



**QUEEN'S  
UNIVERSITY  
BELFAST**

## Functional and structural effects of layer periodicity in chemical solution-deposited Pb(Zr,Ti)O<sub>3</sub> thin films

Brewer, S. J., Williams, S. C., Deng, C. Z., Naden, A. B., Neumayer, S. M., Rodriguez, B. J., ... Bassiri-Gharb, N. (2017). Functional and structural effects of layer periodicity in chemical solution-deposited Pb(Zr,Ti)O<sub>3</sub> thin films. DOI: 10.1111/jace.15057

### Published in:

Journal of the American Ceramic Society

### Document Version:

Peer reviewed version

### Queen's University Belfast - Research Portal:

[Link to publication record in Queen's University Belfast Research Portal](#)

### Publisher rights

© 2017 The American Ceramic Society

This work is made available online in accordance with the publisher's policies. Please refer to any applicable terms of use of the publisher.

### General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

### Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact [openaccess@qub.ac.uk](mailto:openaccess@qub.ac.uk).

# **Functional and Structural Effects of Layer Periodicity and Chemical Heterogeneity in Chemical Solution-Deposited Pb(Zr,Ti)O<sub>3</sub> Thin Films**

Steven J. Brewer<sup>1</sup>, Samuel C. Williams<sup>2</sup>, Carmen Z. Deng<sup>2</sup>, Aaron B. Naden<sup>3</sup>, Sabine M. Neumayer<sup>4</sup>, Brian J. Rodriguez<sup>4</sup>, Amit Kumar<sup>3</sup>, Nazanin Bassiri-Gharb<sup>1,2</sup>

<sup>1</sup> *G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, USA*

<sup>2</sup> *School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA*

<sup>3</sup> *Centre for Nanostructured Media, School of Mathematics and Physics, Queen's University Belfast, Belfast, BT7 1NN, United Kingdom*

<sup>4</sup> *School of Physics and Conway Institute of Biomolecular and Biomedical Research, University College Dublin, Belfield, Dublin 4, Ireland*

## **ABSTRACT**

This work investigates the role of crystallized layer periodicity and thickness on functional response in chemical solution-deposited lead zirconate titanate thin films fabricated with periodic, alternating Zr and Ti gradients normal to the surface of the film. Films were processed with a range of layer periodicities with similar total film thickness, in order to relate the number of layers and compositional oscillations to structural and functional response changes. Trends of increased extrinsic contributions to the dielectric and ferroelectric responses are observed with increasing layer periodicity, but are counterpointed by simultaneous reductions of intrinsic contributions to the same. Transmission electron microscopy reveals in-plane crystallographic discontinuity at individual crystallization interfaces. Samples with smaller periodicity, and thus thinner layers, potentially suffer from out-of-plane grain size refinement and subsequent reduction in domain size, thereby limiting potential extrinsic contributions to the response. The strong compositional oscillations in samples with larger periodicity result in deep fluctuations to the tetragonal side of the phase diagram, potentially reducing intrinsic contributions to the response. On the other hand, piezoresponse force microscopy results suggest the large chemical oscillations in samples with larger periodicity also result in closer proximity to the morphotropic phase boundary, as evidenced by local acoustic softening at switching, signaling potential phase transitions.

## I. INTRODUCTION

Ferroelectric thin films have found ample use in ferroelectric random access memories (FeRAM), thin film capacitors, infrared (IR) detectors, acoustic and ultrasound devices, and microelectromechanical systems (MEMS) sensors and actuators.<sup>1, 2, 3, 4, 5, 6</sup> Traditional processing of such films has often stressed chemical homogeneity in order to maximize dielectric, ferroelectric, and electromechanical responses.<sup>7, 8, 9, 10, 11</sup> In lead zirconate titanate (PZT), the presence of a morphotropic phase boundary (MPB), which separates the rhombohedral and tetragonal (R/T) phases, has further increased interest in compositions with minimal chemical variation: enhanced polarizability arising from the coupling of phases in the vicinity of the MPB results in large increases to dielectric and piezoelectric responses, making compositions in its proximity extremely attractive.<sup>12, 13</sup> While attempts for homogeneous PZT compositions near the MPB have become ubiquitous both in research and industrial applications, recent work on heterogeneous compositions and film structures that traverse the MPB have shown promising enhancements to ferroelectric and piezoelectric responses in increasingly thin films.<sup>14, 15, 16</sup>

A variety of approaches have been implemented to elucidate the effects of chemical heterogeneity in ferroelectric thin films. Theoretical methods have predicted large dielectric and piezoelectric anomalies in heterolayered epitaxial films.<sup>17, 18</sup> Experimental approaches, including discrete heterolayers, graded compositions, bi- and tri-layer superlattices, and other fabrication approaches have been employed to study interactions between dissimilar phases and layers in ferroelectric thin films.<sup>15, 16, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27</sup> The majority of these have demonstrated some degree of enhancement to ferroelectric response, in addition to interesting polarization interactions and thermodynamic properties, such as unusual phase change sequences and nonergodicity.<sup>27</sup> Specifically, ferroelectric hetero-, bi-, and gradient-layers can show large

enhancements of the overall dielectric, ferroelectric, and electromechanical responses of ferroelectric thin films.<sup>15, 16, 23, 27</sup> However, while functional response enhancements are often reported, the mechanisms by which such enhancements are derived are somewhat debated. Anbusathaiah et al., concluded that labile ferroelastic nanodomains in R/T bilayered PZT thin films contribute to giant electromechanical couplings in the films.<sup>16</sup> Work by Mangalam et al., demonstrated nearly coherent strain in PZT R/T bi-layered and graded thin films, contributing to asymmetric bias profiles in the films, thereby resulting in increased tolerance to strain relaxation and enhanced ferroelectric properties.<sup>15</sup> Others have suggested that electrostatic coupling, internal bias fields, interfacial asymmetry, and flexoelectricity contribute to increased polarizability and resulting enhancements of functional properties in ferroelectric superlattices.<sup>14, 15, 17, 18, 21, 24, 28, 29</sup> While the origins of response enhancement are perhaps multifaceted and not unequivocally elucidated, the fact remains that the overwhelming majority of these reports has concentrated on single-layer films with unique B-site cation (Zr/Ti) gradients, or unique bi-layers of rhombohedral and tetragonal compositions.

In this work, we investigate chemical solution deposition (CSD) of periodic PZT thin films deposited with alternating R/T layers across a range of layer periodicities. Attractive response enhancement has clearly been demonstrated for films spanning the MPB and leveraging the resulting phase boundary; by studying films of similar thickness but varying layer periodicity, we can elucidate the contributions of the *periodicity* of fluctuations in chemical heterogeneity to changes in functional response. Furthermore, we can study potential contributions to the functional properties from the mobility of internal interfaces, *e.g.*, phase boundary and domain wall motion, by correlating structural and chemical variations in the films to trends in their dielectric and ferroelectric responses. The study of periodically-layered, chemically-heterogeneous CSD thin

films is expected to shed light on the fundamental interactions and mechanisms for response enhancement of PZT compositions in proximity to and traversing the MPB.

