Nanoscale Phase Mixture and Multifield-Induced Topotactic Phase Transformation in SrFeO$_x$

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ABSTRACT: Nanoscale phase mixtures in transition-metal oxides (TMOs) often render these materials susceptible to external stimuli (electric field, mechanical stress, etc.), which can lead to rich functional properties and device applications. Here, direct observation and multifield manipulation of a nanoscale mixture of brownmillerite SrFeO$_{2.5}$ (BM-SFO) and perovskite SrFeO$_3$ (PV-SFO) phases in SrFeO$_x$ (SFO) epitaxial thin films are reported. The mixed-phase SFO film in its pristine state exhibits a nanoscaffold structure consisting of PV-SFO nanodomains embedded in the BM-SFO matrix. This nanoscaffold structure produces gridlike patterns in the current and electrochemical strain maps, owing to the strikingly different electrical and electrochemical properties of BM-SFO and PV-SFO. Moreover, electric field control of reversible topotactic phase transformation between BM-SFO and PV-SFO is demonstrated by electric-field-induced reversible changes in surface height, conductance, and electrochemical strain response. In addition, it is also shown that the BM-SFO $\rightarrow$ PV-SFO phase transformation can be enabled by applying mechanical stress. This study therefore not only identifies a strong nanometric structure–property correlation in the mixed-phase SFO but also offers a new paradigm for the multifield control of topotactic phase transformation.

KEYWORDS: topotactic phase transformation, SrFeO$_x$ mixed phases, resistive switching, electrochemical strain

INTRODUCTION: Transition-metal oxides (TMOs) exhibit various competing phases and plenty of fascinating properties. A TMO with a rationally designed phase coexistence often displays exotic properties that are unprecedented in its single-phase counterparts, such as giant piezoelectric response,$^{1,2}$ colossal magnetoresistance,$^{3,4}$ superconductivity,$^5$ and enhanced electrochemical activity.$^6$ Therefore, recently, TMOs with mixed phases have been subjected to extensive research in the fields of physics, electronics, chemistry, and so forth.

So far, a variety of approaches have been developed to obtain mixed phases in TMOs, such as chemical alloying,$^{8,9}$ strain engineering,$^{10-12}$ and oxygen stoichiometry tuning.$^{13-17}$ For example, when PbZrO$_3$ is alloyed with PbTiO$_3$ at a Zr/Ti ratio of 52/48, i.e., the so-called morphotropic phase boundary, both tetragonal and rhombohedral phases coexist and anomalously high piezoelectric and dielectric coefficients ($d_{33} > 500$ pC/N and $e_r > 1000$, respectively) arise.$^8$ In addition, when BiFeO$_3$ undertakes a critical compressive strain of 4.5%, a mixture of supertetragonal and rhombohedral phases is formed, which yields giant electromechanical response,$^{11}$ electrically controlled ferromagnetism,$^{18}$ and flexoelectric photovoltaic effect.$^{19}$ Although chemical alloying and strain engineering have proven effective in developing mixed phases, they can apply only to a limited number of TMO systems. Oxygen stoichiometry tuning, however, appears suitable for almost all TMOs, and it can be flexibly applied, either during or after material synthesis.

An ideal platform for implementing the oxygen stoichiometry tuning is a family of TMOs exhibiting two interconvertible topotactic phases, namely, perovskite (PV) ABO$_3$ and brownmillerite (BM) ABO$_{2.5}$ phases. The PV phase comprises corner-linked BO$_6$ octahedra, while the BM phase consists of alternately stacked layers of BO$_6$ octahedra and BO$_4$ tetrahedra.$^{20}$ By gaining or losing oxygen, the BM and PV phases can be reversibly transformed to each other. Such topotactic phase transformation induces not only structural changes but also dramatic changes in electronic and magnetic properties$^{21}$ because, typically, the BM phase is an
antiferromagnetic insulator\textsuperscript{22} and the PV phase is a ferromagnetic metal\textsuperscript{23,24} in their ground states. This promises a wide range of applications such as fuel cells,\textsuperscript{25} catalysts,\textsuperscript{13} resistive switching memories,\textsuperscript{26}−\textsuperscript{28} and magnetoelectric devices.\textsuperscript{29} Therefore, both BM and PV phases, and the topotactic phase transformation between them via oxygen stoichiometry tuning, have attracted great interest and stimulated ongoing research in the past few years.\textsuperscript{15,30}−\textsuperscript{39}

Although the emergence of BM + PV mixed phases during the topotactic phase transformation has been observed previously,\textsuperscript{40}−\textsuperscript{44} the structure–property correlation at the microscopic level in the mixed phases still lacks in-depth research. Moreover, how the mixed phases respond to external stimuli (including electrical and mechanical stimuli) is also important to understand because exotic phenomena such as large resistance change and giant electrochemical strain may arise owing to the electro-chemo-mechanical coupling in the mixed phases.

