

# Engineered $\alpha/c$ domain patterns in multilayer (110) epitaxial $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ thin films: Impact on domain compliance and piezoelectric properties

Cite as: AIP Advances 6, 055104 (2016); <https://doi.org/10.1063/1.4948795>

Submitted: 16 March 2016 • Accepted: 26 April 2016 • Published Online: 03 May 2016

M. Mtebwa, A. Mazzalai, C. S. Sandu, et al.



View Online



Export Citation



CrossMark

## ARTICLES YOU MAY BE INTERESTED IN

[Ferroelectric thin films: Review of materials, properties, and applications](#)

Journal of Applied Physics **100**, 051606 (2006); <https://doi.org/10.1063/1.2336999>

[Ferroelectric or non-ferroelectric: Why so many materials exhibit “ferroelectricity” on the nanoscale](#)

Applied Physics Reviews **4**, 021302 (2017); <https://doi.org/10.1063/1.4979015>

[Domain structure transition in compressively strained \(100\)/\(001\) epitaxial tetragonal PZT film](#)

Journal of Applied Physics **129**, 024101 (2021); <https://doi.org/10.1063/5.0031803>



## Engineered $a/c$ domain patterns in multilayer (110) epitaxial $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ thin films: Impact on domain compliance and piezoelectric properties

M. Mtebwa,<sup>1</sup> A. Mazzalai,<sup>1</sup> C. S. Sandu,<sup>1,2</sup> A. Crassous,<sup>1,a</sup> and N. Setter<sup>1</sup>

<sup>1</sup>*Ceramics Laboratory, Swiss Federal Institute of Technology (EPFL),  
CH-1015 Lausanne, Switzerland*

<sup>2</sup>*3D-OXIDES, 130 rue Gustave Eiffel, Saint Genis Pouilly, 01630, France*

(Received 16 March 2016; accepted 26 April 2016; published online 3 May 2016)

While there is extensive literature on the influence of both compressive and tensile strain on the domain patterns of (001) tetragonal ferroelectric thin films, little is known regarding domain engineering in (110) films. The primary reason is the absence of suitable substrates that allow the growth of epitaxial films with this orientation. However, recent works emphasized the importance of this orientation with the possibility for e.g. to achieve ultra-high ferroelectric domain density. This work reports the controlled growth of  $a/c$  domain patterns in highly tetragonal monocrystalline (110) oriented  $\text{Pb}(\text{Zr}_{0.05}, \text{Ti}_{0.95})\text{O}_3$ . It is demonstrated that while  $a/c$  patterns can easily be realized in the single layer film relaxed under compressive misfit strain, modulation of tensile misfit strain through the use of buffer layers allows for consistent control of domain periodicity, in which case the average domain period was tuned between 630 and 60 nm. The effects of domain density and defects on both switching behavior and piezoelectric properties in single and multilayered structures are also investigated, revealing an optimum composition of the buffer layer for improved domain compliance and piezoelectric properties. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4948795>]

### I. INTRODUCTION

Ferroelectric thin films are currently used in applications previously covered by bulk ceramics including dielectric capacitors, sensors and Microelectromechanical systems (MEMs).<sup>1,2</sup> Piezoelectric properties of ferroelectric materials such as the most commonly used  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) are known to be strongly affected by the domain structures.<sup>3,4</sup> Moreover, the recently discovered and potentially useful functional properties of domain walls such as conductivity<sup>5-8</sup> and the photovoltaic effect<sup>9,10</sup> have brought more attention on the importance of domain engineering in ferroelectric single crystals and thin films.

