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Direct observation of ferroelectric domain switching in varying electric field regimes using *in situ* TEM

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ABSTRACT

In situ Transmission Electron Microscopy (TEM) techniques can potentially fill in gaps in the current understanding interfacial phenomena in complex oxides. Select multiferroic oxide materials, such as BiFeO₃ (BFO), exhibit ferroelectric and magnetic order, and the two order parameters are coupled through a quantum–mechanical exchange interaction. The magneto–electric coupling in BFO allows control of the ferroelectric and magnetic domain structures via applied electric fields. Because of these unique properties, BFO and other magneto–electric multiferroics constitute a promising class of materials for incorporation into devices such as high–density ferroelectric and magnetoresistive memories, spin valves, and magnetic field sensors. The magneto–electric coupling in BFO is mediated by volatile ferroelastically switched domains that make it difficult to incorporate this material into devices.

To facilitate device integration, an understanding of the microstructural factors that affect ferroelastic relaxation and ferroelectric domain switching must be developed. In this article, a method of viewing ferroelectric (and ferroelastic) domain dynamics using *in situ* biasing in TEM is presented. The evolution of ferroelastically switched ferroelectric domains in BFO thin films during many switching cycles is investigated. Evidence of partial domain nucleation, propagation, and switching even at applied electric fields below the estimated coercive field is revealed. Our observations indicate that the occurrence of ferroelastic relaxation in switched domains and the stability of these domains is influenced the applied field as well as the BFO microstructure. These biasing experiments provide a real time view of the complex dynamics of domain switching and complement scanning probe techniques. Quantitative information about domain switching under bias in ferroelectric and multiferroic materials can be extracted from *in situ* TEM to provide a predictive tool for future device development.

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1. Introduction

Ferroelectricity is a key material property for a variety of applications, from piezoelectric sensors and actuators to non-volatile random-access memory to solar energy conversion. There is a special class of ferroelectrics that also exhibit magnetic properties (i.e., multiferroic materials) which provides access to additional functional properties (Fiebig, 2005; Schmid, 1994). Although there has been considerable attention given to multiferroism in materials such as BiFeO₃ (BFO), it is a very rich and complex system and much remains to be learned about the fundamental nature of domain dynamics in this system—especially the factors that control and allow for the manipulation of ferroelectric switching and, in turn, magnetic order in this material (Chu et al., 2007a; Eerenstein et al., 2006; Martin et al., 2008; Ramesh and Spaldin, 2007). In fact, very

little information about the temporal response of domains in multiferroics to external fields is available, despite the importance of this field-dependent evolution for a range of applications. Therefore, by obtaining a better fundamental understanding of the domain dynamics of model multiferroics, such as BFO, and the relationship of these dynamic responses to the microstructure of the material will provide important guidance to the multiferroic community and to future device designs. In particular, a quantitative understanding of the material's coupling processes under electric fields can help to design new devices and to predict and mitigate failures, which will aid optimization of future device designs. This paper presents an approach to directly observe, using *in situ* TEM, the ferroelectric domain switching process in device geometries of the multiferroic BFO. This method reveals the fundamental processes associated with ferroelastic domain switching events at exceptional temporal and spatial scales.

BFO is a rhombohedrally distorted perovskite material with well understood ferroelectric domain structure (Chu et al., 2007b; Streiffer et al., 1998). Recent studies suggest a strong coupling

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between ferroelectric and antiferromagnetism in BFO that is mediated via ferroelastic switching events and enables electric field control of magnetic structures (Chu et al., 2008; Lebeugle et al., 2008; Zhao et al., 2006). Further work has demonstrated that these ferroelastically switched domains in BFO can be unstable due to internal elastic interactions (Baek et al., 2010). As the ability to control magnetic ordering via an applied electric field would provide a broad field for technological innovation, it is thus of great scientific and practical interest to investigate the mechanisms influencing the ferroelastic relaxation process (Béa et al., 2008; Bibes and Barthélemy, 2008).

