Supporting information

Genuinely ferroelectric sub-1-volt-switchable nanodomains in $Hf_xZr_{(1-x)}O_2$ ultrathin capacitors

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Supporting Note 1. Preparation of samples

For this study a series of HZO films with thickness ranging from 7 to 30 nm has been grown by atomic layer deposition (ALD) on Si/SiO_2/TiN substrate stack according to the earlier reported procedure (Ref 28. from the main text). After sputtering 12nm top TiN electrode the multilayer structure was annealed at 600°C in N_2 atmosphere. The sample preparation was completed by sputtering 20nm top layer of Pt and patterning capacitors by photolithography followed by wet etching. Figure S1a represents the schematic cross-section of the resulting capacitor structures, the lateral size of the individual capacitors varied from $50x50\mu m^2$ for the electrical characterization to $5x5\mu m^2$ for PFM analysis. Polarization loops measured using the standard virtual ground circuitry with a commercially available AixACCT ferroelectric tester exhibit hysteretic behaviour as typical for the state-of-art HZO capacitors, with the remnant polarization of 18, 20 and 7 $\mu C/cm^2$ for HZO film thickness of 7, 10 and 30nm, respectively (Fig. S1b). The sharpest hysteresis loop with highest value of remnant polarization was measured on the 10nm layer, which is in line with the reports indicating that this thickness is optimal for ferroelectric phase stabilization. Prior to the experiments presented in this study all capacitors have been cycled with 10000 alternating polarity voltage pulses of 3V/1ms in order to stimulate the wake-up process and ensure that no additional bias-driven phase transition occurs during the measurements.

Supporting note 2. Off-resonance PFM measurements

For measuring local piezoresponse and probing nanometer-size polarization domains we used the PFM technique, which has been adapted for thin film capacitors with extremely weak piezoresponse. The most estabished PFM technique that has been adopted as a standard since early 2000s is resonance PFM, where the cantilever movement is detected at a frequency close to the resonance. Different approaches such as dual AC resonance tracking (DART) or band excitation (BE) are used in order to closely track the resonance frequency during the PFM measurements. The advantage of resonant PFM is obvious: the measured signal is 1-2 orders of magnitude stronger compared to the off-resonance signal. Apart from improved sensitivity this allows for fast data acquisition (useful for collection of large arrays of loops e.g. for PFM spectroscopy). On the downside, the tip-sample interaction near the resonance can be difficult to analyze as the results may depend on the parasitic non-local probe-sample interactions and/or resonance tracking accuracy. Such phenomena can become critical for sub-10nm HfO_2 with the longitudinal piezoelectric coefficient d_{33} of 3-5pm/V or less. In this context, the use of frequency-independent off-resonance PFM represents a significant simplification and allows for a more straightforward analysis of the piezoresponse signal.

The off-resonance PFM, which has been widely used in 1990s, at the early stage of PFM development, is a relatively simple technique. In this method the tip is driven with AC or AC + DC voltage with the frequency that can be arbitrary chosen without approaching the system's resonance frequency. The choice of frequency is only limited by the electrical circuitry and RC-constant, so that the PFM results (both qualitative and quantitative) have to be basically frequency-independent, which is an important criterion of credibility of the measurements. The interpretation of the results in this case is generally more straightforward than in resonance PFM, in particular the amplitude of the tip deflection can be easier calibrated to directly quantify the effective transverse piezoelectric response. The obvious disadvantage of the technique is a relatively low amplitude of detected piezoelectric signal, which dictates using very long times of data acquisition and consequently very slow measurements (typically one to two orders of magnitude longer compared to the standard DART measurements).

All PFM data from the present work were collected using the off-resonance PFM in the capacitor geometry. The experiments were carried out using Asylum Research Cypher AFM system, with the external Zurich Instrument lock-in amplifier unit. For these experiments we used Pt-coated conductive cantilevers from MikroMasch with the tip radius <50nm and nominal spring constant 42N/m. Such extremely high spring constant is essential in order to minimize the nonlocal electrostatic interaction between the sample and cantilever. On the other hand, such stiff cantilevers require a very small deflection for the contact mode operation on order to protect the metallization on the tip.

In order to prove that an electrostatic contribution does not influence the measurements we studied a series of non-ferroelectric samples where d33 has a weak field dependence. Specifically, we used amorphous HfO2 films with extremely weak d33 and Sc-doped AlN films with d_{33}=6-6.5pm/V as confirmed by double-beam interferometry. On these samples we have prepared 5x5um^2 capacitors similar to our HZO samples.