Theoretical works have established that the ferroelastic domain patterns can be controlled by misfit strain.<sup>4,11-14</sup> These predictions have also been supported by experimental works mainly conducted on (001) tetragonal films. Compressive misfit strain favors  $c$  domains for epitaxial films whose thicknesses are below the critical value for relaxation,<sup>15-19</sup> and  $a/c$  patterns for relaxed films.<sup>20,21</sup> On the other hand, depending upon film thickness, substrate lattice parameters and processing conditions, tensile misfit strain can result in formation of either cross-hatched or stripe  $a/c$  patterns,<sup>15,22-24</sup>  $a_1/a_2$  patterns<sup>17</sup> or even more complex superstructures.<sup>25</sup>

Recently, experiments conducted on (110) oriented tetragonal thin films revealed peculiar switching behaviors. For example, a reversible switching between a monodomain state and an

---

<sup>a</sup>arnaud.crassous@epfl.ch

ultra-dense array with an inter-wall spacing of only 10nm was achieved<sup>26</sup> and reconfigurable robust charged domain walls were created without the need of complex poling procedures.<sup>27</sup> However, engineering the as-grown domain structure of films grown in the (110) orientation was much less studied than in its (001) counterpart. To our knowledge, the only reported ferroelastic-ferroelectric domain patterns in single crystalline epitaxial (110) PZT films are those of *a/c*-type created in relaxed films grown on compressive SrTiO<sub>3</sub> (STO) (110) substrates.<sup>28,29</sup> This is due to the fact that currently STO(110) is the only readily commercially available perovskite substrate that can support such an orientation and it imposes a compressive misfit strain for all compositions of the most commonly used PZT.

In this work we apply the strain engineering technique through the use of buffer layers to induce tensile strain in monocrystalline (110) tetragonal Pb(Zr<sub>0.05</sub>Ti<sub>0.95</sub>)O<sub>3</sub> thin films. This PZT composition is chosen since it allows the study of the transition from compressive strain, if directly grown on STO(110) substrate, to tensile strain, if grown on STO(110) substrate with thin PZT buffer layers with higher Zr content. Since the Zr content of the film is only 5%, PZT buffer layers with a wide range of Zr content from 6% to 100% can be used to tune the strain level. We show this is an efficient way to control the periodicity of ferroelastic domains and create dense *a/c* domain patterns. The impact of the *a/c* patterns and the dislocations on both switching behavior and piezoelectric properties is investigated.

## II. EXPERIMENTAL

Tetragonal PbZr<sub>0.05</sub>Ti<sub>0.95</sub>O<sub>3</sub> (PZT05/95) thin films were grown directly on chemically and thermally treated<sup>30</sup> 5% Nb-doped STO(110) substrates (Crystec GmbH) and on buffer layers pre-deposited on the STO(110) substrates. The buffer layers were comprised of PZT compositions with 10, 20, 30, 40, and 50% Zr contents as shown in table I. All layers were deposited by pulsed laser deposition (Coherent KrF excimer laser  $\lambda = 248$  nm). The deposition parameters were 1J/cm<sup>-2</sup> laser energy density, temperature of 550°C, oxygen partial pressure of 200mTorr, laser repetition frequency of 3 Hz, deposition rate of 0.8 nm/min. All films were cooled in an oxygen pressure of 2.0Torr.

Table I shows the theoretical misfit strain of PZT buffer layers on STO(110) substrate. The values are calculated by averaging the strains in the (001) and (1-10) orientations that can be calculated from the formula, respectively:

$$\text{Strain (001) [\%]} = \frac{a - a_s}{a_s} * 100$$

And

$$\text{Strain (1 - 10) [\%]} = \frac{\sqrt{(c^2 + a^2)} - \sqrt{2}a_s}{\sqrt{2}a_s} * 100$$

Where *a* and *c* are the in-plane and out-of-plane lattice parameters of PZT buffer layers and *a<sub>s</sub>* = 3.905 Å is the lattice constant of STO. All buffer layers are compressively strained. On the contrary, similar calculations show tensile strained PZT05/95 films (*a* = 3.9156 Å, *c* = 4.1420 Å) on PZT buffer layers.

