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ORIGINAL ARTICLE

Deterministic Dual Control of Phase Competition in Strained $BiFeO_3$: A Multiparametric Structural Lithography Approach

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Abstract

The realization of a mixed-phase microstructure in strained $BiFeO_3$ (BFO) thin films has led to numerous novel effects derived from the coexistence of the tetragonal-like monoclinic phase (T phase) and rhombohedral-like monoclinic phase (R phase). Strong strain and polarization differences between the phases should result in a high level of transformation plasticity, which enables the continuous alteration of the relative proportion of R and T states in response to external forces. Although the potential for utilizing such plasticity to control mixed-phase populations under external stimuli is evident, direct experimental evidence backed by equilibrium predictions has not yet been fully demonstrated. Here we demonstrate deterministic control of mixed-phase populations in an epitaxially strained BFO thin film through the application of localized stresses and electric fields in a reversible manner. The results illustrate and rationalize deterministic control of mixed phases in strained BFO films, which could be crucial in tuning their functional properties. The findings also highlight a new multiparametric technique in the scanning probe lithography toolbox based on tip-assisted electric and strain field manipulation of functional properties that might find application beyond the ferroelectric domain and structural phase lithography.

Keywords Phase competition · Ferroelectric · Stress · Lithography

1 Introduction

The coexistence of phases in functional materials can be exploited to achieve a rich array of enhanced responses under applied external stimuli. Phases can coexist in a range of material systems via chemical doping, facilitating a wide range of exciting phenomena, such as colossal magnetoresistance in doped manganites [1] and large piezoelectric responses observed in both relaxor ferroelectrics [2] and $Pb(Zr_xTi_{1-x})O_3$ with compositions around the morphotropic phase boundary [3]. Similar scenarios can also be realized in ferroelectric thin films where epitaxial strain can result in coexisting phases reminiscent of eutectic microstructures [4]. The overall functionality of such mixed-phase systems is defined as much by the individual phase populations as the interfaces or boundaries that separate them. As a result, controlling the relative population of the phases and thus the boundaries becomes critical to harness the full potential of mixed-phase systems and achieve highly tuned smart system responses. For each of these material systems, free-energy-based thermodynamic considerations enable the construction of phase diagrams as a function of variables, such as composition, temperature, and epitaxial strain, which predict the regions of stability for the individual phases and the possibility of coexistence of phases. In this context, Pertsev et al. [5, 6] mapped the equilibrium structure of a ferroelectric material versus temperature and misfit strain, producing a "Pertsev phase diagram" of the resulting observable phases through a phenomenological Landau–Devonshire model. These results have since been experimentally verified, and phase-field simulations have illustrated mixed-phase regions in epitaxial thin films of $BaTiO_3$ [7]. In such an epitaxially grown film, the choice of the substrate confines the mixed phases to a narrow range defined by the temperature. However, in principle, external field variables, such as applied

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stresses and electric fields, can be envisaged to tune the population of mixed phases in ferroelectrics and the associated boundaries that separate them. Such control of extrinsic variables on phase composition is already a pertinent approach in structural ceramics and steels with a high level of transformation plasticity, where the solid undergoes a phase transformation accompanied by an irreversible strain under applied stress [8, 9]. As an example, doped zirconia ceramics, such as yttria-stabilized zirconia, exhibit significant fracture toughness as a result of a stress-induced martensitic phase transformation from the metastable tetragonal phase to the monoclinic phase [10, 11]. In this work, we detect a high level of transformation plasticity in an epitaxially strained thin film of $BiFeO_3$ (BFO), which forms a nanoscale mixture of ferroelectric phases under ambient conditions, and exploit this plasticity via localized stresses and electric fields to alter the phase population in a deterministic manner. Electric bias and stress applied via a scanning probe tip are used in a complementary and reversible manner to drive the material into different population states, in essence providing a multiparametric scanning probe lithography technique to engineer associated functional properties. The experimental results illustrate the potential of the developed approach toward deterministic control of mixed phases in functional materials and in turn tuning the overall material response.