Herein, we choose SrFeO\textsubscript{x} (SFO) as a model system to study the BM + PV mixed phases because the small Gibbs free energy difference between SrFeO\textsubscript{2.5} (BM-SFO) and SrFeO\textsubscript{3} (PV-SFO) (~100 meV\textsuperscript{13}) may lead to an easy access to the mixed phases. By finely controlling the oxygen pressure during the growth of SFO epitaxial thin films, we develop a self-assembled nanoscale mixture of BM-SFO and PV-SFO phases. The mixed-phase film (pristine state) exhibits a nanoscaffold structure consisting of PV-SFO nanodomains embedded into the BM-SFO matrix, and this novel structure gives rise to gridlike patterns in both current and electrochemical strain maps. Then, we observe nanoscale phase transformation and associated changes in current and electrochemical strain response upon applications of both electrical and mechanical stimuli, implying great application potential in many electronic devices such as memories, actuators, and sensors.

\section*{RESULTS AND DISCUSSION}

The crystal structures of BM-SFO and PV-SFO are sketched in Figure 1a, showing that BM-SFO contains alternately stacked layers of FeO\textsubscript{6} octahedra and FeO\textsubscript{4} tetrahedra, while PV-SFO consists of only corner-linked FeO\textsubscript{6} octahedra. To obtain the coexistence of these two different phases, the SFO films were grown on SrRuO\textsubscript{3} (SRO)-buffered (001) SrTiO\textsubscript{3} (STO) substrates under a specific oxygen pressure (p\textsubscript{O\textsubscript{2}}) of 3 Pa. The obtained SFO films were first characterized by X-ray diffraction (XRD), as shown in Figure 1b. Two sets of diffractions peaks from SFO are clearly observed: (i) the half-order peaks, including (020)\textsubscript{o}, (040)\textsubscript{o}, (060)\textsubscript{o}, and (0100)\textsubscript{o} from BM-SFO, and (ii) the (001)\textsubscript{pc} and (002)\textsubscript{pc} peaks from bulk PV-SFO (PDF \#40-0905), respectively. AFM topography images of the mixed-phase SFO film (e) in the pristine state and (f) after the +7 V electrical writing.

\begin{figure}[h]
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\caption{Phase analysis of the mixed-phase SFO film. (a) Schematics of crystal structures of BM-SFO and PV-SFO viewed along the (110)\textsubscript{pc} direction. (b) XRD \(\theta\)–2\(\theta\) diffraction pattern, (c) RSM around (103)\textsubscript{pc} reflection of STO, and (d) RSM around (1101)\textsubscript{o} reflection of BM-SFO for a mixed-phase SFO film. The pink and cyan bars in (b) indicate the positions of (0k0)\textsubscript{o} peaks from bulk BM-SFO (PDF \#17-0932) and (00l)\textsubscript{pc} peaks from bulk PV-SFO (PDF \#40-0905), respectively. AFM topography images of the mixed-phase SFO film (e) in the pristine state and (f) after the +7 V electrical writing.}
\end{figure}

formed. According to the peak positions, the lattice constant \( b_0 \) of BM-SFO is calculated as \( \sim 15.67 \) Å. On the other hand, the \((001)_{pc}\) and \((002)_{pc}\) peaks are typical reflections from the PV-SFO phase with the \( c_{pc}\)-axis oriented along the out-of-plane direction. The lattice constant \( c_{pc}\) of PV-SFO calculated from the peak positions is \( \sim 3.85 \) Å. The calculated values of \( b_0 \) and \( c_{pc}\) agree well with their respective bulk values (for bulk BM-SFO: \( b_0 = 15.59 \) Å, \( a_0 = 5.67 \) Å, and \( c_0 = 5.53 \) Å; and for bulk PV-SFO: \( a_{pc} = b_{pc} = c_{pc} = 3.83-3.85 \) Å). Therefore, the XRD results suggest that the SFO film grown under \( pO_2 \) of 3 Pa presents BM + PV mixed phases. Notably, the precise control over \( pO_2 \) during the film growth is critical to obtain the mixed phases because \( pO_2 \) largely controls the oxygen stoichiometry of the deposited film. As \( pO_2 \) decreases (increases), the fraction of the BM-SFO (PV-SFO) phase tends to increase and eventually a pure BM-SFO (PV-SFO) phase is obtained, as shown in Figure S1.