In recent years the study of polarization dynamics at the nanoscale has been aided by the development of a number of new characterization techniques (Chu et al., 2008; Gruverman et al., 2005; Gruverman and Kholkin, 2006; Jesse et al., 2008; Kalinin et al., 2010; Kim et al., 2007), including scanning-probe based characterization methods such as piezoresponse force microscopy (PFM). PFM has, in turn, given us great insight into the nature of polarization switching in ferroelectric materials including studies of nucleation at free surfaces (Jesse et al., 2008) and in capacitor structures (Gruverman et al., 2005), and domain wall dynamics (Kim et al., 2007). Recent PFM experiments revealed the ability to directly observe domains in multiferroics and to control their switching behavior using electric fields (Gruverman et al., 2005; Gruverman and Kholkin, 2006; Jesse et al., 2008; Kalinin et al., 2010; Kim et al., 2007; Zhao et al., 2006). Martin et al. have used this coupling to demonstrate rudimentary electric field control of ferromagnetic domain structures in BFO-based-heterostructures (Chu et al., 2008). Although PFM is the technique most often employed to study ferroelectric switching in thin films, this technique has some limitations which impair the study of small-scale, dynamic events such as ferroelastic relaxation. In particular, scanning-probe studies are limited in resolution based on the tip diameter (which typically have a tip radius of tens of nanometers), direct measurement of kinetics are not possible due to the relatively slow scanning rate of the PFM system (even with exciting recent advances on this front) thus rendering probing processes at short time scales difficult, and the nature of the probe-based process limits results to near-surface information.

Kalinin et al. (2010) summarized the state-of-the-art techniques that can be used to probe ferroelectric domain dynamics, and alluded to the exciting new opportunities in employing transmission electron microscopy (TEM) techniques. True measurements of domain behavior and their interaction with localized microstructural features (e.g., defects) are impossible without using a TEM. The better spatial and temporal resolution of *in situ* TEM as well as the ability to image through the entire sample volume renders this technique capable of imaging the intermediate steps joining the process of domain wall motion, and thus providing new insights about the proposed switching mechanisms. In this paper we present results of *in situ* transmission electron microscopy experiments designed to investigate the dynamics of ferroelastically switched domains in BFO thin films. Our experimental setup (Fig. 1), permits the observation of the response of ferroelectric domains in BFO to in-plane electric fields, and the devices are patterned to permit reversible ferroelastic switching. Epitaxial, thin films of BFO with epitaxial, co-planar SrRuO₃ (SRO) electrodes are grown and patterned on (001) SrTiO₃ single crystal substrates consistent with methods similar to those previously published (Chu et al., 2008). Control over the electrode separation and voltage applied enables the application of electric fields from well below the coercive field to well above the coercive field. During the TEM studies, the sample is tilted away from the [001] zone axis and a two-beam condition is set up to excite reflections with reciprocal lattice vectors parallel to the projection of the polarization. This results in strong diffraction contrast from certain ferroelectric

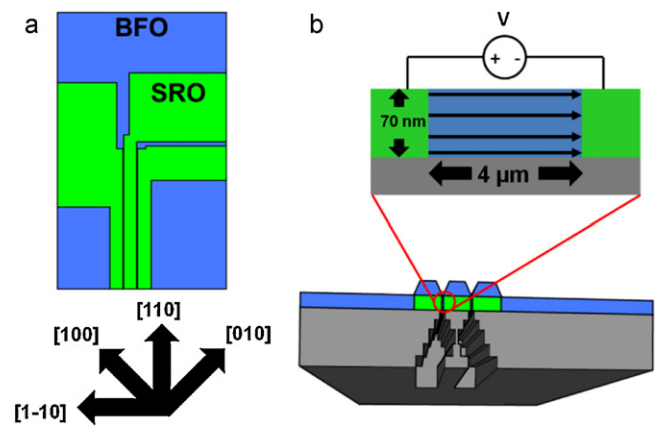


Fig. 1. Schematic diagrams revealing: (a) a plan-view of BFO device structure with SRO electrodes, (b) a side-view of FIB-thinned region of STO substrate with an enlarged schematic showing the planar applied voltage between the SRO electrodes.

domains in the BFO thin film (Streiffer et al., 1998). Thus, diffraction contrast provides clear imaging of domains. Additionally, domain walls, which are twin-type δ -boundaries, can be identified by visible alternating stripes of contrast formed from the inclination of domain walls with respect to the electron beam. This assists in locating domains and their accompanying walls in the film (Streiffer et al., 1998).

