Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic supplementary information

Insights on the piezoelectric response and ferroelectric domain formation of $Hf_{0.5}Zr_{0.5}O_2$ films

Huan Tan,[a] Tingfeng Song,[a] N. Dix,[a] Florencio Sánchez*[a] and Ignasi Fina*[a]

[a]*Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra 08193, Barcelona, Spain. E-mail: fsanchez@icmab.es, ifina@icmab.es*

Electronic supplementary information S1

Volume fraction of orthorhombic phase can not be safely calculated from XRD data. We have estimated it by using the polarization value extracted from Figure 2 and considering that polarization is tilted by 54.7° for the films on LSMO/$SrTiO_3$(001) and (110) and by 24, 66 and 90° (all equally probable) for the films on LSMO/$SrTiO_3$(111) and normalizing the polarization to theoretical calculated value (55 $\mu C/cm^2$,[1, 2]). Therefore, the amount of orthorhombic phase can be extracted, as follows:

- HZO on LSMO/$SrTiO_3$(001): P/ P_{theory} = 18 $\mu C/cm^2$/cos(54.7°)/55 $\mu C/cm^2$ = 56 %
- HZO on LSMO/$SrTiO_3$(110): P/ P_{theory} = 32 $\mu C/cm^2$/cos(54.7°)/55 $\mu C/cm^2$ = 100 %
- HZO on LSMO/$SrTiO_3$(111): P/ P_{theory} = 12 $\mu C/cm^2$ / {1/3 x cos(54.7°) +1/3 x cos(90) 1/3 x cos(90°)} = 55 %

These volume fractions are qualitatively consistent with XRD characterization of the films of similar thickness on LSMO/$SrTiO_3$(001), (110) and (111).[3-5]

Electronic supplementary information S2

Ferroelectric PUND loops (P-V and I-V) for samples grown on LSMO/$SrTiO_3$(001), LSMO/$SrTiO_3$(110), and LSMO/$SrTiO_3$(111) are shown in Figure S1.

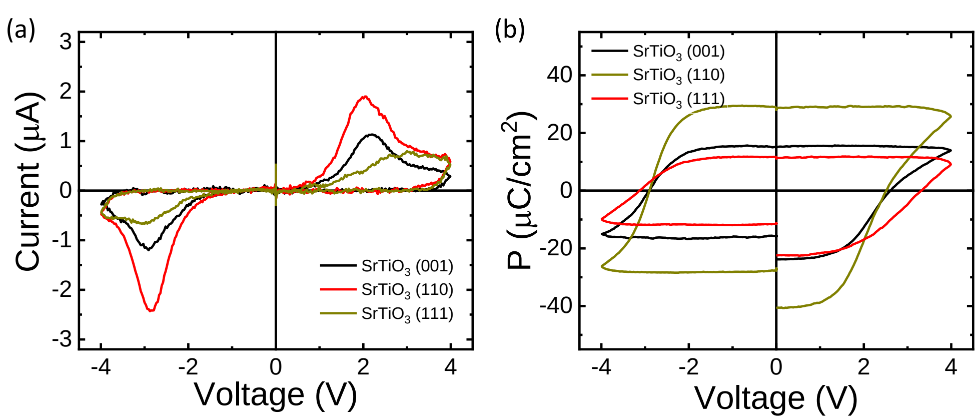

Figure S1. (a,b) Corresponding I-V and P-V PUND loops measured at 1kHz for films on LSMO/$SrTiO_3$(001), LSMO/$SrTiO_3$(110), and LSMO/$SrTiO_3$(111).

Electronic supplementary information S3

Representative 500 x 500 nm^2 regions of out-of-plane signal collected using single-frequency vector PFM are shown in Figure S2(a-f). It can be observed that Figure S2(g) shows the histograms of the amplitude piezoresponse of PFM images of the as grown state.

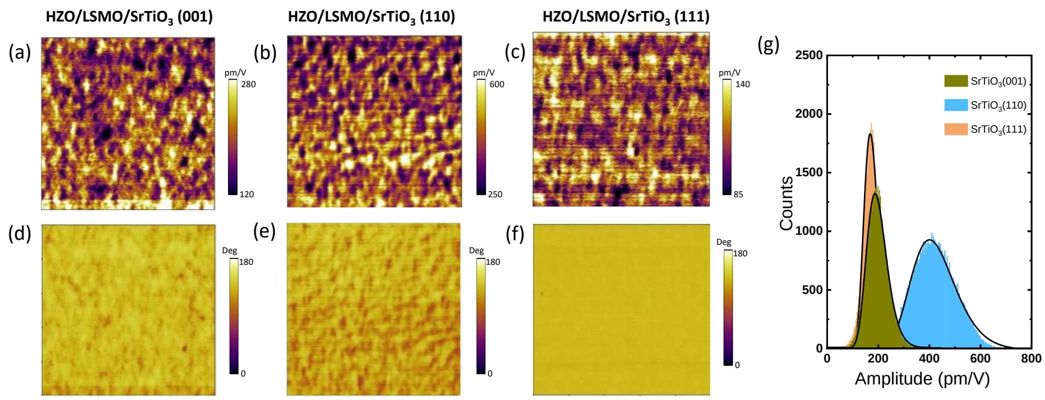

Figure S2. (a,b,c) PFM out-of-plane amplitude 500 x 500 nm images for the HZO films on LSMO/SrTiO₃(001), LSMO/SrTiO₃(110), and LSMO/SrTiO₃(111), respectively. (d,e,f) Idem for the phase response. (g) Histograms of the out-of-plane amplitude PFM of the as-grown representantive regions shown in panels (a-c). Solid line correspond to the lognormal fitting of each histogram.