TABLE I. Lattice parameters and misfit strain on STO(110) substrate for PZT compositions of buffer layers used to control domain patterns of PZT05/95 films. Misfit strain of PZT05/95 films on the different PZT buffer layers.

Lattice constants	Buffer layer				
	PZT10/90	PZT20/80	PZT30/70	PZT40/60	PZT50/50
<i>a</i> = <i>b</i> [Å]	3.9272	3.9539	3.9862	4.0081	4.0303
<i>c</i> [Å]	4.1319	4.1319	4.1331	4.1341	4.1449
Average strain of buffer layer on substrate [%]	-1.9	-2.4	-3.03	-3.45	-3.95
Average strain of PZT 05/95 on buffer layer [%]	0.15	0.65	1.25	1.66	2.13

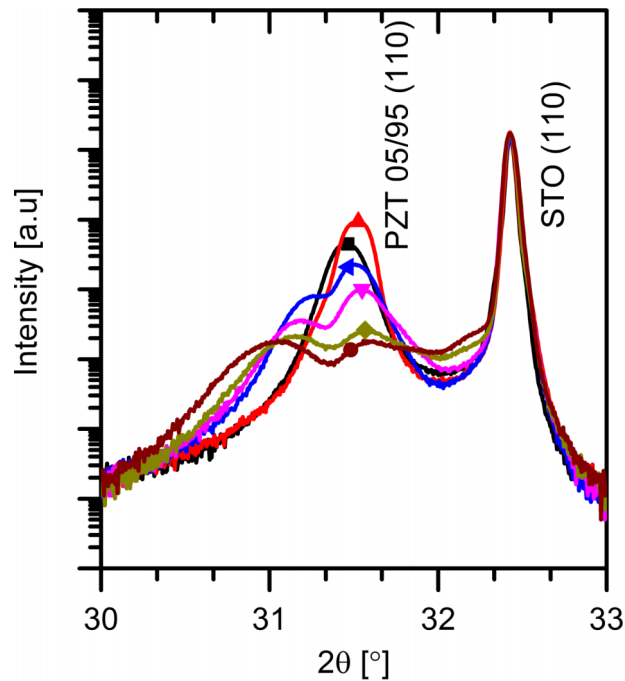


FIG. 1. 2Theta XRD patterns for (110) peak of 150 nm single layer PZT 05/95 (black square) and 100 nm PZT05/95 film on 10 nm buffer layer of PZT10/90 (red up-triangle), PZT20/80 (blue left-triangle), PZT30/70 (magenta down-triangle), PZT40/60 (dark-yellow diamond) and PZT50/50 (brown circle). All films grown on Nb-doped STO(110) substrate.

The orientation of the films was characterized by X-ray diffraction (XRD) using a Bruker D8 Discover. Figure 1 shows the (110) peak of a 150 nm single layer PZT05/95 and 100 nm PZT05/95 films deposited on 10 nm buffer layer of PZT10/90, PZT20/80, PZT30/70, PZT40/60 and PZT50/50. The (110) peaks of PZT 05/95 and 10/90 are merged because of the low mismatch between the two compositions. No thickness fringes are visible in all XRD patterns because of the high films' thicknesses. We note that fringes were typically not observed above 90 nm for PZT05/95 single layers. Additionally, the surface roughness ( $r \sim 0.4$  nm) and the in-depth structural modifications induced by the  $a/c$  domains prevent the interference patterns from occurring.

In the following part, atomic force microscopy (AFM) and piezoresponce force microscopy (PFM) experiments were performed at room temperature using a Cypher Asylum Research AFM in DART (dual a.c. resonance tracking) mode. Commercial silicon tips coated with Ti/Ir (Asylum Research) were used for PFM at typical contact resonance frequencies of 260–300 kHz for vertical PFM and a typical voltage of  $V_{AC} = 1$  V. Transmission electron microscopy (TEM) was carried out with a Tecnai Osiris instrument using an acceleration voltage of 200 kV. Dual-beam laser interferometry was performed on a laboratory made setup.