Selection of the field strength and duration allows for the tuning of the experiments to study specific regimes of ferroelectric switching dynamics. In a high field regime (i.e., applied fields above the coercive threshold, E_c) domain nucleation is initiated in keeping with the Kolmogorov–Avrami–Ishibashi (KAI) model describing domain switching kinetics (Jo et al., 2009; Pantel et al., 2010). Domain nucleation will occur at a time-scale well below the temporal resolution of the TEM and in the high-field regime, the domain propagation velocity may also exceed the time resolution of the microscope (Fatuzzo, 1962; Shin et al., 2007). In a low field regime (i.e., applied fields below E_c) domain propagation speeds can be brought within the temporal resolution of the *in situ* TEM technique. However, dynamics in low fields are complicated by interactions between domain walls and defects such as oxygen vacancies, dislocations, and elastic interactions between domain walls. These interactions can induce non-linear field dependencies of domain dynamics that deviate from the KAI model (Jo et al., 2009). It has been recently reported by Pantel and colleagues that the geometric exponent in the KAI model, n , which describes the effective dimensionality of domain growth in ferroelectrics can take on values that fall outside of the KAI model at low fields (Pantel et al., 2010).

Thus, careful tuning of the field strength to remain within the range of the KAI model while slowing specific domain dynamics to within the temporal capabilities of the *in situ* technique allows for successful investigation of the domain dynamics within these BFO and other ferroelectric films. This paper describes a systematic *in situ* TEM approach to observing ferroelectric domain switching events in real time with increasing applied field.

2. Material and methods

The device structures were produced by first depositing a blanket layer of the epitaxial oxide metal SrRuO₃ (25–75 nm) on a single crystal SrTiO₃ (001) substrate at 680 °C in 100 mTorr of oxygen. Following the growth of the SrRuO₃, a lithography step is used to define the desired planar electrode structure. This is followed by a precision ion-milling step to generate the complex in-plane electrode structures used in the TEM studies for application of in-plane

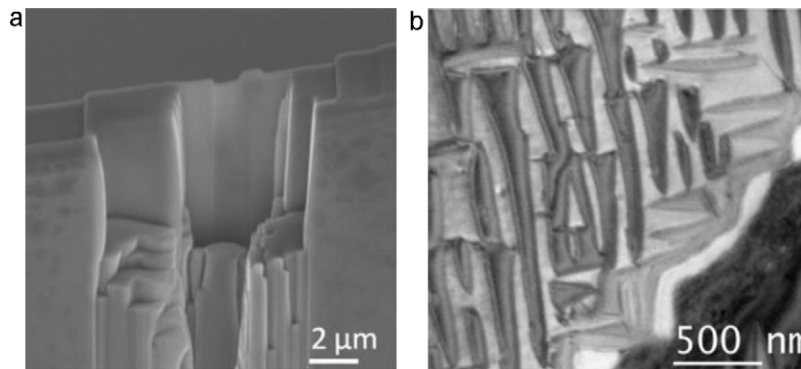


Fig. 2. (a) Secondary electron image of back-thinned sample in the FIB illustrating the large, uniformly thin area beneath the BFO trench. (b) Bright field TEM image revealing ferroelectric domain contrast.

electric fields. The photoresist was then removed and epitaxial films of BFO (35–100 nm) were deposited on the device structure at 700 °C in 100 mTorr of oxygen. Films were deposited so that all the ferroelectric polarization point downward, reducing the number of possible polarization from eight to four. This work builds on previous work that demonstrated the ability to precisely engineer, control and tune the domain structures in complex functional oxide materials such as BFO (Chu et al., 2006, 2009). Overall, due to the geometric limitations of the TEM, the structures studied by *in situ* TEM were engineered to emulate cross-sectional capacitor structures common to device applications. In this work we focus on planar electrode spacing of $\sim 4 \mu\text{m}$.

Dynamic TEM experiments were performed using a Hummingbird Scientific *in situ* electrical biasing holder. The holder is connected to a Keithley Instruments model 2400 voltage source. This source allows for precise control over the applied DC voltages ($\pm 200 \text{ V}$), with voltage step sizes in the microvolt range (10^{-6} V) and current steps sizes in the picoamp range (10^{-12} amps). Minimum pulse widths on the order of 1 ms are also possible with this system. The geometry of the electrical biasing of the sample is shown in Fig. 1.