The results of tests were consistent with the assumption that no electrostatic contribution was detected in our PFM experiments. For both reference samples the field-on and field-off data did not differ. Furthermore, for Sc:AlN sample both field-on and field-off measurements yielded the same d_{33} value of 6 pm/V as the data from the double beam interferometer (with data scattering < 5%).

For PFM measurements performed off resonance one of the key criteria of reliability is the frequency-independence of results within a wide frequency range. Therefore, for each sample investigated in this study we routinely performed PFM loop measurements at three frequencies (all of them being lower than the contact resonance frequency): 12 kHz, 92 kHz and 230 kHz. The choice of these specific frequencies was done based on the noise analysis, similar results could be obtained using other frequencies, with slightly varying noise level. Figure S2 shows the loops of effective d_{33} piezoelectric coefficient and phase of local piezoresponse for 10nm HZO capacitors at different frequencies. The measurements were done on the same spot consequently at AC signal frequencies of 12kHz **(a),** 92kHz **(b),** and 230kHz **(c)**. The AC amplitude was fixed at 0.5V for all measurements. The data for all three frequencies closely reproduce the same fine features of switching behavior and show very close amplitudes of the piezoelectric response. The phase change between the two opposite switched states is close to 180° suggesting that neither dynamic effects nor leakage conduction influence the measured loops.

Electromechanical displacement quantification is one of the most delicate parts of PFM data analysis. Within the off-resonance technique one can assume that the cantilever displacement measured by the sensor directly represents the movement of the material. This assumption is supported by following experimental observation:

-the amplitude of the piezoelectric response in nearly frequency-independent;

-the amplitude of the piezoelectric response is insensitive to the position of the laser spot on the cantilever.

In our study the calibration of cantilever displacement was done based on the reference sample data. As reference samples we have chosen capacitors made of two layers of scandium-doped AlN with thickness of 15nm, 50nm and 100nm, prepared by pulse laser deposition (kindly provided by group of Prof. Paul Muralt). This non-switchable material has relatively low and stable d_{33} of 6-6.5pm/V, which has been carefully measured using the double-beam laser interferometer. PFM measurements on the reference capacitors yielded the calibration factor of 14mV/nm (i.e. 14 μV/pm). In alternative approach, a very close height-to-voltage conversion factor (with the error <5%) was obtained by converting the static deflection signal obtained from the calibration grating with z-feedback disabled.

Knowing the calibration factor (14 μV/pm) we converted the measured piezoresponse amplitude to the displacement in pm. Then, knowing the AC driving voltage amplitude (e.g. 0.5V for 10nm sample) we calculated the effective d_{33} coefficients. The d_{33} values calculated this way appear in Figures S2, S3, as well as in Figures 1-5 in the main manuscript.

Supporting note 3. PFM data for 30nm HZO capacitors

PFM maps collected on the 30nm HZO capacitor exhibited the same essential features as 10nm HZO capacitor shown in Fig.2 in the main manuscript. Fig. S3 shows the topography (a) and PFM data (b,c) for the 30nm capacitor in the partially poled state, which was prepared as follows: the capacitor was poled with the tip voltage of -6V/1sec, then partially switched with + 2.5V/1sec. Both amplitude (Fig. S3b) and phase (Fig. S3c) images show polarization domains, however the amplitude and phase maps appear to be slightly less sharp compared to the other two capacitors shown in Figs. 2,3 in the main manuscript. This difference is understandable considering the fact that the 30nm HZO is close to the phase transition. This implies a lower polarization, wider domain walls and presence of inclusions of the non-ferroelectric phase (the regions where the transition has already occurred). All three effects represent additional complications for PFM imaging and can contribute to some smearing of the amplitude and phase maps.

Supporting note 4. Minimization of thermal drift during the series of slow scans.

Because our PFM data were collected in sequences of slow scans, keeping the thermal drift under control was our priority. To minimize the drift, the full setup including the sample, cantilever and cabling was always prepared at least 24h before the experiment starts. Then some “trial scans” with the same parameters as our experiment were performed in order to reach the best possible stability of the system. As a result, we were able to keep the drift < 5% within the time required for 4-5 scans, 4 hours each. Figure S4 shows two topography images corresponding to the PFM scans (b) and (d) in Fig. 2. The second one was saved >14hours after the first one. By comparing the position of the most prominent topography features (marked with red) one can estimate the impact of the thermal drift, which is rather limited.