### III. RESULTS AND DISCUSSION

#### A. Domain periodicity

Domain patterns of single and multilayered PZT films were characterized by means of AFM and PFM. Figure 2 shows the AFM topography together with vertical PFM amplitude. The vertical PFM amplitude images reveal the  $a-$  domains as black lines due to the absence of signal from these purely in-plane oriented domains. These set of images clearly show the difference in domain periodicity of similar domain patterns with different buffer layers.

The contrast of domains in PFM amplitude images enabled us to quantify the periodicity through averaging several measurements from different areas. Figure 3(a) shows the dependence of domain period with respect to the misfit strain for all films. Remarkably, the periodicity of  $a/c$

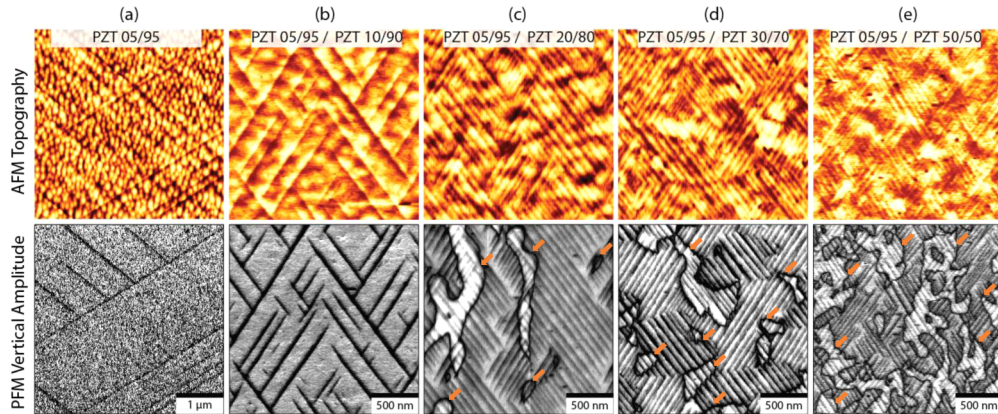


FIG. 2. AFM topography and PFM amplitude of (110) PZT 05/95 thin films. (a) 150 nm PZT 05/95 and multilayered films of 100 nm PZT 05/95 on 10 nm (b) PZT 10/90, (c) PZT 20/80, (d) PZT 30/60 and (e) PZT 50/50. PFM amplitude shows  $a$  domains as black lines in the matrix of  $c$  domains.  $180^\circ$  domains indicated by orange arrows can also be seen in figure 2 (c)-(e). The periodicity of the dense  $a/c$  ferroelastic domain increases with Zr content of the buffer layer from 630 to 60 nm.

domain patterns varies from 630 nm for relaxed single layer film under compressive strain to about 60 nm through increasing tensile misfit strain. Starting from films with a PZT30/70 buffer layer, domain periodicity could not be decreased further and only a small change in domain density was achieved with increasing Zr content. To determine the origin of the abrupt stop in increase of a domain density, TEM was performed on films grown on PZT10/90 and PZT30/70 buffer layers. Due to the moderate lattice mismatch between PZT10/90 and STO (110) and the low lattice mismatch between PZT05/95 and PZT10/90, the heterostructure shows few dislocations, sharp interfaces and  $a$  domains extending through the whole thickness of the films (Fig. 3(b)). On the contrary, in the PZT05/95 / PZT30/70 heterostructure, the PZT30/70 has a large amount of dislocations due to the large strain imposed by the substrate that propagates into the PZT05/95 film which lies above it (Fig. 3(c)). The dislocation-assisted strain relaxation probably hinders the formation of denser  $a$  domain patterns when buffer layers of PZT with Zr content above 30% are used.<sup>22</sup> This is also supported by the curved irregular structures that are non-ferroelastic  $180^\circ$  domains in films grown on PZT20/80, PZT30/70 and PZT50/50 buffer layers (Figs. 2(c)–2(e)), which are the result of poor polarization charge screening at the bottom interface. Poor polarization screening was shown to