## II. EXPERIMENTAL PROCEDURE

Periodic R/T (pR/T) PZT thin films were fabricated via CSD from precursor solutions with nominal composition  $\text{Pb}_{1.2}\text{Zr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ , with concentrations varying from 0.10M to 0.40M. The films were spin-coated on platinized 100-oriented, *p*-type Si wafers (675  $\mu\text{m}$  Si // 500 nm thermal  $\text{SiO}_2$  // 35 nm sputtered  $\text{TiO}_2$  // 100 nm Pt), pyrolyzed at 400° C for 60 seconds to remove solvent and residual organic material, and annealed at 700° C for 60 seconds in a rapid thermal annealer after each deposited layer. A seed layer of 0.15M PZT, approximately 15 nm thick, was deposited first to induce 100-texture in the subsequent PZT layers. The overall target thickness for all samples was ~200 nm. Thermodynamic and kinetic nucleation and growth factors, as described by Brooks *et al.*,<sup>30</sup> and Calame and Muralt,<sup>31</sup> result in films with steep Ti/Zr cation gradients (and expected R/T phases, discussed later) normal to the thickness of the film across each individually-crystallized layer. Measured layer periodicity,  $\Lambda_{\text{meas}}$ , was calculated using contact profilometry (KLA-Tencor P15, subject to 3-5% experimental error), using the formula

$$\Lambda_{\text{meas}} = \frac{d}{n} \quad (1)$$

where  $d$  is the film thickness(subtracting the seed layer thickness from the total measured thickness) and  $n$  is the number of crystallized layers. For comparison of crystallographic orientation, chemical composition, and film microstructure, multiple films were also fabricated using a traditional “multi-layer anneal” (MLA) method, where multiple layers are pyrolyzed together before a final crystallization anneal (see Figure 1).<sup>11</sup> This method yields highly-

homogenous CSD PZT thin films with good dielectric and electromechanical properties, as described elsewhere.<sup>11</sup>

Baseline X-ray diffraction (XRD) analysis of both the pR/T thin films as well as the MLA films for comparison was performed on PANalytical Alpha-1 (Figure 2). The periodicity of the pR/T films is investigated by the presence of satellite peaks centered around the 100- and 200-peaks of PZT (Figure 2a, 2c), as described by Schuller.<sup>33</sup> In addition to the previously-described method of determining each individual layer thickness, the stacking periodicity of the pR/T films were also determined using the Schuller formula:<sup>34</sup>

$$\Lambda_{Schuller} = \frac{\lambda}{2[\sin(\theta_i - \theta_{i-1})]} \quad (2)$$

where  $\lambda$  is the wavelength of the X-ray beam and  $\sin(\theta_i - \theta_{i-1})$  represents the incident angle between two subsequent satellite peaks in the XRD trace. Comparisons of the Schuller periodicities,  $\Lambda_{Schuller}$ , and measured periodicities,  $\Lambda_{meas}$ , are shown in Table 1. Chemical fluctuations across the thickness of the films were studied through use of X-ray photoelectron spectroscopy (XPS) depth profiling (Figure 3) on a Thermo K-Alpha using Ar bombardment to etch the sample between measurements.

**Table 1.** Properties of CSD pR/T films. Comparison of layer periodicities,  $\Lambda$ , as measured via contact profilometry (taking into account the seed layer thickness),  $\Lambda_{meas}$ , and by using the Schuller formula,  $\Lambda_{Schuller}$ .<sup>33</sup> The results show good agreement between  $\Lambda_{meas}$  and  $\Lambda_{Schuller}$ , with a maximum of 8% variation.

Solution Molarity (M)	Layers	Thickness (nm)	Lotgering Factor (100) (%)	$\Lambda_{meas}$ (nm)	$\Lambda_{Schuller}$ (nm)	Error
0.10	16	199 ± 6	93	11.5 ± 0.3	10.9 ± 0.1	6%
0.15	9	201 ± 6	96	20.7 ± 0.6	20.4 ± 1.6	1%
0.20	7	211 ± 6	99	28.0 ± 0.8	26.4 ± 1.2	6%
0.25	6	216 ± 6	98	33.5 ± 1.0	32.3 ± 0.6	4%

0.30	5	$205 \pm 6$	99	$38.0 \pm 1.1$	$41.5 \pm 1.9$	8%
0.35	4	$208 \pm 6$	99	$48.3 \pm 1.4$	$49.1 \pm 2.2$	2%
0.40	4	$241 \pm 7$	98	$56.5 \pm 1.7$	$57.6 \pm 1.7$	2%
0.40	3	$190 \pm 6$	99	$58.3 \pm 1.7$	$58.8 \pm 0.1$	1%

In order to further investigate internal interfaces in the films, including potential phase boundaries and domain walls, transmission electron microscopy (TEM) was performed on selected samples. Cross-sections for TEM were prepared on an FEI Nova 600 dual-beam instrument using standard protocols. (S)TEM and energy dispersive X-ray spectroscopy (EDX) analyses were performed on a Philips TF20 operated at 200 kV and equipped with an EDAX Phoenix EDX system. EDX spectrum images were acquired with low dwell times and summed to improve the signal to noise ratio and minimize damage/contamination. The intensity of the Zr and Ti  $K\alpha$  lines was then determined by background subtraction and integration using Hyperspy.<sup>35</sup> The Zr composition,  $x$  from  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  was estimated using the Cliff-Lorimer analysis of the Zr/Ti ratio.<sup>36</sup> The  $k$ -factor was estimated from the MLA sample assuming a Zr composition,  $x$ , of  $\sim 0.52$  for the median ratio of intensities from the Zr & Ti profiles and applied to both samples.<sup>36</sup> While a rough estimate, this provides good agreement with the XPS data, revealing Zr enrichment in the narrow uppermost portion of each deposited layer, possibly leading to a slightly more rhombohedral structure. Results of bright-field TEM (BF-TEM) imaging, integrated EDX profiles, and high-angle annular dark field (HAADF) imaging are shown in Figure 4 and will be discussed in detail in Section III. Due to the relatively fine spatial fluctuations of composition, balancing the signal-to-noise ratio and sample damage under the electron beam, EDX analysis was not practical on the 0.10M (16-layer) film.

Dielectric, ferroelectric, and piezoelectric characterization were performed on all samples following fabrication. The measurements included, in order, low-field permittivity, polarization-



electric field hysteresis, dielectric permittivity as a function of AC electric field amplitude, dielectric permittivity-DC field tunability characterization, and macroscopic piezoelectric response as a function of DC electric field. Samples were poled with an applied DC bias at ambient temperature for 600 seconds at approximately five times the coercive voltage,  $V_c$ , directly before macroscopic electromechanical measurements in order to maximize out-of-plane polarization contributions to the piezoelectric response. A summary of these measurements for samples across the range of layer periodicities is shown in Table 2.