In its unstrained rhombohedral state, BFO has attracted considerable attention over the years as a room-temperature multiferroic with high remnant polarization, antiferromagnetic order, and domain wall conductivity, among a number of critical developments [12]. Under a sufficiently large compressive epitaxial strain imposed via the substrate, BFO films transform into a tetragonal-like monoclinic phase (T phase) with a substantial increase in the *c*/*a* axis ratio. Upon increasing thickness beyond a critical limit, a nearly dislocation-free nanoscale mixture of the T phase along with a distorted rhombohedral-like monoclinic phase (R phase) is formed [4]. The combination of the unique properties already evident in BFO enhanced by the presence of a strain-driven morphotropic-phase-boundary-like scenario has led to numerous novel effects, such as enhanced spontaneous magnetization confined to the R phase [13], large piezoelectricity due to differences in *c*-axis lattice parameters and commensurate phase boundaries [14–16], shape memory effect [17], and electronic conduction at interfaces in mixed-phase thin films [18, 19]. The various degrees of freedom in this mixed-phase system, namely, spin, charge, and lattice strain, along with the commensurate phase boundaries, make it highly susceptible to control via external fields [20]. Thus, an ideal system for controlling the population of phases is created, resulting in microstructures and boundaries arising out of them. Indeed, studies have been successful in demonstrating local reversible transformations from the R phase to the T phase through the application of localized electric fields [21]. In this context, Sun et al. have shown that R-to-T phase transitions can be reversibly achieved using a direct current (DC) electric field [22]. Studies have also shown that local tip-mediated stresses induce a T to R phase transformation in epitaxially strained BFO, demonstrating local control of the ferroelectric phase [23]. These findings indicate the more general viability of dual reversible control of phases and raise the interesting possibility of achieving various mixtures of phases by combining the two stimuli in a deterministic manner. To address the aforementioned issues and develop an optimal approach toward achieving the desired microstructures in such mixed-phase systems, we present our experimental observations of nanoscale control of phases under tip-induced bias and stress.

2 Experimental Methods

For this study, epitaxial BFO thin films with a thickness of approximately 50 nm were grown using the pulsed laser deposition technique on (001)-oriented $LaAlO_3$ substrate with a 5-nm buffer layer of (La, Sr)CoO_3, which serves as the bottom electrode. The details of the sample preparation technique have been reported elsewhere [24]. The mechanical and electrical writing and imaging of the resulting topography and domain structure were conducted using a Veeco Dimension 3100 atomic force microscopy (AFM) system with a Nanoscope IIIa controller. Mechanical writing was performed by increasing the deflection setpoint (i.e., the cantilever deflection voltage maintained by the atomic force microscope feedback loop proportional to the applied force or stress) to a Pt-coated Si tip (Nanosensors PPP-EFM) while scanning. From a combination of force–distance measurements and subsequent tuning methods, the spring constant was determined to be 2.8 Nm^{-1}. Each 1 V of deflection setpoint from the tip corresponds to a loading force of approximately 150 nN. The obtained images were processed on WSxM (an open-source SPM image processing software) [25]. Piezoresponse force microscopy (PFM) of the investigated regions was undertaken at 20-kHz frequency using a 2-V alternating current.

3 Results and Discussion

3.1 Mixed Phases in Strained BFO and Bias-Induced Control of the T Phase

The typical morphology of the as-grown mixed-phase BFO, which exhibits the characteristic needle-like R phase structures embedded within the smooth T phase matrix, is shown in the topographic image presented in Fig. 1a. The banded needle-like structures shown in the topographic