Figure 2. Hierarchical structures of nanoscale phase mixtures. (a) Low-magnification STEM ABF plan-view image showing two regions, marked as A and B. (b, c) Electron diffraction patterns from the two regions marked as A and B in (a), respectively. The black circles indicate the overlapped reflections from both PV-SFO and BM-SFO phases, while the other superlattice reflections are only from the BM-SFO phase. Particularly, the \( 1/4\{100\}_pc \) and \( 1/2\{100\}_pc \) diffraction spots from the BM-SFO phase are indicated by the red and black arrows, respectively. (d) Medium-magnification STEM ABF image showing one B region surrounded with four A regions. (e) High-magnification STEM ABF image focusing on one A region surrounded with two B regions. (f1, f2) FFT images obtained from the red and green boxes in (e), respectively. (g1, h1) Atomically resolved STEM ABF and HAAADF images from regions A and B, respectively. (g2, h2) FFT patterns corresponding to g1 and h1, respectively. (i1−i3) Atomically resolved STEM HAAADF images of three regions showing the coexistence of BM and PV phases.

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Then, to further characterize the mixed phases, reciprocal space mapping (RSM) was measured around the (103)pc reflection of the STO substrate, as shown in Figure 1c. The middle spot with the highest intensity is the STO (103)pc peak overlapped with the BM-SFO (1121)pc peak. The upper spot corresponds to the (103)pc peak of PV-SFO, while the lower spot corresponds to the SFO (103)pc peak. The in-plane lattice constant \( a_{pc} \) (or \( b_{pc} \) equivalently) of PV-SFO can be directly calculated from the (103)pc peak to be \( \sim 3.91 \) Å. To accurately calculate the in-plane lattice constant \( a_{pc} \) (or \( c_{pc} \) equivalently) of BM-SFO without influence from the peak overlap, an alternative peak of BM-SFO, i.e., the \((1101)_{pc}\) peak, was scanned (see Figure 1d). The value of \( a_{pc} \) is calculated as \( \sim 5.52 \) Å, which is about \( \sqrt{2} \times 3.91 \) Å. Therefore, the lattice parameters of both the BM-SFO and PV-SFO phases are fully determined. The in-plane lattice parameters of BM-SFO and PV-SFO (in pseudocubic unit cells) are quite close to that of STO (\( \sim 3.905 \) Å), suggesting that both the BM-SFO and PV-SFO phases are highly constrained by the STO substrate.

To understand how the BM-SFO and PV-SFO phases are mixed together at the nanoscale, atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM) characterizations were performed. Figure 1e presents an AFM topography image of the mixed-phase SFO film in its pristine state. A novel nanoscaffold structure is observed, where well-ordered pits (dark regions) distribute ubiquitously in the matrix (bright regions). The pits possess an average diameter of \( \sim 150 \) nm and an average depth of \( \sim 0.8 \) nm. The pits and matrix may contain different phases, and the surface height contrast may come from the different out-of-plane lattice spacings \( (d_{oop}) \) of PV-SFO and BM-SFO. For PV-SFO, \( d_{oop} = c_{pc} = \sim 3.85 \) Å. For BM-SFO, two lattice orientations are considered: (i) when the \( b_{pc} \)-axis is oriented along the out-of-plane direction, \( d_{oop} = b_{pc}/a_{pc} = \sim 3.92 \) Å, and (ii) when the \( b_{pc} \)-axis is oriented along the in-plane direction, \( d_{oop} \approx a_{pc} \sqrt{2} = \sim 3.91 \) Å. The first orientation has already been revealed by XRD, while the second one will later be revealed by STEM. Nevertheless, regardless of the orientation, the \( d_{oop} \) values of the BM-SFO phases are always larger than that of the PV-SFO phase. A surface height–phase correlation is therefore speculated: the pit regions might contain mainly PV-SFO whereas the matrix is mainly composed of BM-SFO. This speculation will be verified later by the STEM study, and it is also supported by the observation that the SFO film grown under higher \( p_O2 \) exhibits a higher fraction of the PV-SFO phase and also a larger total area of pit regions (see Figure S1).