Low-field dielectric permittivity ( $\epsilon_r$ ) measurements were conducted at 100 mV and 1 kHz using an Agilent 4284A precision LCR meter. Polarization-electric field (P-E) hysteresis loops were performed up to fields of 300 kV/cm at 100 Hz, using a Radiant P-PM2 ferroelectric test system. Nonlinear AC dielectric permittivity ( $\epsilon_r-E_{AC}$ ) was measured up to approximately 150 kV/cm at 1 kHz. DC electric field-dependent dielectric permittivity ( $\epsilon_r-E_{DC}$ ) measurements were performed up to 300 kV/cm DC bias with an overlapping small-signal 100 mV at 1 kHz. Measurements of the converse, effective longitudinal piezoelectric response ( $d_{33,f}$ ) as a function of DC field ( $d_{33,f}-E_{DC}$ ) were performed on an aixACCT double beam laser interferometer (DBLI) up to 300 kV/cm DC bias with an overlapping AC signal  $V_{AC} \approx 0.5V_c$ . All measurements reported are subject to experimental error up to 3-5%, due to sample variability. The vertical shift in the polarization-field (P-E),  $\Delta P/2$  (Table 2), is calculated using the formula

$$\Delta P/2 = \frac{P_{rem+} + P_{rem-}}{2} \quad (3)$$

where  $P_{rem+}$  and  $P_{rem-}$  are the values of the positive and negative remanent polarization, respectively. Similarly, the horizontal shift of the electric field in both the P-E and  $d_{33,f}-E_{DC}$  hysteresis loops is determined by

$$E_{internal\ bias} = \frac{E_{C+} + E_{C-}}{2} \quad (4)$$

where  $E_{C+}$  and  $E_{C-}$  are the positive and negative coercive fields, respectively. The dielectric tunability is calculated using the expression

$$\text{dielectric tunability} = \frac{\varepsilon_{DC,max} - \varepsilon_{DC,min}}{\varepsilon_{DC,max}} \quad (5)$$

where  $\varepsilon_{DC,max}$  and  $\varepsilon_{DC,min}$  are the maximum and minimum values of the dielectric permittivity-DC field hysteresis measurement, respectively.

The Rayleigh approach was used to study intrinsic and extrinsic contributions to the dielectric response by analysis of the AC field-dependent permittivity.<sup>37, 38, 39, 40, 41</sup> The analysis quantifies reversible contributions ( $\varepsilon_{init}$ ) due to reversible domain wall motion and lattice vibration via the intercept of the AC field-dependent dielectric response; as well as irreversible contributions ( $\alpha$ ), including domain wall and phase boundary motion, via the slope of the response. Accordingly, the ratio  $\alpha/\varepsilon_{init}$  is often employed as a measure of the relative extrinsic contributions to the functional dielectric response.<sup>42</sup>

In order to sample the local piezoelectric response and probe for structural phase transitions, band excitation piezoresponse force microscopy (BE-PFM) was performed using an Asylum Research Cypher atomic force microscope (AFM). BE-PFM switching spectroscopy (BE-SSPFM) was employed to monitor changes in the hysteresis loops and resonant frequency of the films (Figure 5). BE-SSPFM scans were performed on a  $50 \times 50$  grid over a  $2 \mu\text{m} \times 2 \mu\text{m}$  area (Figure 5c right). AFM measurements of the surface topography of selected samples was performed before BE-SSPFM and flattened with a first order fitting to account for variations in the images due to sample mounting (Figure 6).

**Table 2.** Measured dielectric permittivity, loss tangent, polarization, and effective longitudinal piezoelectric responses for periodic R/T PZT thin films. Uncertainties expressed represent standard deviation to one significant figure. Measurement values are reported to the same decimal place as uncertainty for said measurement.<sup>43</sup>

Precursor Solution Molarity (M)	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.40
Number of Layers	16	9	7	6	5	4	4	3
<b>Low-field Dielectric</b>								
$\epsilon_r$	760 $\pm$ 40	800 $\pm$ 30	720 $\pm$ 20	680 $\pm$ 20	690 $\pm$ 40	740 $\pm$ 20	790 $\pm$ 40	690 $\pm$ 30
$\tan(\delta)$ (%)	1.5 $\pm$ 0.1	1.5 $\pm$ 0.1	1.4 $\pm$ 0.2	1.6 $\pm$ 0.2	1.6 $\pm$ 0.1	1.6 $\pm$ 0.2	2.1 $\pm$ 0.1	1.6 $\pm$ 0.1
<b>Rayleigh Analysis</b>								
$\epsilon_{init}$	780 $\pm$ 40	760 $\pm$ 10	730 $\pm$ 40	682 $\pm$ 7	675 $\pm$ 7	740 $\pm$ 30	780 $\pm$ 60	730 $\pm$ 50
$\alpha$ (cm/kV)	2.3 $\pm$ 0.3	2.1 $\pm$ 0.1	2.4 $\pm$ 0.2	2.4 $\pm$ 0.1	2.3 $\pm$ 0.1	2.8 $\pm$ 0.2	3.7 $\pm$ 0.6	2.7 $\pm$ 0.2
$\alpha/\epsilon_{init} \times 10^3$ (cm/kV)	3.0 $\pm$ 0.3	2.8 $\pm$ 0.1	3.2 $\pm$ 0.2	3.5 $\pm$ 0.2	3.4 $\pm$ 0.1	3.8 $\pm$ 0.2	4.8 $\pm$ 0.5	3.7 $\pm$ 0.2
<b>Polarization</b>								
$P_{saturation}$ ( $\mu\text{C}/\text{cm}^2$ )	33.5 $\pm$ 0.9	34 $\pm$ 1	35 $\pm$ 2	34.1 $\pm$ 0.6	35.4 $\pm$ 0.8	36.0 $\pm$ 0.5	36 $\pm$ 1	35.3 $\pm$ 0.8
$P_{remanent}$ ( $\mu\text{C}/\text{cm}^2$ )	12.7 $\pm$ 0.6	12.9 $\pm$ 0.4	14 $\pm$ 1	13.9 $\pm$ 0.2	15.4 $\pm$ 0.4	15.6 $\pm$ 0.1	15.7 $\pm$ 0.6	16.1 $\pm$ 0.8
$E_{C+}$ (kV/cm)	56 $\pm$ 3	56 $\pm$ 5	52 $\pm$ 9	64 $\pm$ 2	62 $\pm$ 2	57 $\pm$ 3	53 $\pm$ 4	53 $\pm$ 1
$E_{C-}$ (kV/cm)	-91 $\pm$ 2	-92 $\pm$ 5	-95 $\pm$ 7	-101 $\pm$ 7	-102 $\pm$ 4	-100.5 $\pm$ 7	-95 $\pm$ 7	110 $\pm$ 2
$E_{internal,P}$ (kV/cm)	-17 $\pm$ 2	-18 $\pm$ 3	-21 $\pm$ 2	-18 $\pm$ 4	-20 $\pm$ 1	-22 $\pm$ 4	-21 $\pm$ 3	-29 $\pm$ 2
$\Delta P/2$ ( $\mu\text{C}/\text{cm}^2$ )	1.9 $\pm$ 0.2	2.0 $\pm$ 0.4	2.5 $\pm$ 0.3	2.0 $\pm$ 0.3	2.5 $\pm$ 0.1	2.8 $\pm$ 0.4	3.0 $\pm$ 0.3	3.4 $\pm$ 0.2
<b><math>\epsilon_r</math>-<math>E_{DC}</math></b>								
% Diel. Tunability	69.1 $\pm$ 0.5	68.5 $\pm$ 0.6	68.2 $\pm$ 0.1	66.8 $\pm$ 0.7	67.4 $\pm$ 0.8	67.4 $\pm$ 0.2	70 $\pm$ 1	68.4 $\pm$ 0.1
$\epsilon_{DC,low-field}$	900 $\pm$ 10	890 $\pm$ 10	842 $\pm$ 4	788 $\pm$ 9	790 $\pm$ 20	815 $\pm$ 3	880 $\pm$ 40	790 $\pm$ 40
<b>Piezoelectric (poled)</b>								
$d_{33,f,saturation}$ (pm/V)	51 $\pm$ 2	52 $\pm$ 2	51 $\pm$ 5	50 $\pm$ 3	52 $\pm$ 2	49 $\pm$ 1	49 $\pm$ 3	49 $\pm$ 3
$d_{33,f,remanent}$ (pm/V)	24 $\pm$ 1	26 $\pm$ 2	29 $\pm$ 1	29 $\pm$ 2	30 $\pm$ 1	29 $\pm$ 1	31 $\pm$ 2	31 $\pm$ 2
$E_{internal,piezo,poled}$ (kV/cm)	-20 $\pm$ 1	-20 $\pm$ 1	-22 $\pm$ 3	-24 $\pm$ 5	-25 $\pm$ 1	-24 $\pm$ 2	-22 $\pm$ 2	-28 $\pm$ 1
<b>Piezoelectric (unpoled)</b>								
$d_{33,f,saturation}$ (pm/V)	48 $\pm$ 2	51 $\pm$ 1	52 $\pm$ 4	50 $\pm$ 1	52 $\pm$ 3	50 $\pm$ 2	50 $\pm$ 1	49 $\pm$ 3
$d_{33,f,remanent}$ (pm/V)	19 $\pm$ 5	22 $\pm$ 3	25 $\pm$ 3	23 $\pm$ 3	24 $\pm$ 2	24 $\pm$ 2	27 $\pm$ 2	27 $\pm$ 2
$E_{internal,piezo,unpoled}$ (kV/cm)	-15 $\pm$ 2	-15 $\pm$ 2	-18 $\pm$ 5	-17 $\pm$ 3	-18 $\pm$ 2	-19 $\pm$ 1	-17 $\pm$ 2	-22 $\pm$ 1

