Supporting Information

Nanoscale design of high-quality epitaxial Aurivillius thin films

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Supplementary note 1. RHEED intensity and pattern variations and their relationship to the structural development during the coalescent layer-by-layer growth

![RHEED pattern and intensity changes during the coalescent layer-by-layer growth of BFTO n=4 film.](image)

**Fig. S1** RHEED pattern and intensity changes during the coalescent layer-by-layer growth of BFTO n=4 film. (1) NGO (001) substrate before the deposition. (2) Completion of 1.5 u.c. (3) Increase in surface roughness due to incomplete coalescence before the completion of 2 u.c. The streaks in the RHEED patterns arise due to the two dimensional growth of crystalline surfaces. Only intensity variations are observed, while the pattern itself remains the same throughout the deposition.
Supplementary note 2. $\theta$-2$\theta$ XRD patterns of $n=4$, 6 and 8 BFTO thin films.

**Fig. S2** $\theta$-2$\theta$ XRD patterns of $n=4$, 6 and 8 homologues of BFTO family confirming the $c$-orientation of the films. The absence of additional peaks corroborates single-crystalline nature of the films.
Supplementary Note 3. Epitaxial matching between unit cells of homologous BFTO series and orthorhombic NGO (001) substrate

For orthorhombic unit cells of BFTO films, the following epitaxial relationships were identified:

\([100]_{\text{BFTO } n=4} \parallel [010]_{\text{NGO}} \text{ and } [010]_{\text{BFTO } n=4} \parallel [100]_{\text{NGO}}\)

\([100]_{\text{BFTO } n=6} \parallel [100]_{\text{NGO}} \text{ and } [010]_{\text{BFTO } n=6} \parallel [010]_{\text{NGO}}\)

\([100]_{\text{BFTO } n=8} \parallel [100]_{\text{NGO}} \text{ and } [010]_{\text{BFTO } n=8} \parallel [010]_{\text{NGO}}\)

Lattice parameters of the BFTO homologues and the resulting lattice mismatch on NGO (001):

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>Mismatch (%)</th>
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<tbody>
<tr>
<td>(a) (b) (c)</td>
<td>[100]_{NGO}</td>
</tr>
<tr>
<td>NGO(^2)</td>
<td>5.428 5.498 7.708</td>
</tr>
<tr>
<td>BFTO (n=4)(^3)</td>
<td>5.470 5.439 41.197</td>
</tr>
<tr>
<td>BFTO (n=6)(^4)</td>
<td>5.470 5.492 57.551</td>
</tr>
<tr>
<td>BFTO (n=8)(^5)</td>
<td>5.504 5.610 76.373</td>
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</table>
Supplementary note 4. Measurement geometry used for piezoresponse force microscopy (PFM) measurements.

Fig. S3 (a) PFM scans displayed in Figure 5 of the main text were recorded with the cantilever aligned perpendicular to the NGO [0 1 0] axis (the axis of the uniaxial in-plane polarization of BFTO films). (b) Topography of the measured area of 1 u.c.-thick BFTO n=4 film. (c) No piezoresponse is detected in the vertical PFM (VPFM) channel, only minor cross-talk from topography and lateral PFM (LPFM). (d) LPFM signal displays the in-plane domain configuration. The piezoresponse is arising purely from the torsion in this measurement geometry.

Supplementary note 5. Ferroelectric switching properties of BFTO n=4 film.

Fig. S4 Macroscopic ferroelectric properties measured for a 8.5 u.c.-thick BFTO n=4 film. (a) Polarization-electric field (P-E) loop of the pristine film. (b) Ferroelectric endurance of the same BFTO film showing the stability of the remnant polarization over switching cycles.
References