Upon electrically writing with an AFM tip bias of \( \pm 7 \) V, the morphology of the mixed-phase SFO film changes into a cracked-earth-like pattern (Figure 1f), manifesting as an assembly of rectangular bulges separated by crossed channels. Again, according to the fact that BM-SFO has a larger \( d_{oop} \) than that of PV-SFO, the bulge and channel regions may mainly contain BM-SFO and PV-SFO, respectively. Comparing Figure 1e,f, the BM-SFO domains expand in area, while the PV-SFO domains shrink in area, pointing to an electrically induced PV-SFO \( \rightarrow \) BM-SFO phase transformation (to be demonstrated later). Therefore, the mixed-phase SFO film can exhibit two types of morphologies: the nanoscaffold type in the pristine state and the cracked-earth type after the \( \pm 7 \) V electrical writing.

While AFM can identify different domains in the mixed-phase SFO film, the microstructure in each domain is largely speculated and direct evidence is still lacking. To directly probe the microstructure, STEM plan views of the mixed-phase SFO film were performed. Figure 2a presents a low-magnification STEM annular bright-field (ABF) plan-view image, which reveals a polydomain pattern containing rectangular domains (marked as B) separated by crossed stripes (marked as A). This pattern well resembles the cracked-earth-type morphology observed under AFM in the mixed-phase SFO film after electrical writing (Figure 1f). The phases in regions A and B were investigated by taking electron diffraction patterns from these two regions. As shown in Figure 2bc, both electron diffraction patterns show the coexistence of BM-SFO and PV-SFO phases. The difference is that Figure 2b from region A shows the PV phase as the majority phase, while Figure 2c from region B shows the BM phase as the majority phase, because the 1/4\{100\}_{pc} diffraction spots (characteristic reflections from the BM phase) are clearly observed in Figure 2c, while they are nearly absent in Figure 2b.

Figure 2d presents a medium-magnification STEM ABF image focusing on a B region surrounded with four A regions, further revealing the nanoscale phase mixtures in both regions. At higher magnification (Figure 2e), one can see that region B contains a large number of superlattice stripes, while region A contains much fewer. Because the superlattice stripes are the fingerprint of the BM phase, regions A and B thus contain PV-SFO and BM-SFO as the majority phases, respectively. To further confirm it, the fast Fourier transformation (FFT) patterns were taken from these two regions. Figure 2f from region B presents strong 1/2\{100\}_{pc} diffraction spots belonging uniquely to the BM phase, but these diffraction spots become much weaker in Figure 2e from region A. It is therefore concluded that the PV-SFO and BM-SFO phases are the majority phases in regions A and B, respectively.

To further investigate the fine structures in regions A and B, aberration-corrected STEM ABF and high-angle annular dark-field (HAADF) imaging modes, which can produce contrast interpretable by mass thickness (the number of atoms) or the Z contrast,47–49 were employed. The atomically resolved STEM images, as shown in Figure 2g1,h1, clearly reveal that the total area of the PV-SFO domains is larger than that of the BM-SFO domains in region A, but the opposite is true in region B. In addition, region B displays much stronger 1/4\{100\}_{pc} diffraction spots than those of region A (see comparison in Figure 2g2,h2), reflecting a higher fraction of the BM-SFO phase in region B than that in region A. These results confirm that the PV-SFO and BM-SFO phases prevail in regions A and B, respectively. Figure 2g1,h1 also shows the superlattice stripes running along two perpendicular \( \langle 100 \rangle \) directions, indicating the presence of BM-SFO domains with in-plane-oriented \( b_{pc} \)-axes (they were not revealed by our previous XRD study, probably because their amount was very low in the pristine state but increased significantly after the STEM sample preparation; see a detailed discussion in Supplementary Note S1). Interestingly, these BM-SFO domains, together with the PV-SFO domains, form different beautiful architectures at the nanoscale, as shown in Figure 2i–i. Detailed analyses on the atomic structure and strain distribution30–33 near the BM/PV interface are provided in Figures S2–S4. Overall, the above STEM results reveal complex hierarchical phase structures in the mixed-phase SFO film, which consists of rectangular domains (region B) with BM-SFO as the majority phase and crossed stripes (region A) with PV-SFO as the majority phase.
By correlating the above STEM results with the cracked-earth-type morphology observed via AFM (Figure 1f), one can deduce that the rectangular bulge regions mainly contain BM-SFO, while the crossed channel regions mainly contain PV-SFO. This well validates the above-mentioned surface height−phase correlation: the regions with a higher (lower) surface height mainly contain BM-SFO (PV-SFO). Note that the BM-SFO phases with different orientations are not further

Figure 3. Correlations between phase, conductance, and electrochemical strain response in the mix-phase SFO film (pristine state). (a) AFM topography image of a 5 × 5 μm² area and (b) C-AFM current map taken over this area (read voltage +3 V). (c) AFM topography image of another 5 × 5 μm² area and ESM (d) amplitude and (e) phase images taken over this area.