Electronic supplementary information S4

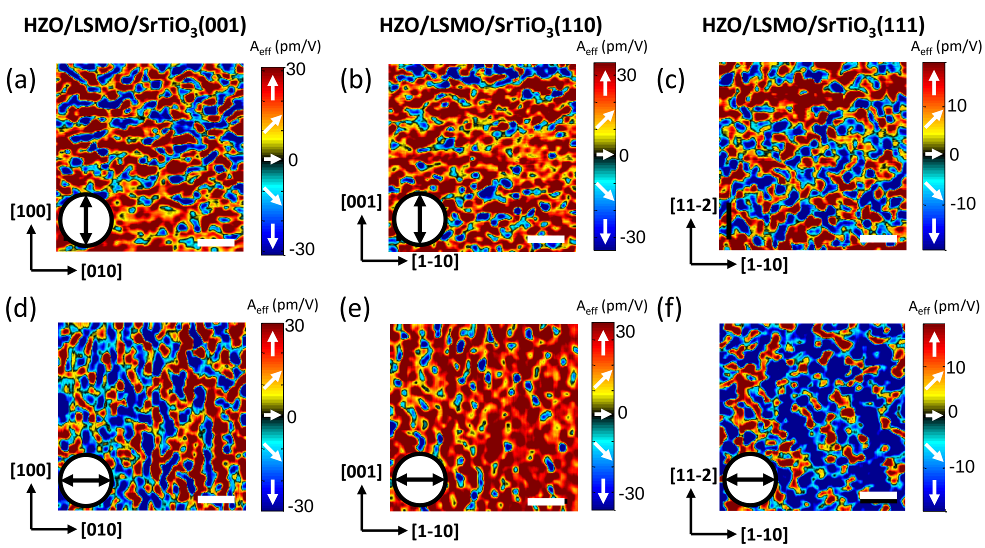

Figure S3. (a,b,c) PFM effective amplitude in-plane amplitude images for the HZO films on LSMO/SrTiO₃(001), LSMO/SrTiO₃(110), and LSMO/SrTiO₃(111), respectively. (d,e,f) Idem while probing along the perpendicular direction as indicated by the arrow. The in-plane substrate main orientations are also indicated. Scale bars in (d-e-f) correspond to 100 nm.

Electronic supplementary information S5

The in-plane polarization projections at different angles (θ) are calculated by the equations described below. φ =54.7°, the angle at which the polarization is tilted with respect to the out-of-plane direction. P_{bulk} is extracted by projecting the P_r empirically collected for each of the indicated samples along the polar axis for each crystalline variant and the three possible polar axis. For the sake of simplicity P_{bulk} values has been normalized to the theoretically expected ones $P_{theory} \approx 55\ \mu C/cm^2$.[1, 2] The amplitude of the in-plane piezoresponse (D) is expected to be proportional to the resulting value.

For HZO/LSMO/STO (001) is:

$$D = 2*\cos(\varphi)*P_{bulk}/P_{theory}*[abs(\cos(45°-\theta)) + abs(\cos(45°-\theta+120°)) + abs(\cos(45°-\theta+240°))] + 2*\cos(\varphi)*P_{bulk}/P_{theory}*[abs(\sin(45°-\theta)) + abs(\sin(45°-\theta+ 120°)) + abs(\sin(45°-\theta+ 240°))]$$

For HZO/LSMO/STO (110) the equation is:

$$D = 2*\cos(\varphi)*P_{bulk}/P_{theory} *[abs(\sin(4.2°-\theta)) + abs(\sin(4.2°-\theta+120°)) + abs(\sin(4.2°-\theta+240°))] + 2*\cos(\varphi)*P_{bulk}/P_{theory}*[abs(\sin(4.2°+\theta)) + abs(\sin(4.2°+\theta+120°)) + abs(\sin(4.2°+\theta+240°))]$$

For HZO/LSMO/STO (111), $\varphi_{1,2,3}$ = 24, 66 and 90° depending on the crystalline variant, and the resulting equation is:

$$D = \sin(\varphi_1)*P_{bulk}/P_{theory}*[abs(\cos(-\theta)) + abs\ (\cos(-\theta\ +120°)) + abs(\cos\text{-}\theta+240°))] + \sin(\varphi_2)*P_{bulk}/P_{theory}*[abs(\cos(-\theta)) + abs(\cos(-\theta\ +120°)) + abs(\cos\text{-}\theta+240°))] + \sin(\varphi_3)*P_{bulk}/P_{theory}*[abs(\sin(-\theta)) + abs(\sin(-\theta+120°)) + abs(\sin(-\theta+240°))]$$

Electronic supplementary information references

1. T. D. Huan, V. Sharma, G. A. Rossetti Jr and R. Ramprasad, *Phys. Rev. B*, 2014, **90**, 064111.
2. F. Delodovici, P. Barone and S. Picozzi, *Phys. Rev. Mater.*, 2021, **5**, 064405.
3. J. Lyu, I. Fina, R. Solanas, J. Fontcuberta and F. Sánchez, *ACS Appl. Electron. Mater.*, 2019, **1**, 220-228.
4. T. Song, H. Tan, S. Estandía, J. Gàzquez, M. Gich, N. Dix, I. Fina and F. Sánchez, *Nanoscale*, 2022, **14**, 2337-2343.
5. T. Song, S. Estandía, N. Dix, J. Gàzquez, M. Gich, I. Fina and F. Sánchez, *J. Mater. Chem. C*, 2022, **10**, 8407-8413.