### III. RESULTS

Fabrication of CSD PZT thin films annealed after deposition and pyrolysis of each layer showed strong evidence of periodic changes in chemical composition (Figures 3, 4d, 4f) and potential structural changes (Figure 2, satellite peaks) through the thickness of the films. Thermodynamic and kinetic factors drive heterogeneous Ti-rich nucleation at the substrate-film interface during crystallization, followed by growth of a Zr-rich phase, thus forming the compositional gradient and the expected accompanying R/T phases in the crystallized PZT film.<sup>31, 44</sup> XPS measurements (Figure 3) confirmed strong Zr/Ti chemical gradients for the films processed in the range of 0.20M to 0.40M precursor solutions. However, the films processed with 0.10M and 0.15M solutions showed flatter, less distinct gradients, potentially due to cation interdiffusion between the relatively thin layers, or insufficient instrumental resolution of chemical fluctuations (individual crystallized layers are 10 to 20 nm in this range). The compositional gradients normal to the surface of the films are further confirmed via EDX as shown in Figures 4d and 4f for selected samples (see also Figure 10b, discussed later), showing up to 4% compositional variation in either direction from the initial composition of  $x = 0.53$ . These chemical variations, especially in the samples with thicker layers, are expected to demonstrate local extremes in composition up to  $\text{Pb}_{1.2}\text{Zr}_{0.57}\text{Ti}_{0.43}\text{O}_3$  and  $\text{Pb}_{1.2}\text{Zr}_{0.49}\text{Ti}_{0.51}\text{O}_3$ , corresponding to purely rhombohedral and tetragonal phases in bulk PZT, respectively. Thus, we expect that the alternating Zr/Ti gradients exhibited by the samples in this work yield some degree of periodic R/T phases.

XRD crystallographic orientation analysis of the films showed distinct satellite peaks for films fabricated in the range of 0.15M to 0.40M precursor solutions (Figure 2), indicating that the interfaces between Zr/Ti regions of each layer and parallel to the substrate exhibit a large degree

of coherency.<sup>33</sup> Calculations of the Schuller periodicities,  $\Lambda_{\text{Schuller}}$ , showed excellent agreement ( $\leq 8\%$  variation) with calculations of the measured periodicity,  $\Lambda_{\text{meas}}$  (Table 1), consistent with the periodic nature of the fabricated films.<sup>33</sup> Both sets of films showed only perovskite peaks with a large degree of 100-texture ( $>93\%$  Lotgering factor for all films, powder diffraction file (PDF) 04-016-2735, Table 1).<sup>32</sup>

Figure 7 shows trends in measured dielectric, ferroelectric, and macroscopic piezoelectric responses as a function of layer periodicity in the films. At low AC electric field, dielectric permittivity ( $\epsilon_r$ ) showed a moderate decreasing trend and the dielectric loss tangent,  $\tan(\delta)$ , exhibited a slight increasing trend (Figure 7a) with increasing periodicity. At intermediate AC electric fields, the results of the Rayleigh analysis show an increase of  $\alpha$  with increasing layer periodicity (Figure 7b). On the other hand,  $\epsilon_{\text{init}}$  (Figure 7b), shows minor decreasing trends with increasing periodicity. Accordingly, trends in the ratio  $\alpha/\epsilon_{\text{init}}$ , generally follow those observed for  $\alpha$ , i.e. overall increasing extrinsic contributions in films with larger layer periodicities (Figure 7c).

Trends in the coercive field, both positive and negative ( $E_{C+}$  and  $E_{C-}$ , Figure 7e), suggest that relatively large internal bias is developed with greater layer periodicity (Figures 8b and 8c). A similar shift in the positive direction of measured polarization on the vertical axis of the  $P$ - $E$  hysteresis measurements,  $\Delta P/2$ , is noted. This shift potentially indicates strong preferential polarization directions in the samples, with this effect augmented in samples with increasing periodicity.<sup>45</sup>

Figures 4a, 4b, 4c, and 4e show representative bright field (BF-)TEM images of selected pR/T films and a multi-layer anneal (MLA) film for comparison of microstructure. Figures 4d and 4f show Zr and Ti elemental maps and corresponding integrated line profiles from the 5-layer 0.30M pR/T and 4-layer 0.40M MLA films, respectively. Due to the polycrystalline nature of the

films, the BF-TEM images of both the pR/T and MLA films show extensive regions of mottled contrast, which are attributed to variations in grain and/or domain structure. The (16-layer) 0.10M pR/T film in Figures 4a and 4b exhibits a relatively continuous contrast throughout the film thickness whereas the (5-layer) 0.30M pR/T and MLA films in Figures 4c and e, respectively, demonstrate somewhat columnar crystallites. However, a stark change in contrast of crystallites at the central crystallization interface in the MLA film (Figure 4e) is observed and likely arises from slight changes in the in-plane crystallographic orientation, resulting in a discontinuity between the layers. This is a representative example and similar variations in contrast are observed throughout the cross-section which is several  $\mu\text{m}$  long, suggesting that this is a common feature to the MLA sample and not simply confined to one location. Similarly, regions of relative discontinuity at film-layer interfaces are observed in the pR/T films (Figures 4b and 4c), further suggesting that the crystallization interfaces play a critical role in determining the properties of these films. In the (5-layer) 0.30M pR/T film, these changes in contrast in the BF-TEM image coincide with large increases in the Zr concentration,  $x$ , of up to  $\sim 0.60$ . Therefore, they likely arise from a combination of both changes in density of the material and slight changes in crystallography since this composition lies towards the rhombohedral portion of the phase diagram.