Figure 4. Electric-field-induced concurrent changes in phase, conductance, and electrochemical strain response. (a, d) AFM topography image and C-AFM current map, respectively, taken after writing a 3.5 × 3 μm² region with +7 V. (b, e) AFM topography image and C-AFM current map, respectively, taken after rewriting an inner 1.5 × 1.5 μm² region with −7 V. In (d) and (e), the read voltage is +3 V. (c) Surface height profile along the red line in (b). (f) Current profile along the blue line in (e). In (c) and (f), the bold black lines are drawn for eye guidance. (g) AFM topography image and ESM (h) amplitude and (i) phase images taken after writing outer (2 × 2 μm²) and inner (1 × 1 μm²) regions with +7 and −7 V, respectively.
distinguished because the $d_{oop}$ values of the BM-SFO phase are always larger than those of the PV-SFO phase, as discussed above. This surface height−phase correlation may also reasonably apply to the nanoscaffold-type morphology, although it is not directly observed in STEM. Why the cracked-earth-type morphology rather than the nanoscaffold-type morphology is observed in STEM may stem from phase transformation caused by the STEM sample preparation (see a detailed discussion in Supplementary Note S1).

As mentioned in the Introduction section, the BM-SFO and PV-SFO phases exhibit starkly different conductivities. It is thus of interest to look into the current distribution in the mixed-phase SFO film. We started with the mixed-phase SFO film (pristine state) that exhibits a nanoscaffold structure. Figure 3a, b presents the topography of a $5 \times 5 \, \mu m^2$ area and the current map taken over this area using conductive AFM (C-AFM), respectively. Interestingly, the current map displays a gridlike pattern having almost one-to-one correspondence with the topography, namely, the pit regions exhibit higher currents ($30−80$ pA), while the matrix exhibits lower currents ($<10$ pA). This in turn confirms that the pit and matrix regions mainly consist of PV-SFO and BM-SFO, respectively, because the PV-SFO phase is more conductive than the BM-SFO phase. Therefore, the mixed-phase SFO film (pristine state) looks like an ordered assembly of nanocables with PV-SFO conducting cores surrounded by BM-SFO insulating shells. Note that the current enhancement in the pits compared to that in the matrix is not simply due to the thickness reduction because the surface height difference between the pits and the matrix is only $\sim 0.8 \, \text{nm}$ ($\sim 1.3\%$ of the total film thickness). The thickness reduction alone is thus unable to cause about 1 order of magnitude enhancement in current. In addition, the topographic crosstalk during tip scanning is excluded as a factor leading to the current enhancement because the enhanced currents are observed in the whole pit regions (rather than only at the boundaries between the pits and the matrix) and these currents are quite stable (Figure SS). It is therefore believed that the phase difference, as discussed above, is the major origin for the different currents measured in the pit and matrix regions.

Besides the different conductivities, the BM-SFO and PV-SFO phases should also exhibit different electrochemical strain responses because of the different oxygen stoichiometries. The electrochemical strain microscopy (ESM) technique was thus utilized to detect the electrochemical strain arising from ionic redistribution and surface electrochemical reaction under an applied tip bias for the mixed-phase SFO film. To minimize influences from the topographic crosstalk on the ESM signals, the dual AC resonance tracking (DART) mode, which can track the resonant frequency, was used. Figure 3c−e presents the topography of a $5 \times 5 \, \mu m^2$ area and the ESM amplitude and phase images taken over this area, respectively. It is not unexpected that both the ESM amplitude and phase images show almost one-to-one correspondence with the topography. The ESM amplitude in the pits is higher than that in the matrix, implying that the PV-SFO phase exhibits a larger electrochemical strain response than the BM-SFO phase. This may be because the PV-SFO phase has either higher oxygen diffusivity or higher activity of oxygen incorporation/extraction near the surface.

While both the conductance and electrochemical strain response are strongly correlated to the phases in the mixed-phase SFO film, an interesting question remains how the phase along with conductance and electrochemical strain response evolves upon applications of electrical and mechanical stimuli. We therefore performed further AFM-based characterizations.