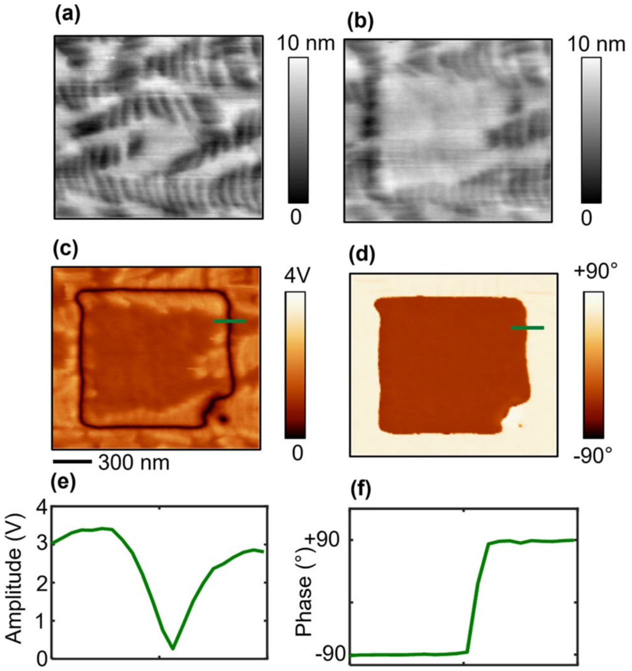

Fig. 1 Creation of a controlled domain structure with the size of 1 μm × 1 μm following the application of a tip-assisted electric field over the 1-μm area. Topographic images **a** before and **b** after electric field application highlight the structural transition from the mixed R and T phase to a T-phase-dominant state (the *dark needles* denote the R phase, whereas the *gray background* denotes the T phase). The corresponding vertical piezoresponse force microscopy (VPFM) amplitude (**c**) and phase (**d**) confirm the existence of 180° ferroelectric switching by the applied bias. Line traces (**e**, **f**) across the boundary of the written region highlight the reduction of the polar component at the point of phase inversion, confirming the presence of ferroelectric switching alongside the crystallographic transition

image represent the R phase, whereas the matrix shown in the topographic image represents the T phase. Notably, the initial microstructure comprises both the R and T phases. For the initial investigations of the electric-field-induced phase switching, which arises in mixed-phase BFO, a uniform – 4-V bias was applied through the tip to facilitate an initial set state within the sample. Topography scans before and after electric field application are presented in Fig. 1a and b, respectively. The writing of a controlled domain structure with the size of 1 μm × 1 μm, is illustrated in Fig. 1c and d. Here, we obtain clear evidence of a field-induced phase transition, with a reordering of the ferroelectric domain structure in the sample occurring through the conversion of the mixed R and T phase state into a locally T-phase-dominant state. The vertical PFM (VPFM) amplitude and phase presented in Fig. 1c and d, respectively, confirm the existence of out-of-plane ferroelectric switching. By taking a simple line trace across the boundary of the written region, we detect a reduction in the amplitude of the implied polar component (Fig. 1e) at the point of phase inversion (Fig. 1f), confirming the presence of ferroelectric switching alongside the transition from a mixed phase to a predominantly T phase (i.e., the out-of-plane polarization was reversed and the phase was changed). The result illustrates that bias drives the phase population toward the T phase.

3.2 Stress-Induced Injection of the R Phase into a Previously Bias-Written T Phase Region

To investigate the stress-mediated injection of the R phase into a previously bias-written T phase region, we imaged the central 2 μm × 2 μm region of Fig. 2a with a – 6-V DC bias from the tip (to maximize the T phase). The R phase needles are observed to have been completely erased from the topography. Moreover, the applied bias has switched the out-of-plane orientation of the region, as presented in the VPFM shown in Fig. 2b and c. Then, the same

