Design and Manipulation of Ferroelectric Domains in $BaTiO_3$ Thin-Films

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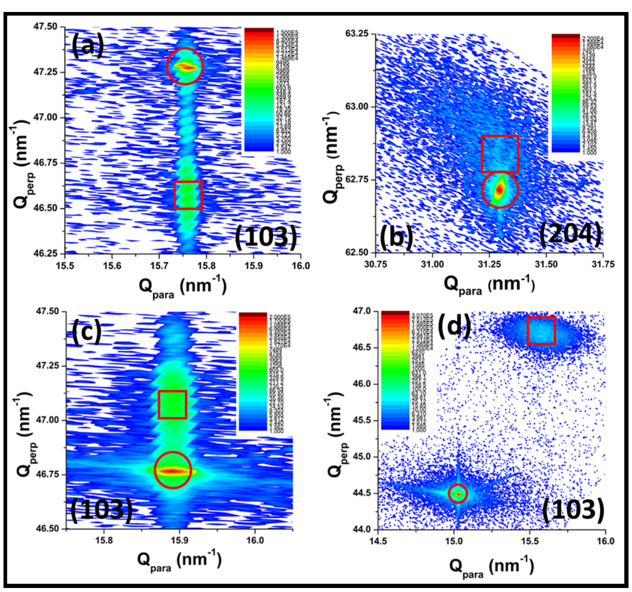
Abstract and Introduction:

As devices miniaturize, the ability to control nanoscale ordering in ferroelectric materials is important for emerging technologies. Ferroelectric materials exhibit spontaneous polarization and respond hysteretically to electric fields making them attractive for incorporation into devices, such as, non-volatile random-access memory (RAM). Additionally, locally ordered polarized regions form domains that are separated by domain walls (DWs) favorably formed from the minimization of electrostatic interactions between domains of opposing polarization. DWs have properties that differ from the ferroelectric domains and are uniquely mobile. For this reason, control of ferroelectric DW formations is desired for future nanoscale devices and functional optimization. Controlled engineering of domain wall patterns in complex ferroelectric oxides provides an avenue to new nanostructured devices realized by writing, erasing, and moving DWs. Mobile ferroelastic DW configurations can be manipulated to control phonon transportation, promoting novel applications in phononics. Here, using strain engineering, we design a variety of phases and DW configurations in ferroelectric $BaTiO_3$ films [1].

Previously, up/down polarization has been exploited in ferroelectric memory devices. However, limited attention has been given to in-plane polarized ferroelectrics. Recently, large lattice parameter substrates capable of inducing tensile strain in $BaTiO_3$ have been developed to promote in-plane polarization. Biaxial strain achieved during epitaxy, where the ferroelectric thin-film adopts the underlying substrate in-plane lattice in the paraelectric phase (a_0 = 4.007 Å), gives two types of strain depending on the lattice mismatch [2]. Substrates with smaller lattice parameter induce compressive strain, leading to up/down polarization, while substrates with larger lattice constants produce tensile strain, promoting in-plane polarization [3].

The substrates investigated were $ReScO_3$ (Re = Gd, Sm, Nd, Pr), La_2LuScO_6, and $LaLuO_3$, which have orthorhombic structures (*Pbnm*; *No.* 62), but can be represented as pseudocubic. Substrate averaged psuedocubic lattice constants, in Ångströms, are as follows, respectively: 3.968, 3.987, 4.008, 4.020, 4.113, 4.184. $BaTiO_3$ films were grown on the above, single crystal perovskite substrates, by reactive molecular



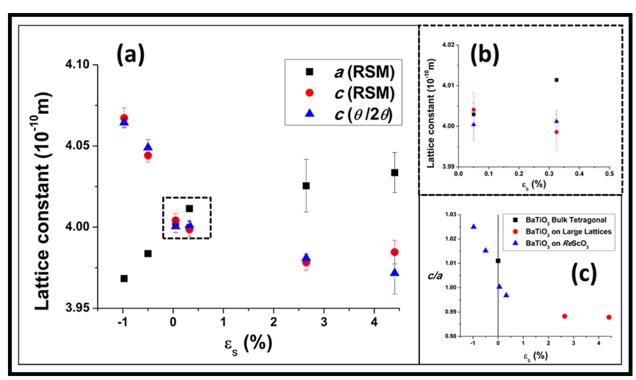


***Figure 1, left:** Reciprocal Space Maps (RSM) of $BaTiO_3$ on various substrates with reflections indicated: $SmScO_3$ (a), $NdScO_3$ (b), $PrScO_3$ (c), and $LaLuO_3$ (d). Film signals identified by squares and substrates by circles. **Figure 2, above:** Lattice constants of $BaTiO_3$ thin-films determined by x-ray diffraction θ-2θ scans and reciprocal space mapping (RSM) as a function of strain, (a), with 0-0.5% misfit strain in (b) for clarity, and tetragonality in (c).*

beam epitaxy, spanning from -0.97% compressive strain to +4.40% tensile strain, with misfit strain defined beforehand [2]. X-ray diffraction (XRD) and piezoresponse force microscopy (PFM) measurements were used to identify different domains and phases in strained $BaTiO_3$ films.

