Electronic Supplementary Information

Large enhancement of ferroelectric polarization in Hf$_{0.5}$Zr$_{0.5}$O$_2$ films by low plasma energy pulsed laser deposition

Tingfeng Song, a Raul Solanas, a Mengdi Qian, a Ignasi Fina, *a and Florencio Sánchez *a

a Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra 08193, Barcelona, Spain

* ifina@icmab.es, fsanchez@icmab.es
S1: Sketches of the P$_{\text{Ar}}$ and P$_{\text{O}_2}$ partial pressures used to grow the films

**Figure S1.** In (a) the three series of films deposited at fixed P$_{\text{O}_2}$ are plotted using black squares (P$_{\text{O}_2}$ = 0.01 mbar), red circles (P$_{\text{O}_2}$ = 0.05 mbar), and blue up triangles (P$_{\text{O}_2}$ = 0.1 mbar). In (b) the four series of films deposited at fixed P$_{\text{Ar}}$ are plotted using black squares (P$_{\text{Ar}}$ = 0 mbar), red circles (P$_{\text{Ar}}$ = 0.05 mbar), blue up triangles (P$_{\text{Ar}}$ = 0.1 mbar), and green down triangles (P$_{\text{Ar}}$ = 0.2 mbar).
S2: XRD θ-2θ scans of the series of films

Figure S2: XRD θ-2θ scans of the series of films deposited under varied $P_{Ar}$ and fixed $P_{O2} = 0.01$ mbar (a), $P_{O2} = 0.05$ mbar (b), $P_{O2} = 0.1$ mbar (c), and the series of films deposited under varied $P_{O2}$ and fixed $P_{Ar} = 0$ mbar (d), $P_{Ar} = 0.05$ mbar (e), $P_{Ar} = 0.1$ mbar (f), $P_{Ar} = 0.2$ mbar (g).
S3: Simulation of Laue oscillations

Figure S3 shows XRD θ-2θ scans of selected samples around the o-HZO(111) reflection. The scans were measured using a longer time than the scans show in Figure 1. The o-HZO(111) reflection is simulated (red curves) according to the equation.\(^1\)

\[
I(Q) = \left( \frac{\sin \left( \frac{QNc}{2} \right)}{\sin \left( \frac{Qc}{2} \right)} \right)^2
\]

where \( Q = 4\pi \sin(\theta)/\lambda \) is the reciprocal space vector, \( N \) the number of unit cells along the out-of-plane direction and \( c \) the corresponding lattice parameter.

Figure S3. XRD θ-2θ scans around the o-HZO(111) reflection. (a) scans of films deposited under \( P_{O2} = 0.01 \) mbar and the \( P_{Ar} \) pressure indicated in each panel. (b) scans of films deposited under \( P_{O2} = 0.05 \) mbar and the \( P_{Ar} \) pressure indicated in each panel. (c) scans of films deposited under \( P_{O2} = 0.1 \) mbar and the \( P_{Ar} \) pressure indicated in each panel. Red lines in each panel are Laue fits. The thickness estimated by the fits is indicated in the corresponding panel.
S4: Thickness and growth rate as a function of $P_{Ar}$

![Graph showing thickness and growth rate as a function of $P_{Ar}$](image)

**Figure S4.** Thickness (solid symbols, left axis) and growth rate (empty symbols, right axis) as a function of $P_{Ar}$ for fixed $P_{O2} = 0.01$ mbar (squares), $P_{O2} = 0.05$ mbar (circles) and $P_{O2} = 0.1$ mbar (triangles). Thickness of the films was estimated by simulation of Laue oscillations as described in Figure S3.

S5: XRD pole figures

![XRD pole figures](image)

**Figure S5.** XRD pole figures of the $P_{O2} = 0.05$, $P_{Ar} = 0.05$ mbar sample, from (a) o-HZO(-111) and (b) STO(111) reflections. (c) Corresponding $\phi$-scans around o-HZO(-111) and STO(111). The pole figures confirm that the orthorhombic phase is epitaxial, presenting four families of crystal variants.
S6: Intensity of the o-(111) reflection, normalized to that of the STO(002) peak

![Figure S6](image)

**Figure S6.** Intensity of the o-(111) reflection, normalized to that of the STO(002) peak, $I_{HZO(111)}/I_{STO(002)}$, as a function of $P_{O_2}$ and $P_{Ar}$. In (a) $P_{Ar}$ is: 0 mbar (black squares), 0.05 mbar (red circles), 0.1 mbar (blue up triangles), and 0.2 mbar (green down triangles). In (b) $P_{O_2}$ is: 0.01 mbar (black squares), 0.05 mbar (red circles), and 0.1 mbar (blue up triangles). The same dependences are obtained normalizing the intensity of the o-(111) reflection to that of the LSMO(002) peak, $I_{HZO(111)}/I_{LSMO(002)}$, as shown in Figure 2 of the manuscript.

S7: The normalized o-(111) reflection

![Figure S7](image)

**Figure S7.** The intensity of the o-(111) reflection, normalized to that of the LSMO(002) peak, $I_{HZO(111)}/I_{LSMO(002)}$, shown in Figure 2 of the manuscript as a function of $P_{O_2}$ and $P_{Ar}$ is normalized to the film thickness. In (a) $P_{Ar}$ is: 0 mbar (black squares), 0.05 mbar (red circles), 0.1 mbar (blue up triangles), and 0.2 mbar (green down triangles). In (b) $P_{O_2}$ is: 0.01 mbar (black squares), 0.05 mbar (red circles), and 0.1 mbar (blue up triangles).
S8: Leakage - voltage curves of films

Figure S8. Leakage - voltage curves of films deposited under varied $P_{Ar}$ and fixed $P_{O2} = 0.01$ mbar (a), $P_{O2} = 0.05$ mbar (b), $P_{O2} = 0.1$ mbar (c), and the series of films deposited under varied $P_{O2}$ and fixed $P_{Ar} = 0.05$ mbar (d), $P_{Ar} = 0.1$ mbar (e), $P_{Ar} = 0.2$ mbar (f).

References