The field of view during TEM experiments is concentrated between the planar SRO electrodes, and voltage can be applied across this region. To ensure that the configuration of the sample is controlled, the samples are prepared using a combination of tripod polishing and FIB milling techniques. In order to have a uniform electric field, the samples are thinned uniformly using a FIB, ensuring a flat surface of BFO between the SRO planar electrodes. Care is taken during FIB milling to ensure minimal sample damage (note that the FIB milling is occurring from the back, substrate side of the sample and which helps minimize damage to the BFO material to be studied). Typical results of the FIB milling process are shown in Fig. 2. During TEM experiments, the samples will be biased, and simultaneously imaged using digital streaming video.

3. Results and discussion

3.1. Ability to observe intermediate processes during domain switching

It was demonstrated that our *in situ* TEM method for studying ferroelectric domain switching in BFO structures described herein is feasible and promising for the understanding of device operation under bias. While the results are comparable with those produced by the PFM, we found that the improved temporal resolution of this *in situ* technique permits study of the intermediate behaviors involved in ferroelastic switching. For example, Fig. 3 shows that we observed particular aspects of domain switching behavior that might not otherwise be able to be seen with techniques that have

lower temporal resolution. More specifically, the improved temporal resolution reveals the evolution of the domains during the switching process, and hints at the ability to view aspects of domain nucleation domain, propagation parallel to the electric field direction, and finally, lateral domain growth perpendicular to the electric field direction.

Fig. 3 contains frames captured from a movie showing a biasing experiment with an application of a -40 V (133 kV/cm , below the estimated E_C of 300 kV/cm), 750 ms long pulse, along the $[-1 -1 0]$. The figure illustrates the ability to view some intermediate steps in the switching process by capturing snapshots during electrical biasing between $t=0$ before the voltage was applied and $t=\infty$ long after the voltage was turned off. Several differences between the images are readily apparent, the most drastic of which are numbered in Fig. 3e–h. For example, domain 3 clearly exhibit a polarization switch and also experience growth, however not all domains follow this exact behavior.

First, a longer, contiguous domain, labeled 2+3 in Fig. 3g and h, has formed from the combination of parts of the separate domain 2 and 3 in Fig. 3e and f. Second, domain tips that point along the $[1 0 0]$ direction, visible in the 500 ms and after images, are found to be nearly formed along the domain walls of the domains numbered 5 and 6. Third, differences in domain morphology and position are witnessed in each of the numbered domains. In Fig. 3f, after 100 ms (the initiation time for the voltage pulse to reach maximum strength), domains 2 and 3 are observed propagating along the $[0 -1 0]$ direction and impinging directly upon the domain walls of domains 5 and 6. It is the result of this apparent and rapid collision that alters the 5 and 6 domains, with domain 5 nearly bifurcating post-collision (Fig. 3d and h). Changes to domain 6 as a result of this collision are more limited as the domains in the vicinity block the motion of the newly-formed domain tips. Domain–domain repulsion plays an important role in determining the final domain configuration post-bias. A marked example of this repulsion can be seen by examining domain 1 in Fig. 3f and g, 100 and 500 ms after the beginning of the bias. This domain moves along the $[-1 0 0]$ direction until it encounters another group of domains, whereupon the red domain elongates along the direction of travel and contracts along the orthogonal $(0 1 0)$ direction as if the two groups of domains were repelling one another.

Efforts to map exact polarization to domains such as those shown in Fig. 3 are underway. This task is complicated by the limitation imposed by the single-tilt axis of the biasing holder. However, because the films are grown such that the polarization all point along the same out-of-plane direction, i.e. up or down, the number of different polarization is reduced from eight to four in the BFO films. The in-plane electrodes and sample geometry minimize the out-of-plane component of the electric field, minimizing any out-of-plane switching and preserving the as-grown four polarization

