Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Flexoelectric Effect in Al-doped Hafnium Oxide

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Methods

The Al doped hafnia films were deposited on HF cleaned 300 mm Silicon wafer (highly doped p-type 10^{20} at/cm^3). The amorphous Al:HfO_2 layer was grown by atomic layer deposition (ALD) using $HfCl_4$, Trimethylaluminum $Al(CH_3)_3$ and H_2O as oxidant (Hf:Al=34:1 pulse ratio) with the reactor at a temperature of 300 °C. The Al:HfO_2 films, having an atomic concentration of 7% at. Al, were capped with 20 nm amorphous Si and crystallized by thermal annealing for 1 min at 850 °C. As conductive top electrode, a ca. 55 nm P doped poly-Si was deposited and finally the film is recrystallized by thermal annealing for 1 min at 850 °C. Furthermore, grazing incident X-ray diffraction and X-ray reflectivity are performed to study the crystalline phases in the material and assess the thickness of the deposited layers. The TEM analysis is performed on a FEI Titan operating at 300kV. For the observation of the surface morphology, standard high aspect ratio Silicon tips (Nanosensor PPP-NCHR) have been used on a Bruker Icon AFM, performing tapping mode, while Pt/Ir tips (k = 7.2 N/m) have been used for C-AFM measurements. Polarization imaging has been performed using Piezoresponse Force Microscopy in an environmental-scope from (e-scope, Bruker) operated in high vacuum (10^{-5} mbar). For all the measurements, in-house developed conductive diamond tips (k = 10 N/m) have been used. For the PFM read-out a DC bias is superimposed on a modulation bias with amplitude 3 $V_{p\text{-}p}$ at 50 kHz. Tip contact forces are calibrated by measuring force-distance curves. Polarization hysteresis loops were obtained by dynamic hysteresis at a 4 kHz frequency by applying a triangular signal (ramp rate fixed at 10μs/V), in capacitors with diameter 100 μm. The value of the coercive field is extracted assuming that the film thickness is 15 nm and that the switching voltage extracted from the Polarization-hysteresis loops is 4 V neglecting shift induced by the different work functions of the electrodes.

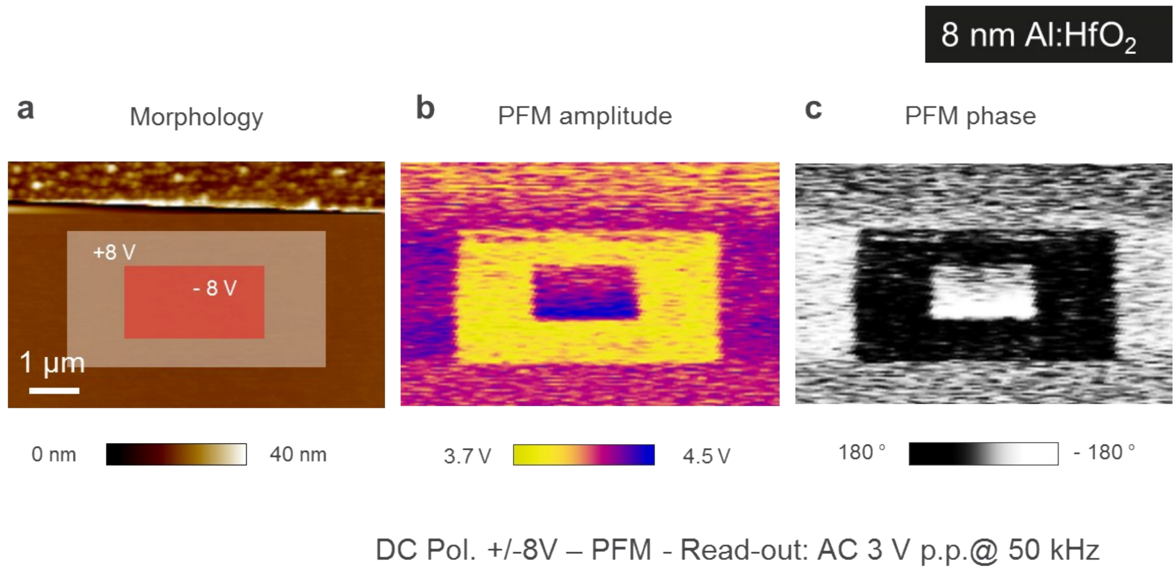

Figure S1 | Appearance of stable ferroelectric in 8 nm-thick Al:HfO_2. Out-of-plane piezoresponce force microscopy shows the morphology (a) amplitude (b) and phase signal (c) of a domain pattern written on a 8 nm-thick Al:HfO_2. The layer is polarized by a DC bias applied by the scanning AFM tip according to the biasing scheme reported in the inset of (a). Similar to the conditions described in the main text, we use a Pt/Ir coated tip which is grounded while the bias is applied to the sample. The application of +/- 8 V DC bias leads to the formation of a stable and reversible electrical polarization as visible in figure (b,c).

