in the section S2 “FORC measurements” below.

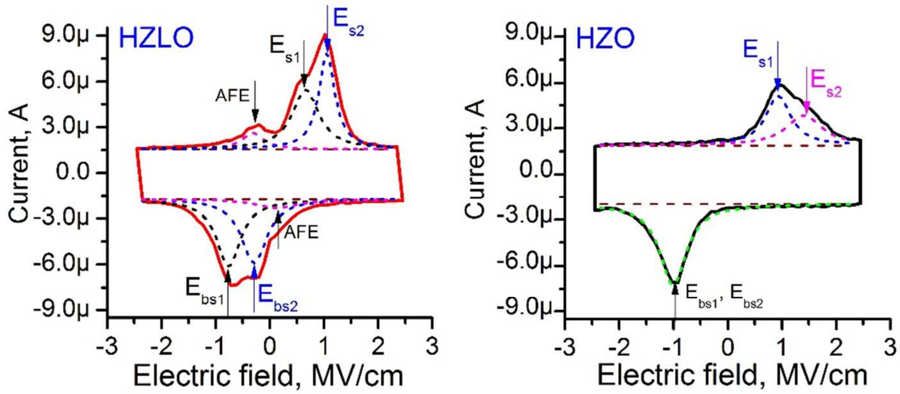

Fig. S1. I_s-E curves for stacks based on HZLO and HZO films after RTP at 450 °C in the awakened state (after 10^5 switching cycles). Dash arrows indicate switching (E_s) and back-switching (E_{bs}) field for both domain groups.

Table S1 Extracted from Fig. S1 E_s and E_{bs} of the two domain groups of the HZLO and HZO films annealed at 450 °C in the awakened state (after 10^5 switches) with calculated coercive fields E_{c1} and E_{c2}.

Film	E_{s1}, MV/cm	E_{bs1}, MV/cm	E_{c1}, MV/cm	E_{s2}, MV/cm	E_{bs2}, MV/cm	E_{c2}, MV/cm
HZLO	0.7	-0.8	0.75	1.2	-0.4	0.8
HZO	0.9	-1.0	0.95	1.4	-1.0	1.2

It is worth to notice also that hysteresis loops obtained from HZLO film and HZO films (in the awakened state, after 450 °C annealing), which are presented in Fig. S2, clearly confirm that "average" coercive field is significantly lower for HZLO film compared to HZO.

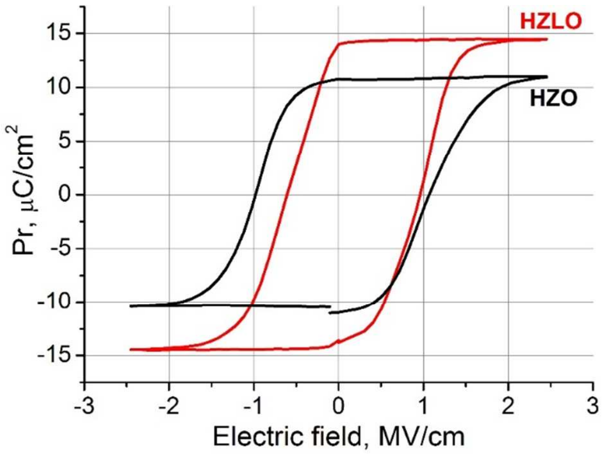

Fig. S2. P-E curves for stacks based on HZLO and HZO films after RTP at 450 °C in awakened state (after 10^5 switching cycles).

S2. FORC measurements

Within the framework of the Preisach model, the total $2P_r$ value can be obtained by integrating the switching current from different grains with their own switching (E_s) and back-switching (E_{bs}) fields, which are called hysterons and characterized by the switching density (ρ). The involvement of different hysterons in the polycrystalline film is induced by different crystallites that are subjected to different local environments and electric fields. Accordingly, the shift in the P_r-E characteristics of a particular grain could occur. To obtain the switching density (ρ) experimentally, it was assumed that charge passing through the ferroelectric capacitor when ramping the voltage from ν_1 to ν_2 (with $\nu_1<\nu_2$) is described by the following equation:

$$Q = \int_{-\infty}^{\nu_1} \int_{-\infty}^{\nu_2} \rho(\nu_l, \nu_h) \times \sigma(\nu_l, \nu_h) d\nu_l d\nu_h \qquad \text{(S2)}$$

where $\rho(\nu_l, \nu_h)$ is the switching density, which characterizes the ferroelectric properties, and $\sigma(v_l, v_h)$ is a state field with values of $\{-1, +1\}$ at each point, which describes film polarization. During such voltage ramping, every point with $v_h < v_2$ changes its value to +1, while values at other points remain unaffected. The analogous rule applied to $v_2 < v_1$. A series of measurements of switching charges at different pairs (v_1, v_2) were performed, and then, Moore-Penrose pseudoinverse was used to solve the integral equation (S1) for the switching density (ρ). Values of σ, which form the kernel, should also be known. They could be established experimentally by starting at the state with all polarization states facing down and then applying the rule described above. To increase the signal-to-noise ratio and reduce the number of stimuli required to recover ρ, a regularization procedure with a regulator induced by the Laplacian of the switching density was adopted. It was also assumed that $\rho(v_l, v_h) = 0$ for $v_h < v_l$, which is an adequate physical assumption.

If $E_s(v_h)$ and $E_{bs}(v_l)$ and related ρ are known from the experiments, the following coordinate transformation can be applied to analyse the ferroelectric hysterons in the film regarding its own effective coercive field (E_c) and effective electric bias (E_{bias})[2,3]:

$$E_c = \frac{E_s - E_{bs}}{2}, E_{bias} = \frac{E_s + E_{bs}}{2} \qquad \text{(S3)}$$

The last one reflects the shift of the ideal symmetrical P_r-E curve along the E axis due to the presence of the local internal field.

S3. DC-IV characteristics of HZLO and HZO films

The DC current density – electric field (J – E) characteristics of the HZLO and HZO films after RTP at 450 °C revealed that the HZLO film has a current density considerably lower (≈1×10^{-8} A/cm^2) than that of HZO (≈1×10^{-5} A/cm^2) at 1 MV/cm (Fig. S3).

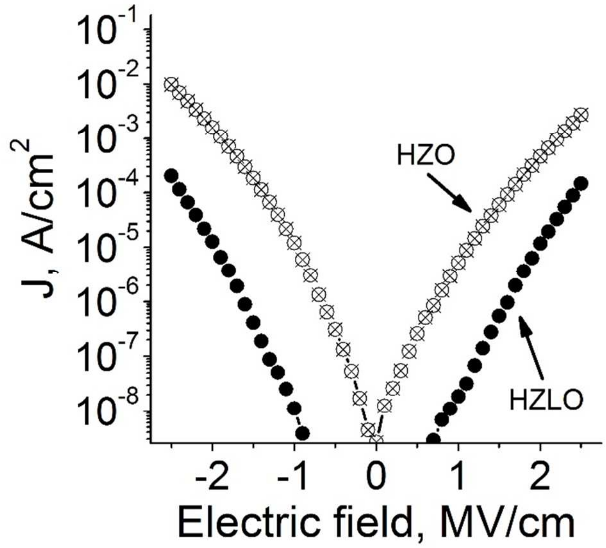

Fig. S3. J-E characteristics for stacks based on HZLO and HZO films after RTP at 450 °C in awakened state (after 10^5 switching cycles)

References

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