As can be seen from Figure 4a (also see Figure 1f), electrical writing with $+7 \, \text{V}$ leads to the cracked-earth-type morphology and a noticeable increase in surface height. Accompanied with the topographic change, a decrease in current is also observed upon $+7 \, \text{V}$ writing (see Figure 4d). The changes in both surface height and conductance can be reversed by an electrical writing with opposite polarity. As shown in Figure 4b, the surface height in the inner $−7 \, \text{V}$ written area is decreased by $\sim 0.8 \, \text{nm}$, compared with that in the outer $+7 \, \text{V}$ written area (note that only the surface height decrease is observed, while the nanoscaffold-type morphology is not recovered; also see Figure 4g). Meanwhile, the current is increased from $\sim 3$ to $\sim 35$ pA, corresponding to an on/off conductance ratio of $\sim 10$ (Figure 4e,f). To exclude the transient current contributions from the charging/discharging effect, the time-dependent current measurements were conducted. As shown in Figure SS, the different currents read in the $+7$ and $−7 \, \text{V}$ written areas are rather stable against time, confirming that the conductivities of these two areas are truly different. Because the BM-SFO phase has a larger $d_{oop}$ and is less conductive compared with the PV-SFO phase, the above results therefore suggest that a reversible phase transformation from PV-SFO to BM-SFO (BM-SFO to PV-SFO) may occur upon $+7 \, \text{V}$ ($−7 \, \text{V}$) writing.

To further characterize the resistive switching phenomenon, local current−voltage ($I−V$) measurements were performed. Figure 5a illustrates typical $I−V$ characteristics measured by locating the tip in the pit and matrix regions and sweeping the voltage as $0 \rightarrow −6 \, \text{V} \rightarrow +6 \, \text{V} \rightarrow 0$. Much smaller $I−V$ hysteresis is observed in the pit region than in the matrix region as the voltage goes along $0 \rightarrow −6 \, \text{V} \rightarrow 0$, indicating that the BM-SFO → PV-SFO phase transformation occurs, while the PV-SFO phase remains unchanged during the application of a negative voltage. After the voltage sweeps from $−6 \, \text{V}$ back to 0, the phases in both pit and matrix regions may become the same PV-SFO phase; therefore, both regions exhibit similar hysteresis as the voltage sweeps along $0 \rightarrow +6 \, \text{V} \rightarrow 0$. These local $I−V$ hysteresis loops are well consistent with the above C-AFM mapping results, confirming that the topotactic phase transformation between PV-SFO and BM-SFO can be driven by the electric field and it can cause resistive switching.

The topotactic phase transformation also triggers a significant change in electrochemical strain response. As shown in Figure 4g−i, $+7 \, \text{V}$ ($−7 \, \text{V}$) writing leads to a decrease (increase) in ESM amplitude and noticeable changes in the phase contrast, concurrently with the topographic changes. This observation is consistent with the scenario of topotactic phase transformation between BM-SFO and PV-SFO because the PV-SFO phase is shown to have larger electrochemical strain response than the BM-SFO phase (see Figure 3d).

Besides the ESM mappings, local ESM amplitude loops were also recorded. Figure 5b shows the comparison of ESM amplitude hysteresis loops measured in the pit and matrix regions by applying a voltage cycle of $0 \rightarrow +6 \, \text{V} \rightarrow −6 \, \text{V} \rightarrow 0$. The matrix region shows negligible hysteresis, while the pit region exhibits a butterfly winglike hysteresis as the voltage sweeps from 0 to $+6 \, \text{V}$ and back to 0, suggesting that a positive voltage induces the phase transformation from PV-SFO to BM-SFO while keeping the BM-SFO phase unchanged. After the voltage sweeps from $+6 \, \text{V}$ back to 0, the phases in both pit
If the strain is defined as $\Delta h/d$, where $d$ is the film thickness, the $\Delta h$ of 800 pm observed at +9 V with a scan rate of 1 Hz corresponds to a strain of $\sim$1.3%. This huge electrochemical strain is on the same order of magnitude as the highest strains achieved in state-of-the-art relaxor ferroelectrics, which may have potential applications in actuators.