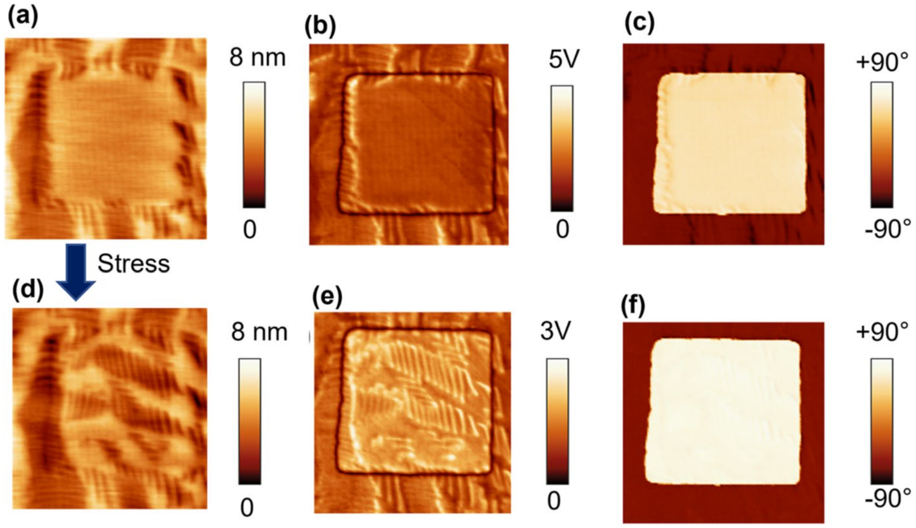

Fig. 2 Stress-induced injection of the R phase into a previously bias-written T phase region: **a** initial topography obtained after imaging the central region with – 6 V, **b** VPFM amplitude and **c** phase obtained after bias writing, **d** topography after the application of 750 nN tip loading force to the same region, **e** piezoresponse force microscopy amplitude, and **f** phase reveal stress-injected R phase needles

region was imaged with a 750 nN loading force, driving the film into an R-phase-dominated state seen clearly in the topography (Fig. 2d). The resulting PFM images illustrate that the stress-written R phase possesses a similar level of contrast compared with the pre-existing domains, thus emphasizing their ferroelectric nature. Notably, the stress-induced injection of the R phase retains the same polarity as the prepoled T phase (in the upward direction). This effect is different from the electric-field-induced reversibility of R and T phases observed by Sun et al. [22] where the electric field is used to drive the tetragonal phase between up and down states and R–T phase mixtures are obtained as intermediate outcomes at subsaturation voltages during ferroelectric switching of the T phase. In contrast to the 180° flexoelectric switching investigated in ultrathin (< 5 nm) films by Lu et al. [26] no reversal in VPFM is observed in thick (50 nm) films of mixed-phase BFO where the associated strain gradient from the tip is expected to permeate a minimal fraction through the thickness of the film. Thus, this study focused on the competition between the phases under applied stresses and electric fields. The result illustrates the clear effect of stress, which drives a predominant T phase into an R-phase-rich region, indicating that phase competition can be shifted toward favoring the R phase over the T phase using stress (in this regard, we observe that the native state of the films is mainly the T phase).

3.3 Effect of Varying Applied Stress on the Electrically Written Region

The effect of varying the applied stress on the induced transformation from the electrically written T phase to the R phase was tested. The 4 µm × 4 µm region shown in Fig. 3a was written with a DC bias exceeding the coercive voltage of the film of – 3 V applied from the metallic tip to create a region mainly consisting of the T phase (Fig. 3b). Then, the bias-written area was scanned with the AFM tip while increasing the tip force in different segments of the image from 150 nN to 1200 nN (or an estimated 0.35 to 2.9 GPa stress assuming the tip to be a flat disk with a radius of 11.5 nm) with a constant scan rate of per line 0.2 Hz. The resulting topography is displayed in Fig. 3c. Critical stress is required to induce a T to R phase transformation. Once the critical stress is surpassed, the density of the created R phase rapidly increases. The concentration of the R phase levels off as opposed to linearly increasing until a completely R phase region is created. This finding highlights the limiting case where a further increase in the proportion of the R phase would likely force the film to dislocate from the substrate and relax to a bulk rhombohedral state.