BE-SSPFM results show characteristic piezoresponse hysteresis loops, with switching voltages in the range of 2 to 15 V, and generally increasing with film layer periodicity. The effects of charging in the 0.10M and 0.30M samples are noted in the piezoresponse hysteresis loops at high electric field through the noses at the end of the loops (Figures 5a right, 5b right). The contact resonant frequency extracted from simple harmonic oscillator (SHO) fitting of the measured piezoresponse versus excitation frequency was monitored, as it is sensitive to changes in lattice stiffness.<sup>46</sup> Namely, “acoustic softening,” or reductions in the stiffness of the locally-interrogated

material can be indicative of potential phase transitions, especially if accompanied by local enhancements of the piezoelectric response, as demonstrated by Vasudevan *et al.*<sup>46</sup> It has been reported that some degree of acoustic softening is typically observed at ferroelectric switching, but that such softening is expected to increase dramatically when it is the result of field-induced phase transitions.<sup>46</sup> Substantial acoustic softening (~4% reduction to contact resonant frequency) was observed in local regions in the pR/T film processed with 0.40M (4 layer) precursor solution (Figures 5c and 5d). Similar effects were not observed in other samples at both low and high applied tip voltages (Figure 5a, 5b, 5d).

#### IV. DISCUSSION

The observed trends of greater dielectric irreversible Rayleigh coefficient ( $\alpha$ ) with increasing layer periodicity signal potentially increased extrinsic contributions, *e.g.*, from domain walls or phase boundary motion, in samples with thicker crystallized layers. However, these results are counterpointed by the slight tendency of decreasing  $\epsilon_{init}$  contributions to the dielectric response with increasing film periodicity, suggesting a complex interaction of the compositional interfaces in the films. Grain and domain size effects, pinning of hysteretically and nonlinearly mobile internal interfaces, chemical heterogeneity, and residual stresses inevitably play critical roles in determining the effects of crystallized layer thickness in the periodic-layered pR/T PZT films studied here. In the following discussion, we consider several of the possible contributions to the observed trends in functional response.

Variations in processing conditions and indivisible layer thicknesses (*e.g.*, a 0.40M precursor solution results in individual layer thickness of ~60 nm, hence the total film thickness is either ~180 nm or ~240 nm (discounting the seed layer)) resulted in deviations from the 200-nm

target film thickness by up to ~20%. Numerous previous reports have studied scaling effects in perovskite-phase ferroelectrics, showing strongly-decreasing trends of functional properties with reduced film thickness.<sup>47, 48</sup> Figure 9 shows literature data from a variety of studies on polycrystalline thin-film ferroelectrics, compared to the present work. Logarithmic trendlines are fit to the data from this work to guide the eye in the inset plots. Neither  $\epsilon_r$  or  $d_{33,f,sat}$  showed a strong trend correlated to scaling effects, comparable to those observed in the literature. These results suggest that scaling effects are limited in the pR/T films studied in this work, and are not the root cause for the observed trends in functional response as a function of layer periodicity.

Discontinuity at the crystallization interfaces, both in the grain/domain structure and crystallite orientation are readily visible in the TEM analyses (Figures 4b, 4c, and 4e). Despite the strong columnar texture of the films (Figures 4c and 4e), the crystallites extending through the thickness of the film do not necessarily maintain consistent in-plane crystallography, as evidenced in the contrast changes across the crystallization interface (Figure 4e). This observation is important since these abrupt discontinuities in the MLA film suggest that the density of such interfaces and the number of anneals can have a substantial impact on the crystallography throughout the film thickness, and hence the overall functional properties of the film. Based on the observations here, the most abrupt discontinuities arise for films with thicker as-deposited layers and hence fewer anneals. This is likely due to spatial confinement of the phase segregation of Zr- and Ti-rich regions of the solid solution of  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  and the greater overall time afforded to crystallization and diffusion when annealing more frequently in low-periodicity (thinner layer) films, resulting in the reduction of the presence of satellite peaks in the corresponding XRD data (Figure 2). Such non-uniform crystallography throughout the film thickness may result in grain and domain size refinement for samples with smaller layer periodicity. Numerous reports have



shown that domain size (and thus wall mobility) in ferroelectric materials scales with grain size.<sup>47</sup>  
<sup>49</sup> In smaller grains where smaller domains are expected, domain walls are bound to exhibit reduced mobility, due to greater chances of interaction with other domain walls – potentially resulting in diminished extrinsic contributions to the dielectric response. These scaling effects are consistent with reduced  $\alpha$  and lower polarization ( $P_{sat}$  and  $P_{rem}$ ) and remanent piezoelectric response ( $d_{33,f,rem}$ ) in samples with thinner crystallized layers. However, while grain size reductions can explain trends in extrinsic contributions to the dielectric and ferroelectric responses, it cannot fully account for the trends in intrinsic contributions shown in Figure 7. Below, we consider other factors impacting observed trends in the intrinsic and extrinsic contributions to the response.

While the proximity of the PZT composition to the morphotropic phase boundary generally results in favorable enhancements of dielectric and electromechanical responses, there are differences in intrinsic and extrinsic contributions for compositions on either side of the MPB. Rhombohedral compositions ( $Zr > 0.53$ ) generally demonstrate greater values of  $\alpha$  than tetragonal compositions at an equal distance from the phase boundary.<sup>50, 51</sup> Coupled with the magnitude of chemical oscillations through the thickness of the film, such asymmetry can lead to additional dependence of functional response on periodicity. Chemical fluctuations from the mean composition will inevitably traverse regions of the phase diagram that offer varying levels of both extrinsic and intrinsic dielectric response. For samples with higher periodicity (thicker layers), these deviations from the mean composition are of greater magnitude than for samples with smaller periodicity, as illustrated in Figure 10a. Hence, the latter show, on average, a more homogeneous composition. On the other hand, as noted in the EDX data, the spatial extent of Ti chemical fluctuations are greater than those of Zr, and is especially apparent in the films processed with larger layer periodicity. Results of higher spatial resolution EDX analysis for a single layer of the

(5 layer) 0.30M pR/T film in Figure 10b show that normal to the thickness of the film, the Ti-rich zones are significantly thicker ( $> 60\%$  of the layer thickness) than the corresponding Zr-rich regions with a notable compositional gradient stretching over several nm. These significant chemical oscillations in the direction of the Ti-rich composition (*i.e.*, greater compositional heterogeneity) correlate with the substantial reductions to the intrinsic response,  $\epsilon_{init}$ , with increased layer periodicity discussed above.<sup>52, 53</sup> For the samples with small periodicity, their more homogeneous composition prevents compositional oscillations of similar magnitude, and corresponding reductions to the intrinsic response are relatively absent.

Thermal loading during crystallization can potentially result in large variations in residual stress in ferroelectric thin film material stacks. Numerous studies have shown that residual stresses can effectively shift the MPB, thus modifying the transition temperature,  $T_C$ .<sup>54, 55, 56, 57</sup> In PZT thin films, biaxial compressive stresses can result in a T to R phase transition, while tensile stresses have been shown to shift MPB compositions towards the tetragonal phase.<sup>54, 55</sup> Given the initial proximity of the PZT precursor solutions to the MPB, the expected tensile stresses in 200 nm-thick films (reported up to 180 MPa)<sup>58</sup> can potentially push the effective composition into the tetragonal region of the phase diagram. This concept is demonstrated in Figure 10c, showing initial composition  $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ , and an effective “stressed composition” after crossing the MPB. From the stressed composition on the tetragonal side of the MPB, the previously-discussed effects of large chemical excursions towards the tetragonal side of the phase diagram further exacerbate the potential reductions to intrinsic dielectric response.