We now focus on the possible mechanism underlying the electric-field-induced topotactic phase transformation. According to previous studies, a chemical equilibrium is generally reached near the SFO film surface:

$$O_2 + 4e^- + 2V_0 \rightleftharpoons 2O_0^4$$

(1)

By applying a negative bias on the film surface, the forward reaction of eq 1 occurs. The oxygen atoms in the ambient are thus incorporated into the film, filling the vacancy sites in BM-SFO. Consequently, the BM-SFO phase transforms into the PV-SFO phase. The region with the PV-SFO phase then gradually grows as the oxygen ions migrate toward SRO under the negative bias. On the contrary, applying a positive bias on the film surface triggers the reverse reaction of eq 1. The oxygen atoms in the lattice are pulled out, creating oxygen vacancies. This leads to the conversion of the PV-SFO phase into the BM-SFO phase.

The above mechanism is different from that proposed by Ferreiro-Vila et al. They proposed that the oxygen vacancies migrate and accumulate underneath the tip when applying a negative tip bias, leading to the PV-SFO $\rightarrow$ BM-SFO phase transformation. However, since the reverse phase transformation (BM-SFO $\rightarrow$ PV-SFO) induced by the negative bias was observed in our sample, we think that the oxygen incorporation from the ambient into the SFO film [see eq 1] may play the dominant role. Indeed, both oxygen migration and oxygen incorporation/extraction may co-work and which one dominates depends on the sample and the electric field distribution. Their and our samples (both in the pristine state) mainly contain the PV-SFO phase and the mixed phases, respectively. In addition, no bottom electrode was used in their sample, while we used SRO as the bottom electrode, which should lead to different electric field distributions. Considering these differences, we think that both their and our observations are explainable, and the oxygen incorporation/extraction is a more suitable mechanism for our sample. To further verify it, checking whether the $O_2$ in the ambient is an indispensable medium for the BM-SFO $\rightarrow$ PV-SFO phase transformation is of necessity. Hence, the topographic changes in the SFO film after applying $\sim$7 V in different atmospheres were examined. Figure S8 shows that the topographic change becomes less observable as the volume fraction of $O_2$ decreases, confirming the critical role played by $O_2$ in the topotactic phase transformation and also supporting our proposed mechanism.

Mechanical stimuli were also applied to trigger the topotactic phase transformation and property changes in the mixed-phase SFO film. A region of $10 \times 10 \text{ mm}^2$ was initially written with +7 V. Consequently, this region contains mainly BM-SFO and has a relatively large surface height. This pretreatment was used because it can result in a larger contrast between the regions with and without mechanical writing in the topography image. Then, three small regions of $3 \times 3 \text{ mm}^2$ inside the pretreated region were scanned with loading forces of $\sim$9, $\sim$22, and $\sim$40 $\mu$N, respectively, while applying zero tip bias. Figure 6a shows the topography image taken after the mechanical writing. As the loading force increases from $\sim$9 to $\sim$40 $\mu$N, the sink of the film surface emerges and becomes

![Figure 5. Hysteretic responses of current and electrochemical strain and dependences of topographic change on write voltage magnitude and duration time. (a) Hysteretic I–V characteristics measured in pit and matrix regions. (b) ESM amplitude hysteresis loops measured in pit and matrix regions. The red arrows indicate the starting step of a voltage cycle, while the black arrows indicate the following steps of this voltage cycle. Insets show the locations where hysteresis loops were measured. AFM topography images obtained after the positive write voltage and (f) scan rate. The data in (d) and (f) are the statistical results obtained from (c) and (e), respectively.](image-url)
increasingly noticeable. Along with the topographic change, the conductance also becomes higher with an increase in loading force (see Figure 6c). The simultaneous changes in topography and conductance suggest that the BM-SFO → PV-SFO phase transformation may occur during mechanical writing. After rewriting the whole 10 × 10 μm² region with +7 V, both the surface height and conductance of the mechanically written regions are largely recovered to be similar to those of the surrounding regions (see Figure 6b,d). The recovery of both the surface height and conductance further confirms the occurrence of topotactic phase transformation, rather than plastic deformation or wear, induced by mechanical writing.

In terms of the underlying mechanism, one can also refer to eq 1. The mechanical pressure applied by a tip can lower the formation energy of lattice oxygen,62,63 promoting the forward reaction of eq 1. In addition, the pressure may push oxygen vacancies away from the region underneath the tip.64 Both effects may contribute to the occurrence of BM-SFO → PV-SFO phase transformation under mechanical pressure. However, since the tip cannot apply tensile forces to the sample, the PV-SFO → BM-SFO phase transformation is not available.