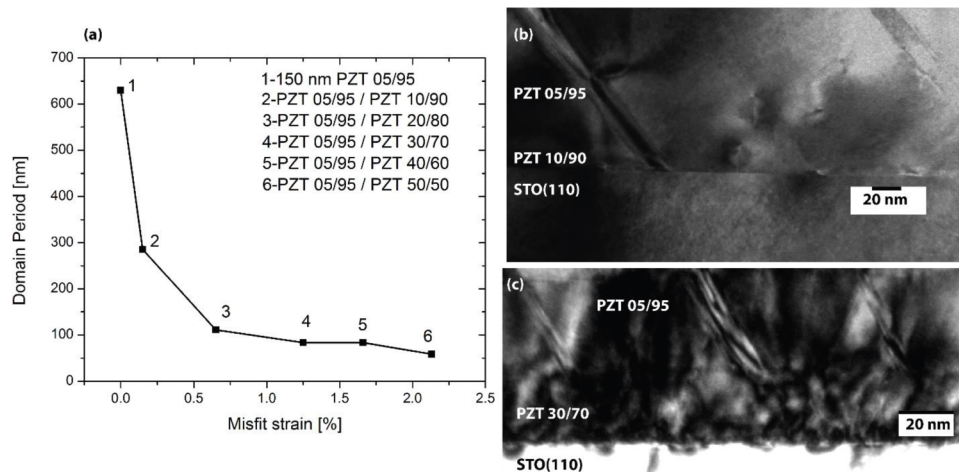


FIG. 3. (a) Dependence of  $a/c$  domain period on the misfit strain for (110) PZT 05/95 thin films. TEM images showing low-defect density cross-section for (b) PZT 05/95 on PZT 10/90 buffer layer and a high defect density for (c) PZT05/95 on PZT30/70 buffer layer.

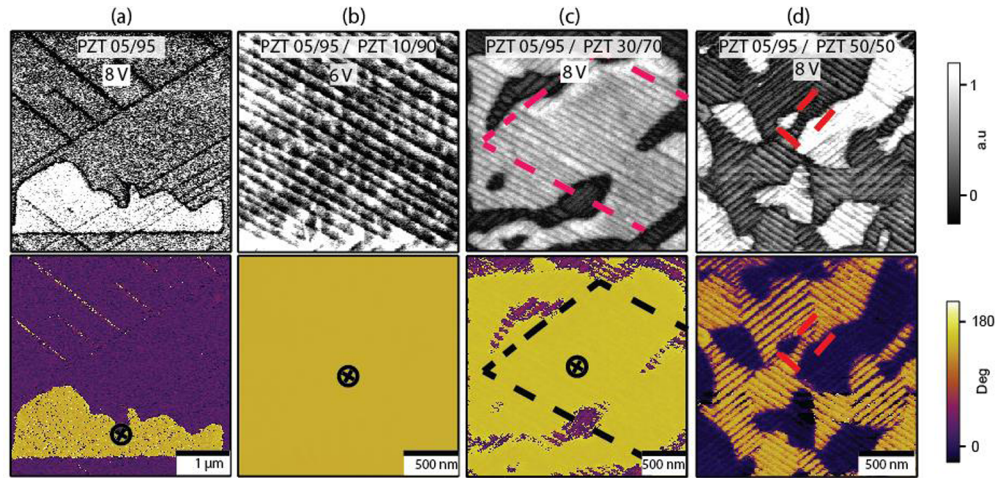


FIG. 4. Modified domain patterns after poling (a) 150 nm thick PZT05/95 film on STO(110), (b) 100 nm thick PZT05/95 film on 10 nm PZT10/90, (c) on 10 nm PZT30/70 and (d) on 10 nm PZT50/50 buffer layers. The poling bias voltages applied on the AFM tip is indicated in each case and dotted lines encircle the area with noticeable *a*-domains switching in (c) and (d).