The results of BE-SSPFM experiments show evidence of localized potential phase transitions that further support the hypothesis of deeper chemical excursions, and thus, closer proximity to the MPB in the sample with the highest periodicity. A relatively dramatic reversible

acoustic softening occurs specifically in the 0.40M, 4-layer sample (Figure 5c), where Zr/Ti cation gradients are enhanced over a wide region. However, while evidence of possible phase transitions is apparent in the acoustic softening of the 0.40M sample, the corresponding changes to piezoresponse observed are somewhat limited (Figure 5c left, notable as small steps corresponding to ferroelectric switching). Meanwhile, similar effects are not observed in other films; we discuss multiple size- and chemical heterogeneity-related potential causes for this. First, in the samples with thinner layers, deficient chemical fluctuations do not result in sufficient proximity to the MPB to yield an R/T phase transition. The individual layers of the 0.40M, 4-layer sample are nearly 20% thicker than the 0.35M sample (Table 1), allowing for a greater level of chemical fluctuation in the 0.40M samples. Second, the 0.40M, 4-layer is the sample with the greatest total thickness, and 10 to 20% thicker than all other films studied here. Thinner films are likely more susceptible to the previously-mentioned effects of residual stress. The effective composition of PZT in thinner films conceivably shifts even further from the MPB composition compared to the thicker 0.4M, 4-layer sample, to the point that even large chemical oscillations are not close enough to the MPB to observe R/T phase transitions and accompanying acoustic softening. Third, we consider the effects of Vegard strains as a result of applied pressure from the PFM probe. Defect motion as a result of applied pressure from PFM probe tips has been strongly correlated to grain size and chemical composition, and can result in changes to the ferroelectric transition temperature.<sup>59, 60</sup> It is possible that the previously-discussed grain size differences as a function of layer periodicity result in local fluctuations of the transition temperature with the pressure of the applied probe during BE-SSPFM measurements, potentially masking evidence of phase transitions in those experiments. We also note that the observed softening of the resonant frequency is unlikely to be the effects of local charge injection, the effects of which are typically associated with thinner films. Comparison of

the two samples processed with 0.40M solutions showed that substantially greater softening occurs in the *thicker* of the two samples: 241 nm with 4 crystallized layers *vs.* 190 nm thick from 3 deposited layers (not shown), and is thus not likely to result from simple charge injection.

Finally, possible contributions of the flexoelectric effect – *i.e.*, polarization generated in a solid through application of a strain gradient – to the observed trends in functional response as a function of periodicity should also be considered.<sup>28</sup> While flexoelectric contributions are typically small and difficult to fully separate from piezoelectric properties in ferroelectric-phase materials, their presence has been proposed in (heterostructured) epitaxial PZT thin films.<sup>14, 15</sup> Specifically, large strain gradients in thin films potentially arise from misfit lattice strain and due to the presence of internal interfaces, leading to flexoelectric couplings in the material. The strain-induced flexoelectricity can subsequently create large internal bias fields, breaking internal field symmetry and resulting in changes to the functional properties of such films.<sup>14</sup> In the pR/T PZT thin films studied here, large Zr/Ti chemical gradients (and the expected R/T phase transitions) inevitably lead to some amount of lattice mismatch, exacerbated in samples with greater layer periodicity. In fact, in the pR/T samples, the greater magnitude of chemical fluctuations is correlated with increasing levels of internal bias, both in the P-E and  $d_{33}$ - $E_{DC}$  hysteresis loops (Figure 8b and 8c).

## V. CONCLUSION

Successful processing of polycrystalline PZT thin films with periodic heterogeneous Zr/Ti oscillations has been demonstrated across a range of layer periodicities, with compositional gradients normal to the surface. Crystallographic phase analysis and application of the Schuller formula shows good agreement of satellite peak locations with measured layer periodicities, suggesting some degree of superlattice-like coherency between phases in the material, and

rhombohedral/tetragonal phases are expected to correspond to the Zr-/Ti-rich zones of individual layers, respectively. Trends in the measured functional response show strong dependencies of dielectric, ferroelectric, and electromechanical response on layer periodicity. Notably, remanent and saturation polarizations, remanent piezoelectric response, and extrinsic contributions to the dielectric response show strong increasing trends with increasing layer periodicity, suggesting increased mobility of internal interfaces, such as domain wall and phase boundary motion. On the other hand, minor decreasing tendencies are noted for the low-field permittivity and intrinsic contributions to dielectric response with increasing layer periodicity, suggesting a complex interaction in the samples that exceeds simple variations in domain wall mobility.

Crystallization interfaces are thought to strongly influence grain size and structure, resulting in grain and domain size refinement in samples with thinner layers, and corresponding reductions to domain wall motion. On the other hand, the magnitude of chemical fluctuations greatly affects functional response: asymmetric chemical oscillations towards the tetragonal side of the MPB result in decreased intrinsic contributions to the dielectric response in samples with larger chemical gradients, *i.e.*, larger periodicity. Residual stress effects potentially push the effective composition of the films further to the tetragonal side of the MPB, additionally exacerbating the effects of compositional oscillations. Large internal electrical bias is observed, suggesting that flexoelectric effects potentially affect functional response in samples with large chemical (and thus, strain) gradients. The results play an important role in elucidating the effects of layer periodicity on functional response in polycrystalline ferroelectric thin films, and suggest that crystallization interface number density and compositional gradients are the primary contributors to functional responses trends of CSD-processed ferroelectric thin films. Furthermore, these findings can be employed to tailor the functional response of ferroelectric thin films for

microelectronics applications, by engineering the chemical heterogeneity and number of crystallization interfaces within the film.

## **ACKNOWLEDGMENTS**

S.B., S.W., C.D., and N.B.G. acknowledge funding from the U.S. National Science Foundation (NSF) under grant numbers DMR-1255379 and CMMI-1537262. A.B.N. and A.K. acknowledge support by Department of Education and Learning, Northern Ireland through the US-Ireland R&D partnership grant no. USI-082 and funding support from the Engineering and Physical Sciences Research Council (EPSRC) through contract EP/N018389/01. S.N. and B.J.R. acknowledge support from Science Foundation Ireland (14/US/I3113). A portion of this research was conducted at the Center for Nanophase Materials Science which is a DOE Office of Science User Facility, under proposal number CNMS2014-282. The authors gratefully acknowledge Ronald G. Polcawich and Joel Martin of the U.S. Army Research Laboratory for providing the platinized Si substrates for this work.