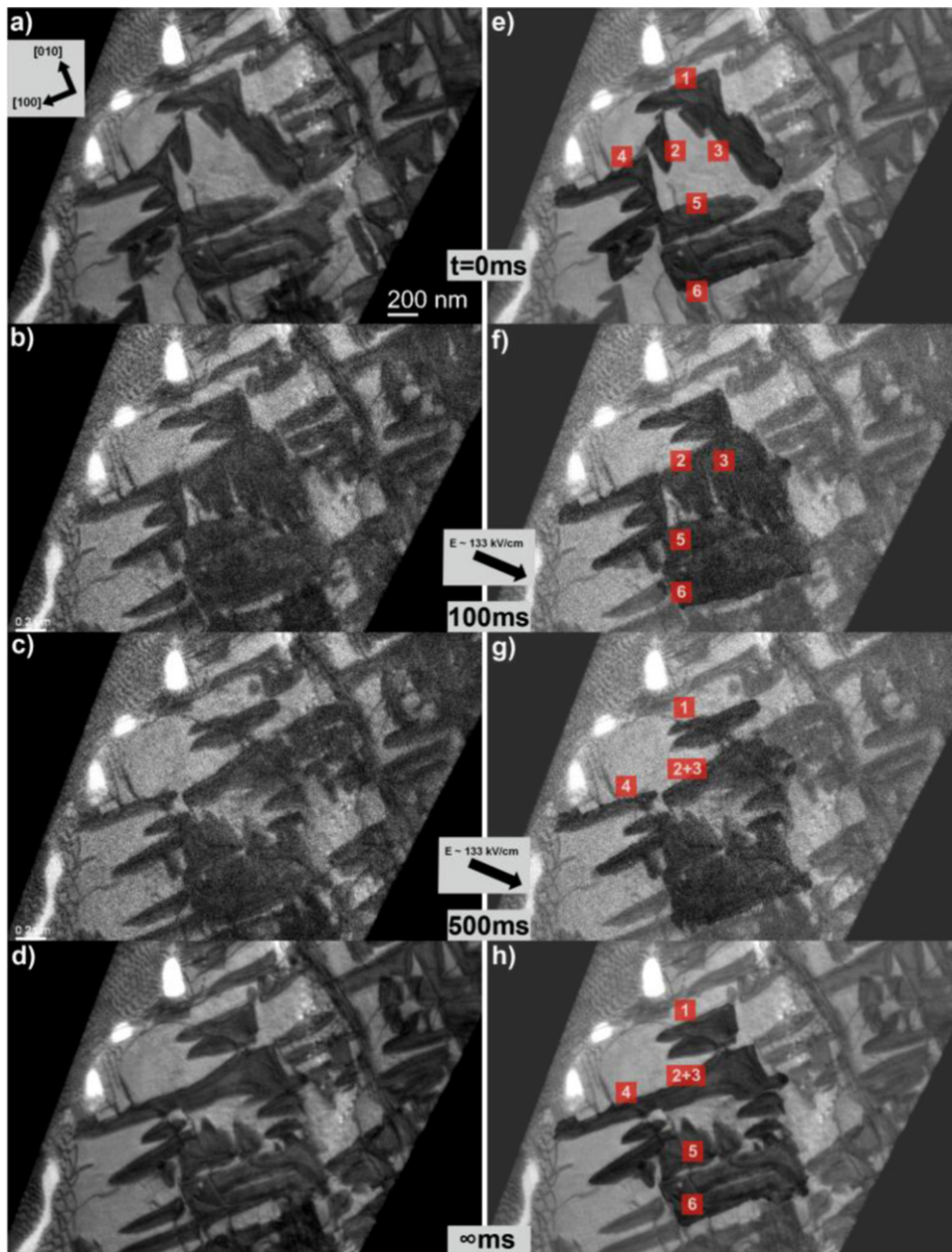


Fig. 3. Images extracted from an *in situ* biasing experiment captured in bright field TEM, (a)–(d). Domains are numbered to guide the eye in (e)–(h), and reveal intermediate processes caught at 100 and 500 ms, respectively, not shown in pre and post images.

states. With careful mounting of the sample in the biasing holder, the sample can be tilted to excite a set of $\pm\{110\}$ planes. The projection of the $\langle 111 \rangle$ polarization in BFO falls upon these $\{110\}$ planes in plan view, and thus a set of domains with polarization which project onto the excited $\{110\}$ planes become strongly diffracting. This provides a qualitative understanding of the polarization and its evolution under biasing.

3.2. Role of coercive field in switching dynamics

We took advantage of the ability to view this “evolutionary” domain switching behavior in real time with *in situ* TEM to examine the differences in the process as a function of applied field. We found that studying switching necessitates an increase in the applied electric field strength to that near or above the coercive field strength of the BFO films, which is estimated at 300 kV/cm. At field strengths between 150 kV/cm and 200 kV/cm domain

relaxation behaviors are witnessed. This behavior may be related to the observed relaxation of ferroelastic domains in BFO, which is thought to occur due to a high energy barrier prohibiting direct ferroelectric switching (Baek et al., 2010). The high spatial and temporal resolution of this *in situ* technique compared to PFM is again instrumental in observing this domain relaxation behavior, as it occurs over a short length span and is not observed in the post-bias images.