create a competition between electrostatic and elastic energies and hence prevent the formation of denser *a* domain patterns to favor  $180^\circ$  domains.<sup>22</sup>

## B. Compliance of *a/c* domain walls and piezoelectric properties

Positive bias voltages were applied to the conductive tip of an AFM to switch the polarization of the samples downwards. Despite a high switching voltage of 8 V, only a small fraction of the single layer PZT05/95 thin film undergoes  $180^\circ$  switching (Fig. 4(a)). The *a* domains are unaffected by switching. On the other hand, a smaller voltage of 6 V was enough to completely switch and concurrently modify the *a/c*-domain patterns of a PZT05/95 with a 10 nm PZT10/90 buffer layer (Fig. 4(b)). By comparing figures 2(b) and 4(b) we see that domain pattern modification by poling resulted in an increase in domain density as new *a*-domains appeared. These *a*-domains are created to compensate the erased ones due to elastic reasons, because the locally erased ferroelastic domains were globally responsible for the minimization of elastic energy.<sup>31</sup>

The dotted lines in figures 4(c) and 4(d) indicate the regions modified after poling with 8V in PZT films on PZT30/70 and PZT50/50 buffer layers, respectively. The domain modification by poling in multilayered structure is increasingly difficult as the tensile strain increases. Denser and clamped *a* domains and a higher amount of defects are most likely responsible for this. The latter would explain why films grown on PZT50/50 are harder to switch than those grown on PZT30/70 despite a very similar *a* domain density. We can conclude from this switching experiment that an additional buffer layer is beneficial for domain compliance if the balance between *a* domain density and low-defect density is found. This is achieved here with the PZT10/90 buffer layer in which the *a/c*-domain pattern modification occurs through the elimination of one of the two energetically equivalent *a* domains.

We then measured the effective piezoelectric coefficient  $d_{33,f}$  of the single and multilayered films by dual-beam laser interferometry. Figure 5 shows the effective piezoelectric coefficients taken with an a.c. voltage of 0.1 V at 5 kHz and a d.c. electric field varied between  $\pm 500$  kV/cm. Piezoelectric loops of the single layer PZT film (Fig. 5(a)) and PZT films grown on PZT20/80 (Fig. 5(c)) and PZT30/70 (Fig. 5(d)) buffer layers present a significant vertical shift supported by the difficulty in switching shown in the PFM images. No switching was observed for the film grown on the 50/50 buffer layer (Fig. 5(e)). Its piezoelectric response was however higher than the ones of the films with identical *a* domain density but grown on different buffer layers. This might be related to the buffer layer being of a weaker tetragonality (a composition closer to the morphotropic phase boundary). Finally, we note that the film grown on a PZT10/90 has the most symmetric

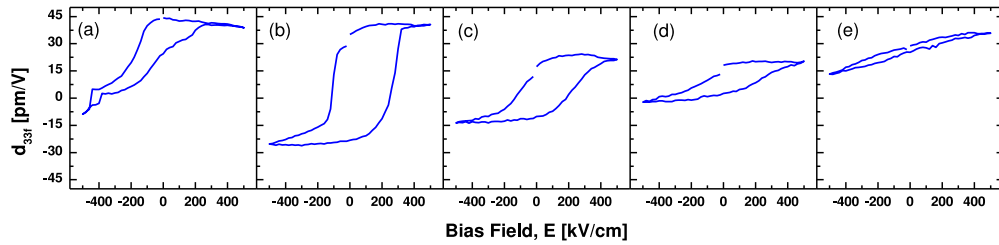


FIG. 5. Effective piezoelectric coefficient as a function of electric field for (a) 150 nm PZT05/95 film and 100 nm PZT05/95 films on (b) PZT10/90, (c) PZT20/80, (d) PZT30/70 and (e) PZT50/50 buffer layers.

loop (Fig. 5(b)) consistent with the domain switchability determined by PFM and a piezoelectric coefficient equivalent to the one of the single layer film. This result emphasizes that the careful choice of the buffer layer does not only allow structural modification and domain engineering but has clear effect on properties.