## REFERENCES

1. C. Chang and C. Tang, "An integrated pyroelectric infrared sensor with a PZT thin film," *Sensors and Actuators a-Physical*, 65[2-3] 171-74 (1998).
2. R. Schwartz, T. Schneller, and R. Waser, "Chemical solution deposition of electronic oxide films," *Comptes Rendus Chimie*, 7[5] 433-61 (2004).
3. T. Otsuki and K. Arita, "Quantum jumps in FeRAM technology and performance," *Integrated Ferroelectrics*, 17[1-4] 31-43 (1997).
4. R. Schwartz, P. Clem, J. Voigt, E. Byhoff, M. Van Stry, T. Headley, and N. Missert, "Control of microstructure and orientation in solution-deposited BaTiO<sub>3</sub> and SrTiO<sub>3</sub> thin films," *Journal of the American Ceramic Society*, 82[9] 2359-67 (1999).
5. R. Schwartz, T. Reichert, P. Clem, D. Dimos, and D. Liu, "A comparison of diol and methanol-based chemical solution deposition routes for PZT thin film fabrication," *Integrated Ferroelectrics*, 18[1-4] 275-86 (1997).
6. P. Clem, B. Tuttle, J. Ruffner, C. Brinker, R. Schwartz, M. Rodriguez, W. Warren, R. Jones, S. Summerfelt, and I. Yoo, "Investigation of PZT//LSCO//Pt/aerogel thin film composites for uncooled pyroelectric IR detectors," *Ferroelectric Thin Films VII*, 541 661-66 (1999).
7. S. K. Dey, K. D. Budd, and D. A. Payne, "Thin-film ferroelectrics of PZT of sol-gel processing," *IEEE Trans Ultrason Ferroelectr Freq Control*, 35[1] 80-1 (1988).
8. K. D. Budd and D. A. Payne, "Sol-Gel Processing of Thin-Layer Dielectrics in Lead-Titanate-Based Systems," *Institute of Physics Conference Series*[103] 13-22 (1989).
9. K. D. Budd, S. K. Dey, and D. A. Payne, "Sol-gel processing of PbTiO<sub>3</sub>, PbZrO<sub>3</sub>, PZT, and PLZT thin films," *British Ceramic Proceedings*, 36 107-21 (1985).
10. G. Trefalt, A. Bencan, M. Kamplet, B. Malic, Y. Seo, and K. Webber, "Evaluation of the homogeneity in Pb(Zr,Ti)O<sub>3</sub>-zirconia composites prepared by the hetero-agglomeration of precursors using the Voronoi-diagram approach," *Journal of the European Ceramic Society*, 34[3] 669-75 (2014).
11. N. Bassiri-Gharb, Y. Bastani, and A. Bernal, "Chemical solution growth of ferroelectric oxide thin films and nanostructures," *Chemical Society Reviews*, 43[7] 2125-40 (2014).
12. S. Zhang, R. Xia, and T. Shrout, "Lead-free piezoelectric ceramics vs. PZT?," *Journal of Electroceramics*, 19[4] 251-57 (2007).
13. S. Mabud, "The Morphotropic Phase Boundary in PZT Solid Solutions," *Journal of Applied Crystallography*, 13[JUN] 211-16 (1980).
14. J. Karthik, R. Mangalam, J. Agar, and L. Martin, "Large built-in electric fields due to flexoelectricity in compositionally graded ferroelectric thin films," *Physical Review B*, 87[2] (2013).
15. R. V. K. Mangalam, J. Karthik, A. R. Damodaran, J. C. Agar, and L. W. Martin, "Unexpected Crystal and Domain Structures and Properties in Compositionally Graded PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> Thin Films," *Advanced Materials*, 25[12] 1761-67 (2013).
16. V. Anbusathaiah, D. Kan, F. C. Kartawidjaja, R. Mahjoub, M. A. Arredondo, S. Wicks, I. Takeuchi, J. Wang, and V. Nagarajan, "Labile Ferroelastic Nanodomains in Bilayered Ferroelectric Thin Films," *Advanced Materials*, 21[34] 3497-+ (2009).
17. Z. Ban, S. Alpay, R. Guo, K. Nair, W. WongNg, A. Bhalla, D. Viehland, D. Suvorov, C. Wu, and S. Hirano, "Lattice misfit as a design parameter for enhanced dielectric response and tunability in epitaxial barium strontium titanate films," *Morphotropic Phase Boundary Perovskites, High Strain Piezoelectrics, and Dielectric Ceramics*, 136 333-43 (2003).

18. A. Roytburd, S. Zhong, and S. Alpay, "Dielectric anomaly due to electrostatic coupling in ferroelectric-paraelectric bilayers and multilayers," *Applied Physics Letters*, 87[9] (2005).
19. I. Vrejoiu, Y. L. Zhu, G. Le Rhun, M. A. Schubert, D. Hesse, and M. Alexe, "Structure and properties of epitaxial ferroelectric  $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3/\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$  superlattices grown on  $\text{SrTiO}_3$  (001) by pulsed laser deposition," *Applied Physics Letters*, 90[7] (2007).
20. F. Pontes, E. Longo, E. Leite, and J. Varela, "Improvement of the dielectric and ferroelectric properties in superlattice structure of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  thin films grown by a chemical solution route," *Applied Physics Letters*, 84[26] 5470-72 (2004).
21. H. Lee, H. Christen, M. Chisholm, C. Rouleau, and D. Lowndes, "Strong polarization enhancement in asymmetric three-component ferroelectric superlattices," *Nature*, 433[7024] 395-99 (2005).
22. C. Wang, Q. Fang, Z. Zhu, A. Jiang, S. Wang, B. Cheng, and Z. Chen, "Dielectric properties of  $\text{Pb}(\text{Zr}_{20}\text{Ti}_{80})\text{O}_3/\text{Pb}(\text{Zr}_{80}\text{Ti}_{20})\text{O}_3$  multilayered thin films prepared by rf magnetron sputtering," *Applied Physics Letters*, 82[17] 2880-82 (2003).
23. Z. Zhou, J. Xue, W. Li, J. Wang, H. Zhu, and J. Miao, "Heterolayered lead zirconate titanate thin films of giant polarization," *Journal of Applied Physics*, 96[10] 5706-11 (2004).
24. V. Cooper, K. Johnston, and K. Rabe, "Polarization enhancement in short period superlattices via interfacial intermixing," *Physical Review B*, 76[2] (2007).
25. C. Bungaro and K. Rabe, "Epitaxially strained  $[\text{001}](\text{PbTiO}_3)(1)(\text{PbZrO}_3)(1)$  superlattice and  $\text{PbTiO}_3$  from first principles," *Physical Review B*, 69[18] (2004).
26. W. Tian, J. Jiang, X. Pan, J. Haeni, Y. Li, L. Chen, D. Schlom, J. Neaton, K. Rabe, and Q. Jia, "Structural evidence for enhanced polarization in a commensurate short-period  $\text{BaTiO}_3/\text{SrTiO}_3$  superlattice," *Applied Physics Letters*, 89[9] (2006).
27. I. A. Kornev and L. Bellaiche, "Unusual thermodynamic properties and nonergodicity in ferroelectric superlattices," *Physical Review Letters*, 91[11] (2003).
28. L. Cross, "Flexoelectric effects: Charge separation in insulating solids subjected to elastic strain gradients," *Journal of Materials Science*, 41[1] 53-63 (2006).
29. R. Ahluwalia, A. Tagantsev, P. Yudin, N. Setter, N. Ng, and D. Srolovitz, "Influence of flexoelectric coupling on domain patterns in ferroelectrics," *Physical Review B*, 89[17] (2014).
30. K. Brooks, I. Reasney, R. Klissurska, Y. Huang, L. Bursill, and N. Setter, "Orientation of Rapid Thermally Annealed Lead Zirconate Titanate Thin Films on (111) Pt Substrates," *Journal of Materials Research*, 9[10] 2540-53 (1994).
31. F. Calame and P. Muralt, "Growth and properties of gradient free sol-gel lead zirconate titanate thin films," *Applied Physics Letters*, 90[6] (2007).
32. E. Araujo, E. Lima, J. Guerra, A. dos Santos, L. Cardoso, and M. Kleinke, "Evidence for the monoclinic-tetragonal phase coexistence in  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  thin films," *Journal of Physics-Condensed Matter*, 20[41] (2008).
33. I. K. Schuller, "New Class of Layered Materials," *Physical Review Letters*, 44[24] 1597-600 (1980).
34. D. H. Bao, R. Scholz, M. Alexe, and D. Hesse, "Growth, microstructure, and ferroelectric properties of  $\text{Pb}(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3/\text{PbZrO}_3$  superlattices prepared on  $\text{SrTiO}_3$  (100) substrates by pulsed laser deposition," *Journal of Applied Physics*, 101[5] (2007).
35. F. de la Peña, T. Ostasevicius, V. T. Fauske, P. Burdet, P. Jokubauskas, M. Sarahan, D. Johnstone, and M. Nord, "HyperSpy 1.1.2." in: Zenodo, 2017.