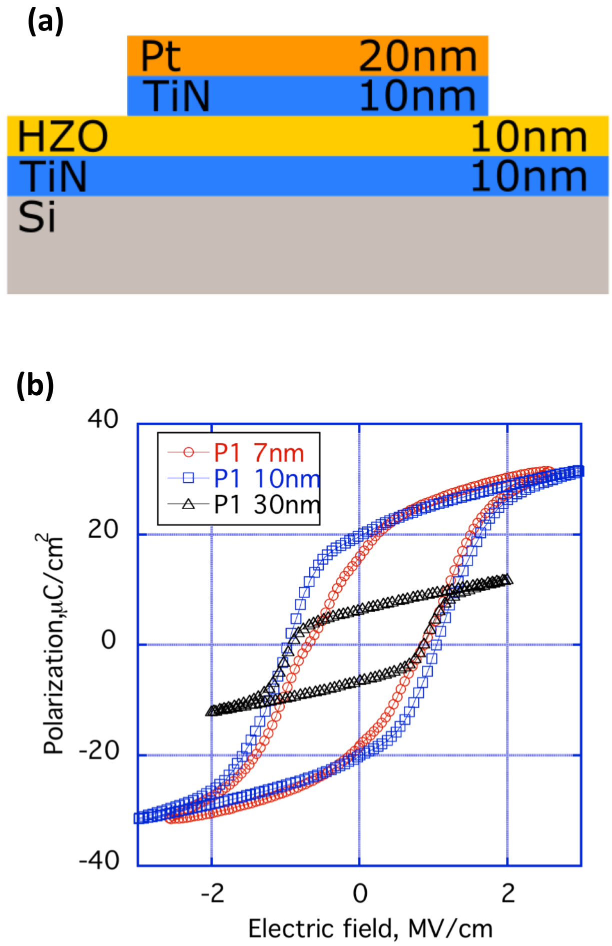

Figure S1. **a,** Schematic cross-section of the HZO capacitors used for the experiments. The top electrode size was 5x5μm^2 for the PFM analysis and 50x50μm^2 for P-V loop measurements. **b**, Polarization hysteresis loops measured on HZO capacitors with thickness of 7, 10 and 30nm at 1kHz.