Up to this point, it has been demonstrated that the conductance and electrochemical strain response are strongly coupled with the phase in the mixed-phase SFO film, and reversible phase transformation between PV-SFO and BM-SFO can be driven by the electric field. The mixed-phase SFO film with well-ordered nanosized PV-SFO and BM-SFO domains may therefore work as a high-density dual-functional memory device that can store the information of both conductance and electrochemical strain response. Besides, the giant electrochemical strain of 1.3% makes the mixed-phase SFO film potentially useful for actuator applications. In addition, the topotactic phase transformation in the mixed-phase SFO film can also be induced by the mechanical field, making it attractive for pressure sensing. One last thing worth mentioning is that the AFM technique is a facile tool to study the topotactic phase transformation. As demonstrated here and also in Ferreiro-Vila’s work,65 an AFM tip with mild applied electrical and mechanical stimuli (several volts and several micronevents, respectively) can readily trigger the topotactic phase transformation, unlike thermal annealing,13,31 ionic liquid gating,14,15,32 and plasma-assisted ion implantation,35 which require high-temperature heating, long-term electric poling, and introducing foreign ions, respectively.

### CONCLUSIONS

In summary, SFO epitaxial thin films with a nanoscale mixture of BM-SFO and PV-SFO phases have been fabricated on the SRO-buffered STO substrates by finely controlling the oxygen pressure during the film growth. The mixed-phase SFO film (pristine state) exhibits a nanoscaffold structure, where PV-SFO nanodomains are embedded in the BM-SFO matrix. Coupled with this novel structure, gridlike patterns are formed in both current and electrochemical strain maps. Applying a positive (negative) tip bias can drive a phase transformation from PV-SFO to BM-SFO (BM-SFO to PV-SFO), resulting in an increase (decrease) in surface height as well as a decrease (increase) in conductance and ESM amplitude. Particularly, an on/off conductance ratio of ∼10 is obtained upon applying ±7 V, and an electrochemical strain as large as ∼1.3% is achieved at +9 V with a scan rate of 1 Hz. In addition, a mechanical pressure exerted by the tip is also able to trigger the BM-SFO → PV-SFO phase transformation, which manifests as a decrease in surface height and an increase in conductance. The ability to exhibit significant changes in both conductance and electrochemical strain in response to electrical and mechanical stimuli promises the mixed-phase SFO films a wide range of applications such as memories, actuators, and sensors.

### METHODS

#### Film Deposition.

Mixed-phase SFO thin films were epitaxially grown on SRO-buffered (001)-oriented STO substrates using pulsed laser deposition (PLD) with a KrF excimer laser (λ = 248 nm). SRO bottom electrode layers (~30 nm) were first deposited at a substrate temperature of 680 °C in an oxygen atmosphere of 15 Pa. Subsequently, ~60 nm mixed-phase SFO films were deposited at 660 °C under a pO2 of 3 Pa. For comparison, the SFO films were also grown under pO2 of 1, 2, 5, and 10 Pa. During deposition, the energy fluence of the laser was fixed at 1.2 J/cm² with a repetition rate of 4 Hz. After deposition, the samples were cooled to room temperature at 10 °C/min in an oxygen atmosphere the same as that used for SFO deposition.

#### Structural Characterizations.

The crystalline phases were examined using XRD and RSM (XPert PRO, PANalytical). STEM was conducted on a Jeol ARM200F microscope equipped with a cold field-emission gun and ASCOR probe corrector. The STEM planeview specimens were prepared by grinding/polishing and ion milling from the substrate side.

#### AFM-Based Characterizations.

Nanoscale observation and manipulation of phases and physical properties were conducted using an integrated AFM system (Asylum Cypher, Oxford Instruments) with conductive Pt-coated silicon tips (EFM, Nanoworld). More specifically, AFM, C-AFM, and ESM were used to characterize the surface morphology, electrical conduction, and electrochemical strain response, respectively. When performing C-AFM, a read voltage of +3 V was used for current mappings. In the ESM measurements, the dual AC resonance tracking (DART) mode with an AC drive amplitude of 1.5 V was employed. Unless otherwise specified, all of the AFM-based characterizations were performed at ambient conditions and the voltage is defined to be positive when the Pt tip is positively biased.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c03684.

AFM and XRD results of SFO films grown on different pO\textsubscript{2}; detailed analyses on the atomic structure and strain distribution near the BM/PV interface; time-dependent current measurements; surface height change induced by negative writing; retention of phase transformation; electrical writing in different atmospheres; and origin for the observation of the cracked-earth-type morphology in STEM (PDF)

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Notes
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