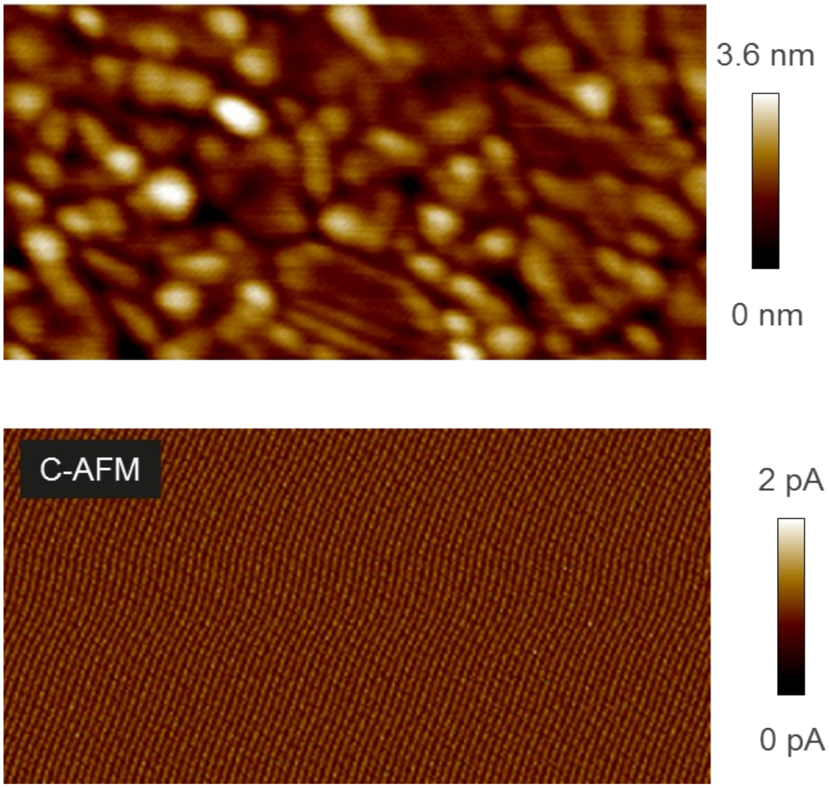

Figure S2 | C-AFM leakage current in 15 nm-thick Al:HfO_2. To exclude any possible role of local charge injection during the PFM polarization, we monitor the electronic current flowing in the tip-sample system by C-AFM (1 pA current sensitivity). The latter is achieved by combining the PFM with a C-AFM setup, therefore selecting a different sensing amplifier respectively lock-in or linear transimpedence. While the crystalline morphology of the sample is clearly visible in topography, no current leakage is detected in the area during the +/- 8 V polarization as visible in the C-AFM current map showing only the noise level of the amplifier (scan area 500 x 250 nm). The same level of leakage is observed also during high force scans used for pressure-induced polarization reversal.

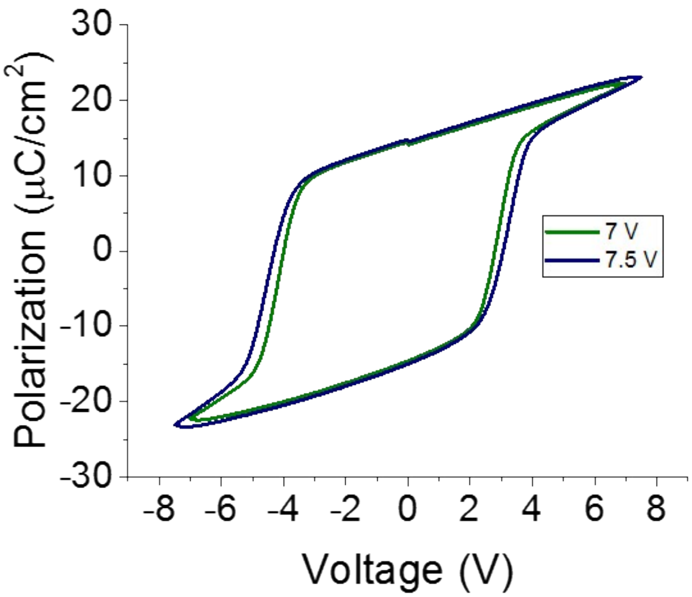

Figure S3 | Dynamic piezoelectric hysteresis loop. Dynamic piezoelectric hysteresis loop are acquired on capacitors of size (100 μm diameter). From the window observed in the graph, we can extract a coercive field in the order of 2.6 MV/cm which in our case needs to be comparable to the one induced by the flexoelectric field when the tip-induced reversal is induced. Therefore, considering our observation of Fig. 2b (main text) a comparable value is induced at a load force of 100 nN which is the minimum value to measure the polarization reversal. Note that the leakage observed in the P-V curves can be ascribed to the larger size of the capacitors compared to the tip-sample system (orders of magnitudes smaller) for which we do not sense electrical losses (1 pA resolution).