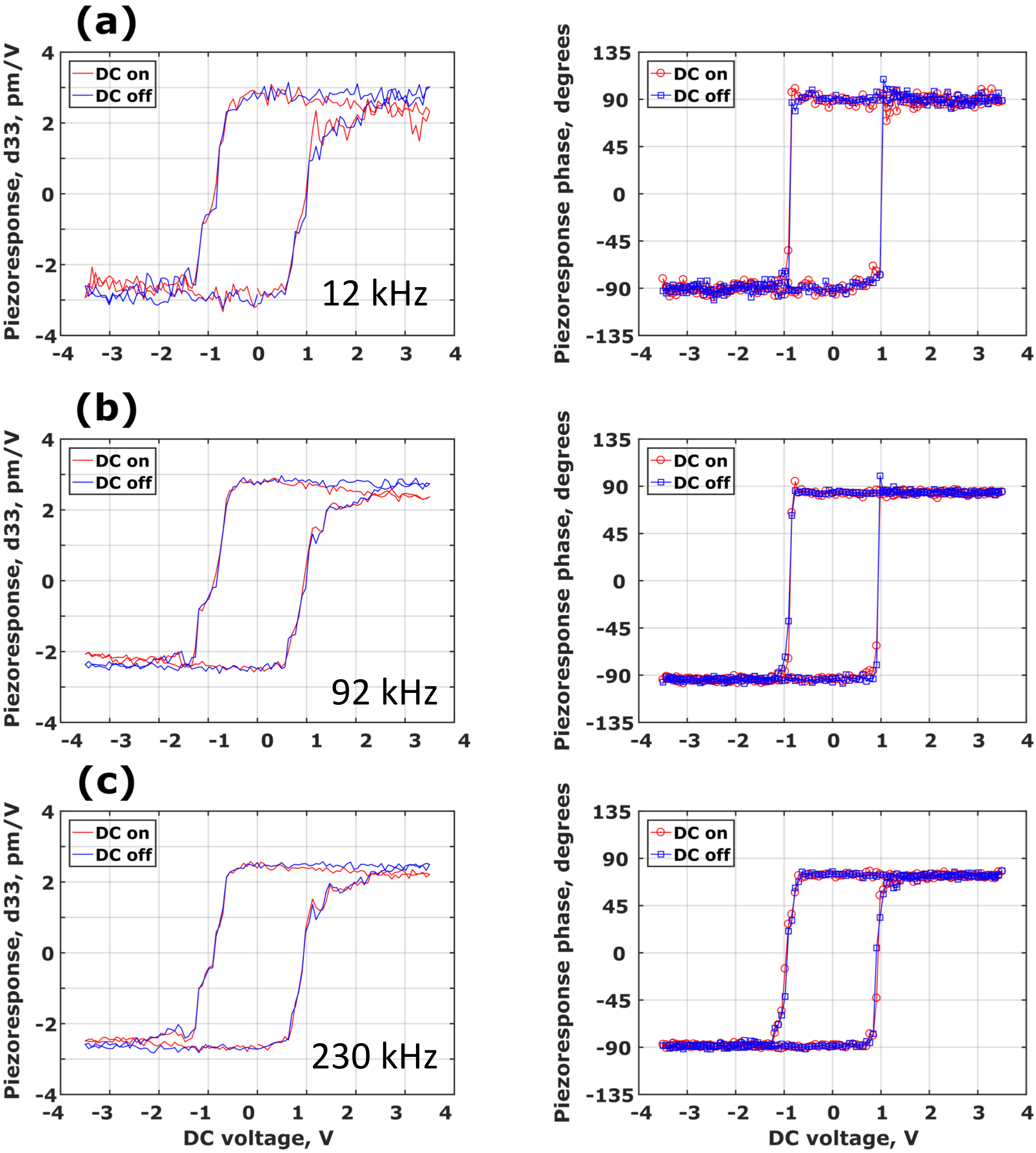

Figure S2. Loops of effective d_{33} (left) and phase of local piezoresponse (right) for 10nm HZO capacitors measured on the same spot at AC signal frequencies of 12kHz **(a),** 92kHz **(b),** and 230kHz **(c)**. The AC amplitude was 0.5V for all measurements. Effective d_{33} was calculated based on the calibration procedure described in the Supporting note.