Results and Conclusions:

Structural Characterization. XRD θ-2θ scans and reciprocal space mapping (RSM) techniques were employed to determine how the $BaTiO_3$ structure varied with epitaxial strain and the resulting phase. From RSM of a compressive film, seen in Figure 1a, the signal of $BaTiO_3$ appears below the $SmScO_3$ signal, indicating a fully strained, coherent film, stabilizing a *c*-domain with polarization along the [001]. Low strain tensile in $BaTiO_3$ on $NdScO_3$ was resolved using the (204) reflection, seen in Figure 1b. RSM of $BaTiO_3$ on $PrScO_3$, in Figure 1c, shows fully strained, coherent tensile strain in the film stabilizing an orthorhombic *aa*-phase with in-plane polarization along the [110] direction. $BaTiO_3$ on $LaLuO_3$ shows relaxation, seen in Figure 1d, from disagreeing $\mathbf{Q}_{para}$ vectors.

From θ-2θ scans, the out-of-plane lattice constant, *c*, was calculated using Bragg's Law from the (002) reflection while RSM signals afford both *c* and *a* lattice constants relative to the signal of the underlying substrate, plotted in Figure 2a, b. In Figure 2c, tetragonality, the ratio of *c* and *a*, reveals the evolution of the strained structure and realized relaxation of $BaTiO_3$ on La_2LuScO_6 and $LaLuO_3$, where the tetragonal phase is favored in-plane, since $a/c \approx c/a$ of bulk tetragonal $BaTiO_3$. Thus, relaxed thin-films on La_2LuScO_6 and $LaLuO_3$ exhibit in-plane polarization in the [100] and [010] directions. When tetragonality is greater than one, as in compressive strained films, out-of-plane polarization is enhanced along the [001], whereas, in tensile strained films, tetragonality is less than one, indicating in-plane polarization.

Domain Mapping and Manipulation. PFM was used to map domain polarization in nanoscale regions and selectively pole local regions upon application of an electric field. Vertical PFM verified *c*-domain formation in compressively strained films of $BaTiO_3$ on $GdScO_3$ and $SmScO_3$, supporting RSM findings. Selective manipulation of a compressively strained, 10 nm $BaTiO_3$ on $SmScO_3$ with a fully strained 6 nm $SrRuO_3$ Inner Back Electrode (IBE) depicts controllable switching, shown in Figure 3, where a 750-nm region was poled using an applied -3-Volt vertical bias to the area in a slow raster and mapped immediately thereafter.

Tensile strained orthorhombic in-plane polarized films with rectangular domains and DW along the [100] and [010] directions can be seen in $BaTiO_3$ on $PrScO_3$ and resemble others [4]. Remarkable out-of-plane local hysteretical switching using a 3-Volt bias waveform on a tensile strained 40 nm $BaTiO_3$ on $PrScO_3$, with an IBE as before, can be seen in Figure 4a, despite having in-plane domains, seen from lateral PFM amplitude response, in Figure 4b, and phase mapping, in Figure 4c. Local switching of the [110] polar axis to [001] shows controlled formation of a tetragonal *c*-domain from an orthorhombic *aa*-phase. Evidence of polarization manipulation using PFM depicts nanoferroelectric functionalities promoting future devices with the ability to controllably write and switch domains using electrical biases.

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References:

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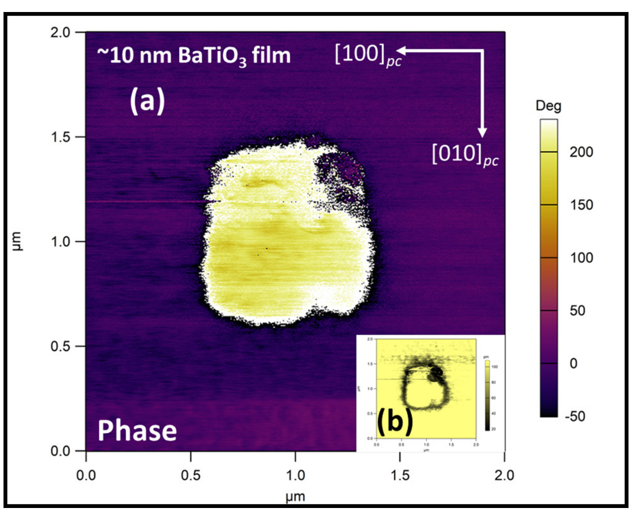

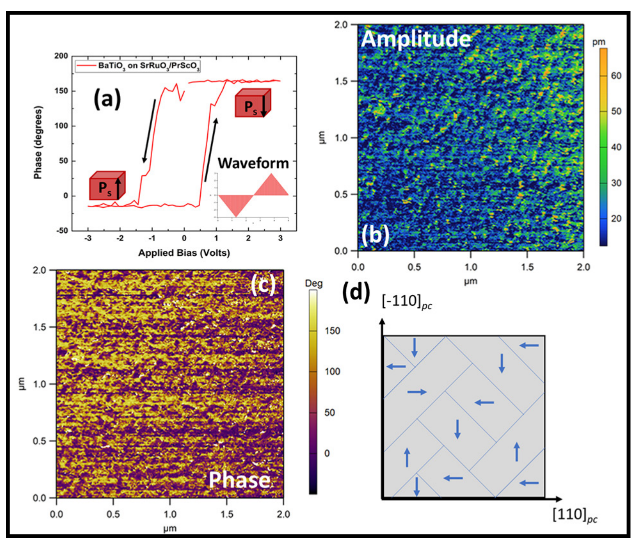

Figure 3, left: Locally poled $BaTiO_3$ thin-film, (a) and the written domain wall seen in PFM amplitude, (b). Figure 4, right: Out-of-plane hysteresis (a) of $BaTiO_3$ on $PrScO_3$, lateral PFM mapping amplitude response (b), the corresponding phase (c), and a derived model depicting truncated aa*-domains with in-plane polarization (d).*