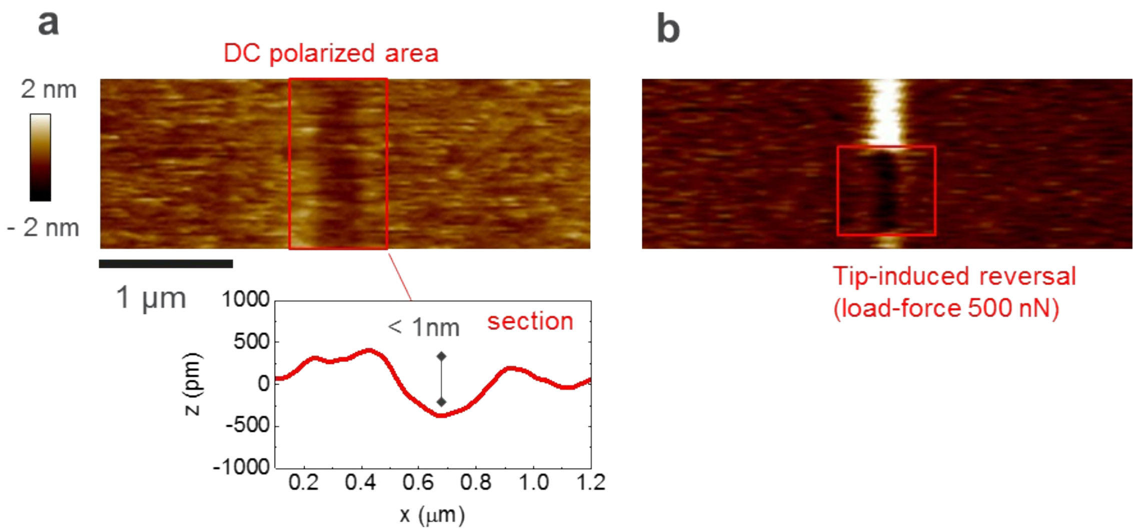

Figure S4 | Impact of tip-induced reversal on the surface morphology. The surface morphology (a) and PFM amplitude (b) show the effects of pressure-induced polarization reversal on the material using a load force ca. 500 nN. As visible, a reduced < 1nm removal of material is observed in the region which is electrically polarized by the tip (red box in a). In comparison, the portion of surface which is reversed by tip-induced pressure shows a negligible material removal (red box in b). The latter indicates that the material is removed already during the static DC polarization phase, and not during the pressure-induced reversal. A very distinct situation is visible in Fig. S5 using forces over 500 nN.

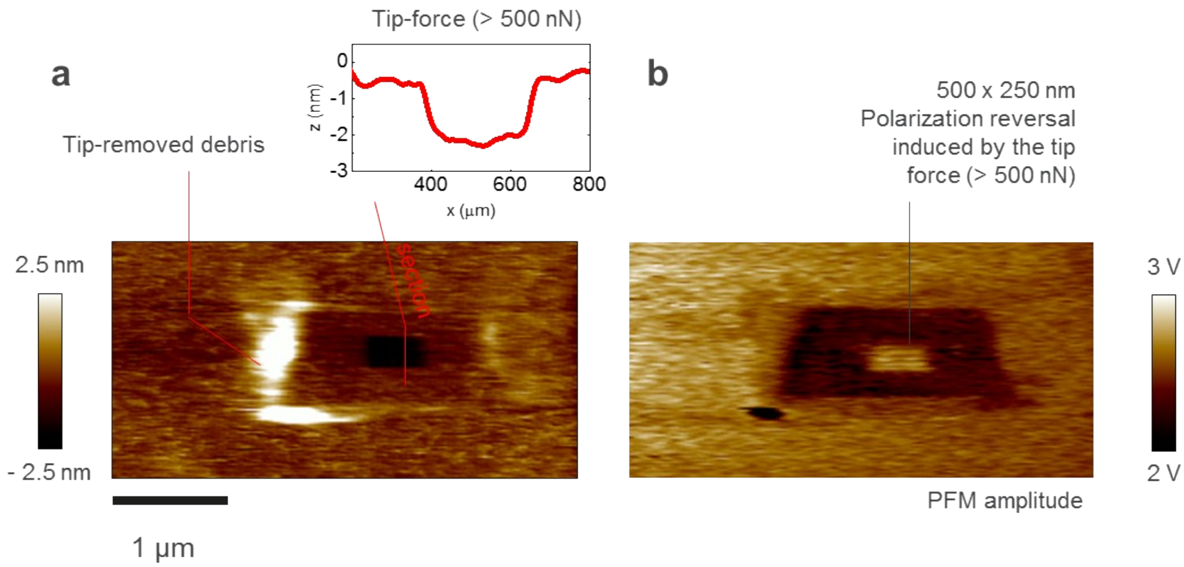

Figure S5 | Impact of tip-induced reversal on the surface morphology at high force. The surface morphology (a) and PFM amplitude (b) show the effects of pressure-induced polarization reversal on the material using a load force ca. 1 µN. In this case we can clearly see the effect of the high-force scan on the morphology of the sample in which a deep (~ 2 nm) trench is dug by the tip-induced reversal. The removed debris accumulates on the side of the scan area. Although the surface modification is not desirable, the electrical polarization reversal is clearly visible also in this case.