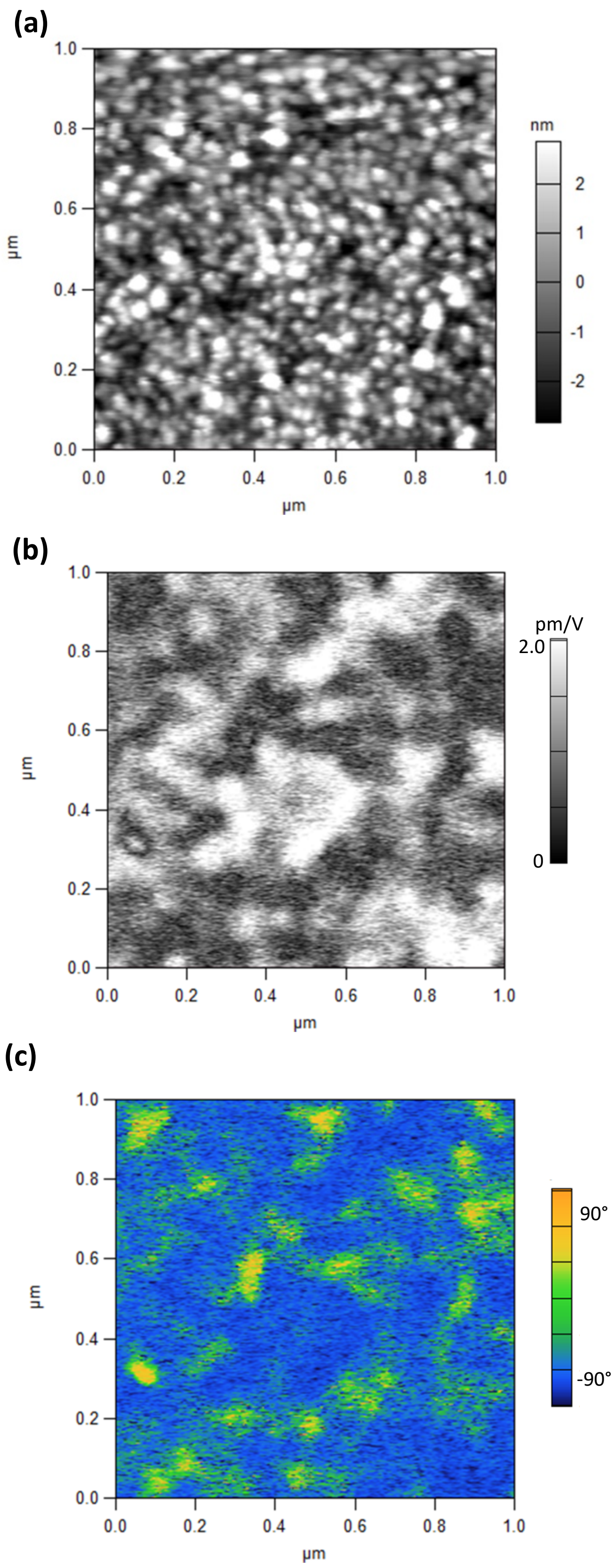

Figure S3. 1x1μm^2 AFM/PFM scans of topography **(a)**, piezoelectric response amplitude **(b)** and phase **(c)** for the 30nm HZO capacitor in the off-resonance mode. The AC signal amplitude was 0.8V/92kHz.

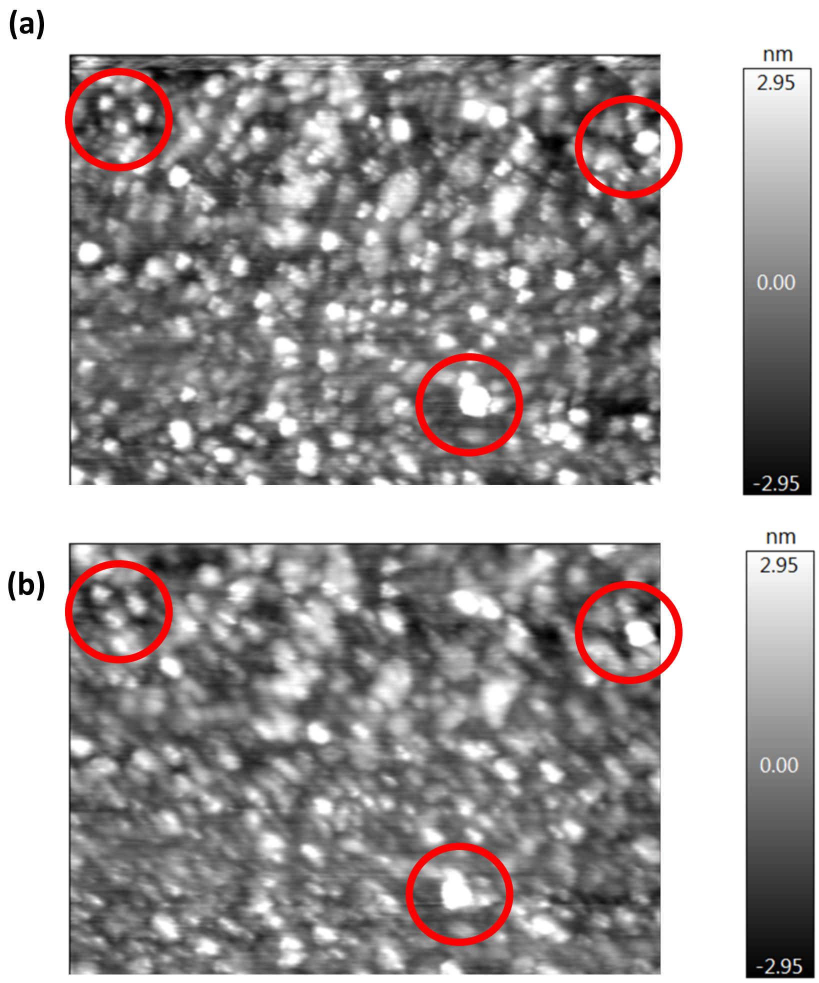

Figure S4. 1x1.4μm^2 topography images measured concurrently with the PFM data shown in Figs 2b and 2d in the manuscript. The delay between acquisition of the two topography images (a) and (b) was >14 hours. The very small change in the position of the prominent topography features marked with red circles shows that there was no significant thermal drift.