#### IV. SUMMARY AND CONCLUSIONS

Domain periodicity in tetragonal monocrystalline (110) oriented PZT05/95 thin films was controlled by imposing different tensile misfit strain levels. Due to unavailability of suitable substrates with appropriate lattice parameters, thin PZT buffer layers with different Zr compositions were used.  $a/c$  domain patterns obtained in the relaxed single layer films under compressive misfit strain had average periodicity of 630 nm. As for the multilayered structures, it was found that domain density can conveniently be controlled through modulation of tensile misfit strain. In this respect, the average periodicity of  $a/c$  patterns was reduced to 60 nm. An optimum buffer layer composition of PZT10/90 was found, allowing the improvement of domain compliance and the piezoelectric properties. This approach is not restricted to PZT and can be potentially used with other ferroelectric-ferroelastic materials for which lack of substrates is detrimental to tuning their domain patterns and properties.

#### ACKNOWLEDGEMENT

The authors thank the Swiss National Science foundation and the Lithuanian-Swiss cooperation program to reduce economic and social disparities within the enlarged European Union under project agreement No. CH-3- $\hat{S}$  MM-01/02 for the financial support of this work.

- <sup>1</sup> P. Muralt, *Ultrasonics, Ferroelectrics and Frequency Control, IEEE Transactions on* **47**, 903 (2000).
- <sup>2</sup> N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N. Y. Park, G. B. Stephenson *et al.*, *J. Appl. Phys.* **100**, 051606 (2006).
- <sup>3</sup> D. Damjanovic, *Reports on Progress in Physics* **61**, 1267 (1998).
- <sup>4</sup> A. K. Tagantsev, L. E. Cross, and J. Fousek, *Domains in ferroic crystals and thin films* (Springer, 2010).
- <sup>5</sup> J. Seidel, P. Maksymovych, Y. Batra, A. Katan, S.-Y. Yang, Q. He, A. P. Baddorf, S. V. Kalinin, C.-H. Yang, J.-C. Yang *et al.*, *Phys. Rev. Lett.* **105**, 197603 (2010).
- <sup>6</sup> J. Guyonnet, I. Gaponenko, S. Gariglio, and P. Paruch, *Adv. Mater.* **23**, 5377 (2011).
- <sup>7</sup> P. Maksymovych, A. N. Morozovska, P. Yu, E. A. Eliseev, Y.-H. Chu, R. Ramesh, A. P. Baddorf, and S. V. Kalinin, *Nano letters* **12**, 209 (2012).
- <sup>8</sup> T. Sluka, A. K. Tagantsev, P. Bednyakov, and N. Setter, *Nat. Commun.* **4**, 1808 (2013).
- <sup>9</sup> S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C.-H. Yang, M. D. Rossell, P. Yu, Y.-H. Chu, J. F. Scott, J. W. Ager *et al.*, *Nat. Nanotech.* **5**, 143 (2010).
- <sup>10</sup> A. Bhatnagar, A. R. Chaudhuri, Y. H. Kim, D. Hesse, and M. Alexe, *Nat. Commun.* **4**, 2835 (2013).
- <sup>11</sup> N. A. Pertsev and A. G. Zembilgotov, *J. Appl. Phys.* **78**, 6170 (1995).
- <sup>12</sup> V. G. Koukhar, N. A. Pertsev, and R. Waser, *Phys. Rev. B* **64**, 214103 (2001).
- <sup>13</sup> Q. Y. Qiu, V. Nagarajan, and S. P. Alpay, *Phys. Rev. B* **78**, 064117 (2008).
- <sup>14</sup> Q. Y. Qiu, S. P. Alpay, and V. Nagarajan, *J. Appl. Phys.* **107**, 114105 (2010).
- <sup>15</sup> B. S. Kwak, A. Erbil, J. D. Budai, M. F. Chisholm, L. A. Boatner, and B. J. Wilkens, *Phys. Rev. B* **49**, 14865 (1994).
- <sup>16</sup> I. Vrejoiu, G. Le Rhun, L. Pintilie, D. Hesse, M. Alexe, and U. Gösele, *Adv. Mater.* **18**, 1657 (2006).