The $t=0$ image (Fig. 3a and e) shows the as-grown morphology of a set of striped ferroelectric domains that are in a diffracting condition, and thus appear dark in contrast. A complicated array of individual domains and domain clusters point along the $\langle 100 \rangle$ and $\langle 010 \rangle$ directions. Some domain tips are squared-off while many others have sharp tips, which is generally indicative of charge accumulation at those curved tips, and is it those tips that are expected to be strongly driven by the applied electric field. All induced switching events are expected to be of the ferroelastic type, with

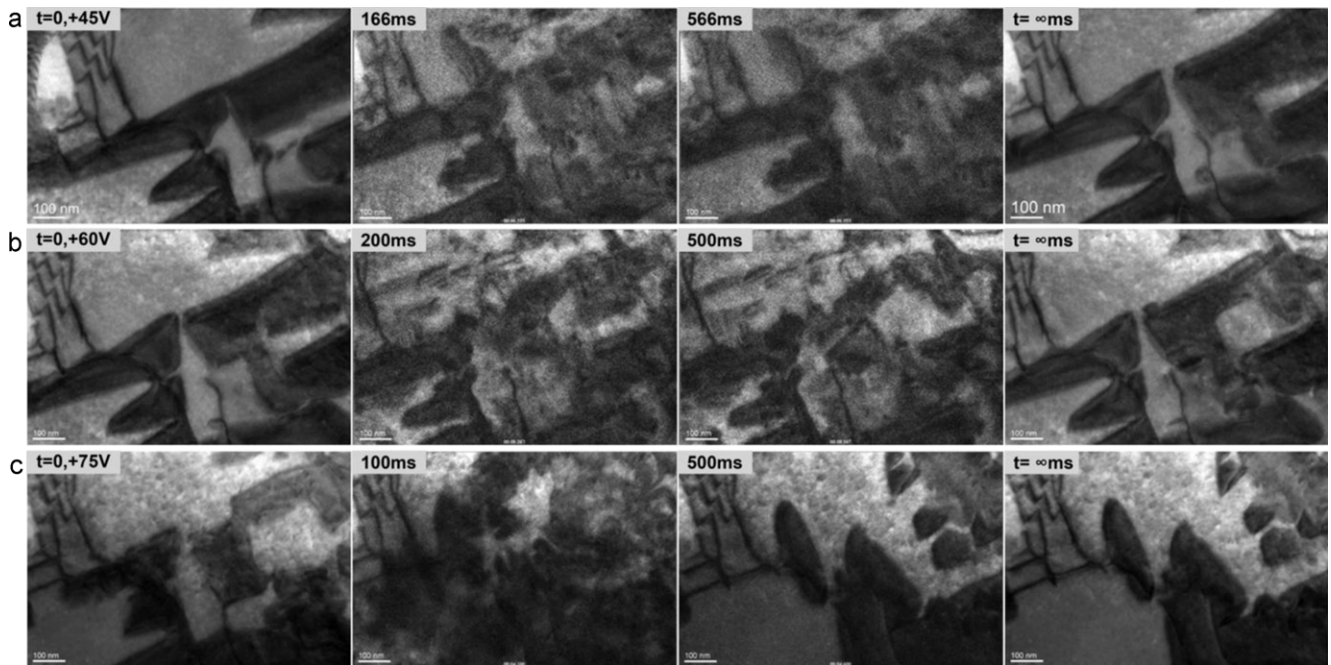


Fig. 4. Montage of three *in situ* biasing series in bright-field TEM. Pre-bias and Post-bias images are indicated by “ $t=0$ ” and “ $t=\infty$ ”, respectively. All series were taken from the same region in the same sample, and reveal the progression of the switching process with increased applied voltage (and thus increased coercive field).

71° switching, or a switch of polarization along a unit cell face edge, and 109° switching events, which entails a change along a unit cell face diagonal. We witnessed different regimes of domain switching dynamics at increasing applied electric fields (e.g., beginning at ~ 133 kV/cm) below the coercive field (>200 kV/cm). For these studies, the field was calculated by using the equation $V_{\text{app}}/W = E_c$, where W = the trench width between the two SRO electrodes and V_{app} is the applied DC bias. An experiment with a similar electrode geometry found switching to occur at a higher coercive field, which was thought to be as a result of a small electrode area (Shafer et al., 2007). In a localized area of tens of square micrometers of nearly uniform thickness, and thus nearly constant electric field, it is evident that the domains in the BFO film exhibit different responses to the applied electric field.