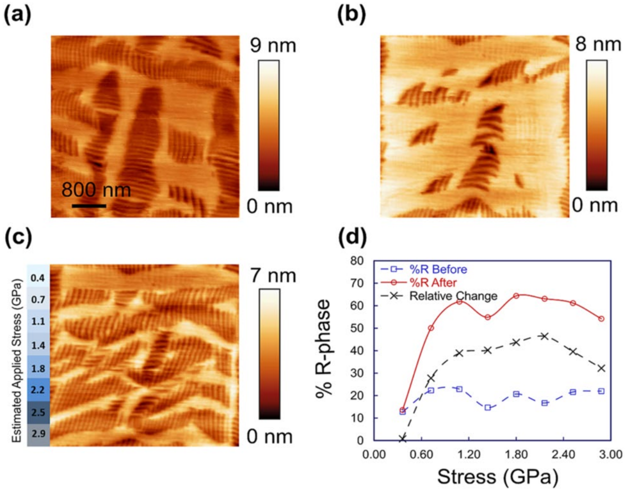

Fig. 3 **a** Atomic force microscopy (AFM) topographic image showing the initial state of the film and **b** after application of – 3-V DC bias. **c** Resulting topography after applying increasing tip stress in the segments shown while the region was scanned with the AFM tip. **d** Image-analysis-based quantitative estimation of the R phase concentration present at the surface of the film before and after the application of stress and thus the relative change in the R phase plotted as a function of the applied stress

3.4 Dual Control of Phases in Epitaxially Strained BFO via Selective Application of Stresses or Electric Fields

The key to achieving precise control over the relative populations of R and T phases in epitaxially strained BFO is establishing an effective experimental method that can reversibly and reliably transform the two phases in the system. The coexistence of two low-symmetry phases [27] with different strain and polarization orientations in an energetically mixed-phase space, combined with the commensurate interfaces between them, should result in substantial susceptibility to external stimuli, creating an ideal system for controlling the resulting phase populations. Previous literature has well established that local R to T phase transformations can occur under appropriate levels of applied electric fields from conductive AFM tips [4, 21, 22, 28, 29]. In a similar manner to the work conducted by Lu et al. [26] recent studies have demonstrated local T to R phase transformations under local uniaxial stress [23, 30]. Here, these two stimuli are applied selectively in a dual control method that can reversibly drive localized regions of the film into different population states.

Figure 4a shows the initial topography of the 2 µm × 2 µm region investigated, which consists of a nearly equal proportion of R and T phases. Imaging the region demarcated by the white dashed line in Fig. 4a while applying – 5-V DC bias from the AFM tip results in the topography shown in Fig. 4b, which is now nearly completely dominated by the T phase.