- <sup>17</sup> F. Borodavka, I. Gregora, A. Bartasyte, S. Margueron, V. Plausinaitiene, A. Abrutis, and J. Hlinka, *J. Appl. Phys.* **113**, 187216 (2013).
- <sup>18</sup> M. Mtebwa, L. Feigl, and N. Setter, in *IEEE International Symposium on the Applications of Ferroelectrics and Workshop on the Piezoresponse Force Microscopy (ISAF/PFM)* (IEEE, 2013), pp. 73–75.
- <sup>19</sup> J. Chen, H. Lu, H.-J. Liu, Y.-H. Chu, S. Dunn, K. K. Ostrikov, A. Gruverman, and N. Valanoor, *Appl. Phys. Lett.* **102**, 182904 (2013).
- <sup>20</sup> C. S. Ganpule, V. Nagarajan, H. Li, A. S. Ogale, D. E. Steinhauer, S. Aggarwal, E. Williams, R. Ramesh, and P. De Wolf, *Appl. Phys. Lett.* **77**, 292 (2000).
- <sup>21</sup> V. Nagarajan, C. S. Ganpule, H. Li, L. Salamanca-Riba, A. L. Roytburd, E. D. Williams, and R. Ramesh, *Appl. Phys. Lett.* **79**, 2805 (2001).
- <sup>22</sup> L. Feigl, P. Yudin, I. Stolichnov, T. Sluka, K. Shapovalov, M. Mtebwa, C. S. Sandu, X.-K. Wei, K. Tagantsev, and N. Setter, *Nat. Commun.* **5**, 4677 (2014).
- <sup>23</sup> L. Feigl, L. J. McGilly, and N. Setter, *Ferroelectrics* **465**, 36 (2014).
- <sup>24</sup> J. Ouyang, J. Slusker, I. Levin, D.-M. Kim, C.-B. Eom, R. Ramesh, and A. L. Roytburd, *Adv. Funct. Mater.* **17**, 2094 (2007).
- <sup>25</sup> R. Xu, J. Karthik, A. R. Damodaran, and L. W. Martin, *Nat. Commun.* **5**, 3120 (2014).
- <sup>26</sup> M. Mtebwa, L. Feigl, P. Yudin, L. J. McGilly, K. Shapovalov, A. K. Tagantsev, and N. Setter, *Appl. Phys. Lett.* **107**, 142903 (2015).
- <sup>27</sup> L. Feigl, L. J. McGilly, A. Crassous, T. Sluka, C. S. Sandu, and N. Setter, Submitted (2016).
- <sup>28</sup> R. Xu, S. Liu, I. Grinberg, J. Karthik, A. R. Damodaran, A. M. Rappe, and L. W. Martin, *Nat. Mater.* **14**, 79 (2014).
- <sup>29</sup> K. Lefki and G. J. M. Dormans, *J. Appl. Phys.* **76**, 1764 (1994).
- <sup>30</sup> A. Biswas, P. B. Rossen, C.-H. Yang, W. Siemons, M.-H. Jung, I. K. Yang, R. Ramesh, and Y. H. Jeong, *Appl. Phys. Lett.* **98**, 051904 (2011).
- <sup>31</sup> L. Feigl, L. J. McGilly, C. S. Sandu, and N. Setter, *Appl. Phys. Lett.* **104**, 172904 (2014).