Fig. 4 shows a series of three biasing experiments with increasing applied voltage, and thus, increasing coercive field. The three applied voltages for the experiments were +45 V (a), +60 V (b), and +75 V (c). These experiments were performed in the same region of the sample for direct comparison of switching behavior. Differences between the pre and post images for the +45 V and +60 V series are subtle, whereas the pre and post images in the +75 V series are vastly different. Examination of the images captured hundreds of milliseconds into the biasing experiment reveal intermediate structures that are striking in their difference with either the pre or post domain patterns. It is clear that changes in the switching dynamics and relaxation patterns are strongly influenced by applied field. At an applied field of +45 V, images taken at 166 and 566 ms reveal domain switching events, but a nearly full relaxation of these the domains to the $t=0$ configuration after the field is brought to zero and nearly 3 seconds are allowed to pass. At an applied bias of +60 V, the 200 and 500 ms frames reveal (1) markedly different behavior during the switching process, and (2) a slightly altered post-bias image. It is not fully understood as to whether or not local defect concentration played a role in the differences seen in domain motion and morphology in the 566 ms and 500 ms images from the +45 V and +60 V series, respectively. When subject to +75 V of applied bias, the switching behavior was

completely different from that observed in the lower field series. At 100 ms, an intermediate stage was observed, much like that in the +45 and +60 V series, however, the domains were altered to the point where individual domains are barely discernable to the naked eye. This could be attributed to the speed of the domain motion as well as the switching process altering the domain morphology. At 500 ms, however, the domains have been completely switched, which was not observed in the previous series. This result is far more similar to that seen in BFO switched by PFM techniques in Chu et al. (2008). Thus, there appears to be a critical coercive field at which full domain switching can be achieved, however this is not independent of local microstructure in the film.

The complex interplay of mechanical and electrical fields associated with the motion of ferroelastic domains complicates interpretation of these results, yet many of the behaviors witnessed fit within the developed framework of the theory of ferroelectric and ferroelastic switching. The strain energy associated with dislocations and ferroelastic domain walls promotes the nucleation and stabilization of domains at these sites (Jesse et al., 2008). Work is in progress to use convergent beam electron diffraction techniques to map the polarization of the ferroelectric domains in the se BFO films, allowing us to quantify the type of switching and preferred nucleation sites. Additionally, defects that can only be detected below the spatial resolution of the instrument used for these experiments are known to strongly influence domain and propagation. For example, point defects, such as oxygen vacancies, are believed to impede domain wall motion. Inhomogeneous distribution of these defects in a film will thus result in non-uniform domain behaviors to an applied uniform electric field. Higher magnification biasing experiments will enable the visualization of how defects interact with domain walls.

4. Conclusions

We are able to observe domain propagation and relaxation at relevant time and length scales using our *in situ* biasing experiments. The results are comparable with those produced by the

piezoresponse force microscopy, yet the superior temporal resolution of this *in situ* technique permits study of the intermediate behaviors involved in ferroelastic switching. The range of spatial resolutions available in the TEM and the sensitivity of the technique to defects and dislocations enables the capturing of domain–defect interactions, an advantage over PFM. We witnessed a variety of intermediate domain behaviors, including domain repulsion, domain collision, and domains stabilized by dislocations, during these biasing experiments. The images and movies captured provide insight into the processes of ferroelastic domain switching in BFO films. Despite the fact that more domains experienced more complete reversible switching behavior if high enough voltages are applied, similar to that that was found in PFM studies by [Chu et al. \(2008\)](#), our *in situ* TEM experiments revealed that domains did not move in coordinated motion. Each domain experienced different morphological changes at different rates, as is shown in [Fig. 3](#).

Overall, the results herein indicate that *in situ* TEM is an ideal tool to investigate the intermediate processes of domain switching under bias. The temporal resolution of this *in situ* technique is sufficient to capture the intermediate steps of domain motion. The techniques and instrumentation used this research can be extended to investigate the nanoscale properties of other important classes of materials, such as piezoelectrics, pyroelectrics, and ferroelastics.

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