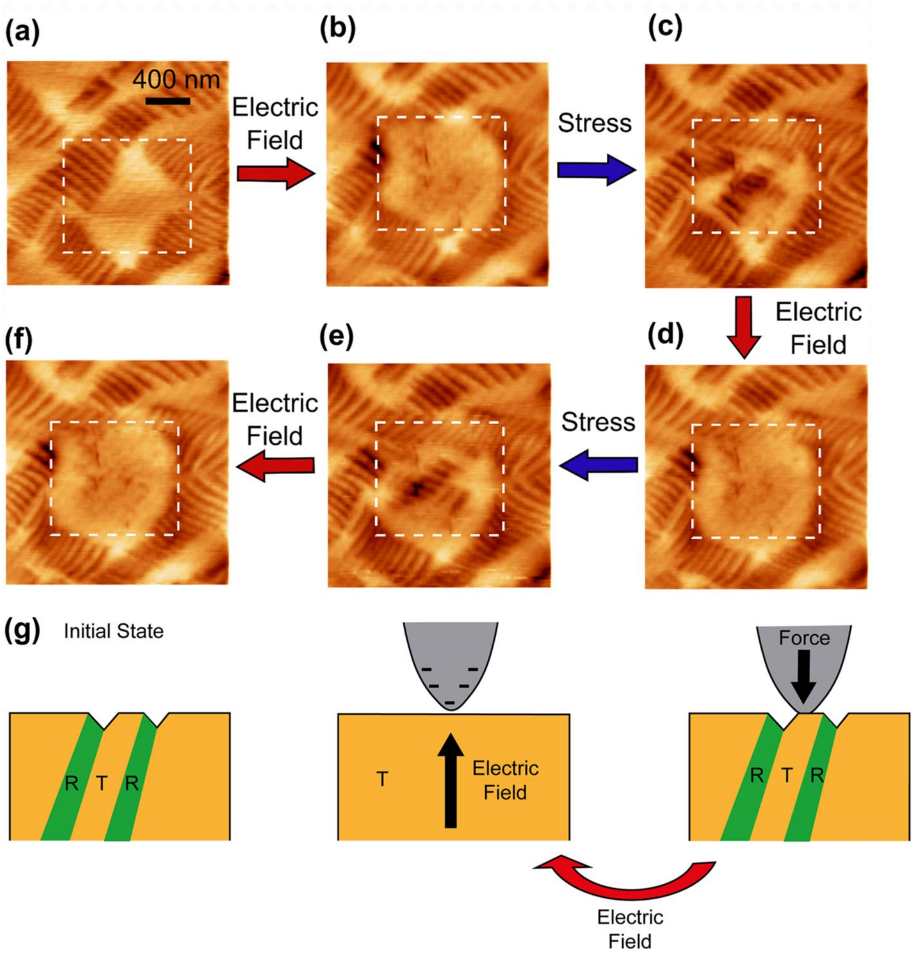

Fig. 4 Dual reversible control of phases in epitaxially strained BiFeO$_3$: **a** Initial AFM topography of the region showing a mixture of R and T phases. **b** After imaging the region (demarcated by the *white dashed line*) with − 5-V DC from the tip. **c** After imaging the same region with a 750-nN loading force. **d**–**f** Demonstration of the reversible and repeatable nature of the method. The *Z*-height *scale bar* is 8 nm for all images. **g** Schematic illustration of the dual control method

Then, the region was imaged while applying 750 nN loading force from the same AFM tip, corresponding to applied stress of approximately 1.8 GPa (assuming the tip to be a flat disk with a radius of 11.5 nm). As evident in the resulting topography (Fig. 4c), the localized stress was sufficient to cause the region to become inundated with R phase needles (previously illustrated in Fig. 2). Hence, to drive the film back into a T-phase-dominated state, the region is again imaged with a − 5-V DC bias from the tip (Fig. 4d). Crucially, this demonstrates reversible control over the phase populations in the film. Furthermore, the process is repeatable. Thus, the application of 1.8 GPa brings back a similar R-phase-dominated microstructure, which can again be erased with the same applied bias, as shown in Fig. 4e and f. Such reversible and repeatable control confirms the viability of the approach to systematically control the coexisting phase populations.

4 Conclusions and Outlook

We have demonstrated reversible dual control of mixed ferroelectric phases in an epitaxially strained film via the application of external stimuli. The dual approach shown here has similarities in terms of achieving reversible R-to-T phase transitions as previously undertaken via electric field exclusively but also reveals subtle differences in terms of the polarity of the injected R phase and its tunability with increasing levels of applied stress. Well-controlled modifications of mixed-phase populations have been shown where electric field, stress, and misfit strain can be used as simultaneous handles to control the final microstructure. Direct experiments show the clear potential of the approach toward deterministic control of mixed phases. With the increasing realization of the unique role of the mixed-phase boundaries in strained BFO system in controlling functional properties, such as R–T phase boundary conductance [31], enhanced electromechanical response [32], and magnetoelectricity [13], deterministic dual control can be used as a powerful tool to control the functionality of the ferroelectric film, opening up potential applications in piezotronic and magnetoelectric devices. Beyond mixed-phase ferroelectrics, the combinatorial manipulations of mixed-phase systems via external variable fields (as shown here) could have significant implications for the effective control of functionality associated with mixed phases. The findings also highlight a new option in the scanning probe lithography toolbox based on tip-assisted electric and strain field manipulation of functional properties that might find application beyond the ferroelectric domain and structural phase lithography.

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Conflicts of interests There are no conflicts to declare.

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