36. G. Cliff and G. Lorimer, "Quantitative analysis of thin specimens," *Journal of Microscopy-Oxford*, 103[MAR] 203-07 (1975).
37. N. Bassiri-Gharb, I. Fujii, E. Hong, S. Trolier-McKinstry, D. V. Taylor, and D. Damjanovic, "Domain wall contributions to the properties of piezoelectric thin films," *Journal of Electroceramics*, 19[1] 49-65 (2007).
38. D. Taylor and D. Damjanovic, "Domain wall pinning contribution to the nonlinear dielectric permittivity in Pb(Zr, Ti)O<sub>3</sub> thin films," *Applied Physics Letters*, 73[14] 2045-47 (1998).
39. D. Taylor and D. Damjanovic, "Evidence of domain wall contribution to the dielectric permittivity in PZT thin films at sub-switching fields," *Journal of Applied Physics*, 82[4] 1973-75 (1997).
40. D. Damjanovic, "Contributions to the piezoelectric effect in ferroelectric single crystals and ceramics," *Journal of the American Ceramic Society*, 88[10] 2663-76 (2005).
41. D. Damjanovic and D. Taylor, "Contributions to the nonlinear dielectric and piezoelectric response of ferroelectric thin films and ceramics," *Ferroelectrics*, 221[1-4] 137-46 (1999).
42. S. P. Li, A. S. Bhalla, R. E. Newnham, and L. E. Cross, "Quantitative-Evaluation of Extrinsic Contribution to Piezoelectric Coefficient D<sub>33</sub> in Ferroelectric Pzt Ceramics," *Materials Letters*, 17[1-2] 21-26 (1993).
43. J. R. Taylor, "An introduction to error analysis : the study of uncertainties in physical measurements," pp. xvii, 327 p. 2nd ed. University Science Books: Sausalito, Calif., (1997).
44. P. Muralt, "Texture control and seeded nucleation of nanosize structures of ferroelectric thin films," *Journal of Applied Physics*, 100[5] (2006).
45. M. Alexe, C. Harnagea, D. Hesse, and U. Gosele, "Polarization imprint and size effects in mesoscopic ferroelectric structures," *Applied Physics Letters*, 79[2] 242-44 (2001).
46. R. Vasudevan, H. Khassaf, Y. Cao, S. Zhang, A. Tselev, B. Carmichael, M. Okatan, S. Jesse, L. Chen, S. Alpay, S. Kalinin, and N. Bassiri-Gharb, "Acoustic Detection of Phase Transitions at the Nanoscale," *Advanced Functional Materials*, 26[4] 478-86 (2016).
47. J. Ihlefeld, D. Harris, R. Keech, J. Jones, J. Maria, and S. Trolier-McKinstry, "Scaling Effects in Perovskite Ferroelectrics: Fundamental Limits and Process-Structure-Property Relations," *Journal of the American Ceramic Society*, 99[8] 2537-57 (2016).
48. T. M. Shaw, S. Trolier-McKinstry, and P. C. McIntyre, "The properties of ferroelectric films at small dimensions," *Annual Review of Materials Science*, 30 263-98 (2000).
49. C. Randall, N. Kim, J. Kucera, W. Cao, and T. Shrout, "Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics," *Journal of the American Ceramic Society*, 81[3] 677-88 (1998).
50. D. Damjanovic and M. Demartin, "Contribution of the irreversible displacement of domain walls to the piezoelectric effect in barium titanate and lead zirconate titanate ceramics," *Journal of Physics-Condensed Matter*, 9[23] 4943-53 (1997).
51. D. M. Marincel, H. R. Zhang, J. Britson, A. Belianinov, S. Jesse, S. V. Kalinin, L. Q. Chen, W. M. Rainforth, I. M. Reaney, C. A. Randall, and S. Trolier-McKinstry, "Domain pinning near a single-grain boundary in tetragonal and rhombohedral lead zirconate titanate films," *Physical Review B*, 91[13] 134113 (2015).
52. M. Haun, E. Furman, S. Jang, and L. Cross, "Thermodynamic theory of the lead zirconate-titanate solid solution system, 1. Phenomenology," *Ferroelectrics*, 99 13-25 (1989).

53. M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, "Thermodynamic Theory of the Lead Zirconate-Titanate Solid-Solution System, .5. Theoretical Calculations," *Ferroelectrics*, 99 63-86 (1989).
54. A. Amin, R. Newnham, and L. Cross, "Effect of Elastic Boundary Conditions on Morphotropic Pb(Zr,Ti)O<sub>3</sub> Piezoelectrics," *Physical Review B*, 34[3] 1595-98 (1986).
55. J. Cheng, W. Zhu, N. Li, and L. Cross, "Electrical properties of sol-gel-derived Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> thin films on a PbTiO<sub>3</sub>-coated stainless steel substrate," *Applied Physics Letters*, 81[25] 4805-07 (2002).
56. S. Oh and H. Jang, "Ferroelectric phase transitions and three-dimensional phase diagrams of a Pb(Zr,Ti)O<sub>3</sub> system under a hydrostatic pressure," *Journal of Applied Physics*, 85[5] 2815-20 (1999).
57. S. Oh and H. Jang, "Epitaxial Pb(Zr,Ti)O<sub>3</sub> thin films with coexisting tetragonal and rhombohedral phases," *Physical Review B*, 63[13] (2001).
58. T. Berfield, R. Ong, D. Payne, and N. Sottos, "Residual stress effects on piezoelectric response of sol-gel derived lead zirconate titanate thin films," *Journal of Applied Physics*, 101[2] (2007).
59. A. Morozovska, I. Golovina, S. Lemishko, A. Andriiko, S. Khainakov, and E. Eliseev, "Effect of Vegard strains on the extrinsic size effects in ferroelectric nanoparticles," *Physical Review B*, 90[21] (2014).
60. A. Kumar, S. Kalinin, and Y. Kim, "Exploring Electro-Chemo-Mechanical Phenomena on the Nanoscale Using Scanning Probe Microscopy." in *Electro-Chemo-Mechanics of Solids*,. Edited by Springer, 2017.