Publication information

Title	Effect of dislocation walls on the polarization switching of a ferroelectric single crystal
Author(s)	Wu, H.H.; Wang, J.; Cao, S.G.; Zhang, T.Y.
Source	Applied physics letters , v. 102, (23), June 2013, article number 232904
Version	Published version
DOI	http://dx.doi.org/10.1063/1.4809945
Publisher	American Institute of Physics (AIP) Publishing

Copyright information

This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing. The following article appeared in "Wu, H.H., Wang, J., Cao, S.G., & Zhang, T.Y. (2012). Effect of dislocation walls on the polarization switching of a ferroelectric single crystal, Applied physics letters, 102(23), article number 232904." and may be found at <http://dx.doi.org/10.1063/1.4809945>

Notice

This version is available at HKUST Institutional Repository via
<http://hdl.handle.net/1783.1/55317>

If it is the author's pre-published version, changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published version.

Effect of dislocation walls on the polarization switching of a ferroelectric single crystal

H. H. Wu, J. Wang, S. G. Cao, and T. Y. Zhang

Citation: *Applied Physics Letters* **102**, 232904 (2013); doi: 10.1063/1.4809945

View online: <http://dx.doi.org/10.1063/1.4809945>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/102/23?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Ferroelectric domain structure and c-axis polarization switching in monoclinic Bi₄Ti₃O₁₂ single crystals](#)

Appl. Phys. Lett. **90**, 202904 (2007); 10.1063/1.2740114

[Domain wall broadening mechanism for domain size effect of enhanced piezoelectricity in crystallographically engineered ferroelectric single crystals](#)

Appl. Phys. Lett. **90**, 041915 (2007); 10.1063/1.2435584

[Dynamical systems analysis for polarization in ferroelectrics](#)

J. Appl. Phys. **100**, 114106 (2006); 10.1063/1.2388124

[Polarization-switching characteristics of flux-grown KTiOPO₄ and RbTiOPO₄ at room temperature](#)

J. Appl. Phys. **97**, 124105 (2005); 10.1063/1.1940135

[Study of ferroelectric domain switching by domain wall induced light scattering](#)

J. Appl. Phys. **97**, 074102 (2005); 10.1063/1.1882772

Want to publish your paper in the
#1 MOST CITED journal in applied physics?
With *Applied Physics Letters*, you can.

AIP | Applied Physics
Letters

THERE'S POWER IN NUMBERS. Reach the world with AIP Publishing.

Effect of dislocation walls on the polarization switching of a ferroelectric single crystal

H. H. Wu,¹ J. Wang,² S. G. Cao,¹ and T. Y. Zhang^{1,a)}

¹Department of Mechanical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

²Department of Engineering Mechanics, School of Aeronautics and Astronautics, Zhejiang University, Hangzhou 310027, China

(Received 5 March 2013; accepted 19 May 2013; published online 11 June 2013)

Phase field simulations were conducted to study the influence of dislocation walls on the domain configuration and polarization switching behavior of a ferroelectric single crystal. The simulation results show that the domain configuration and polarization switching behavior depend highly on the dislocation spacing in the dislocation wall. The ferroelectric properties can be greatly improved by reducing the coercive field and meanwhile enhancing the remanent polarization if an appropriate density of dislocations is introduced at high temperature. The phase field simulations also put insights into the mechanism of polarization switching. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4809945>]

Ferroelectric materials exhibit spontaneous electric polarization and spontaneous strain. The electric polarization can be switched by an electric field or/and a mechanical load. The polarization switching is characterized by the hysteresis loop of polarization versus applied electric field. The remanent polarization and coercive field determined from the hysteresis loop are the basic properties for ferroelectric nonvolatile memories.^{1,2} The remanent polarization and coercive field are dependent on crystal defects, such as dislocations,^{3,4} oxygen vacancies,^{5,6} and grain boundaries.^{7–9} Dislocations can be introduced into ferroelectric ceramics during the fabrication process at high temperature,^{10–13} which are experimentally observed in ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin film.¹¹ The pre-existed dislocations play important roles in the ferroelectric switching behavior, acting as the nucleation center of new domains or/and pinning the domain wall motion.^{3,4,14,15} *In situ* Transmission Electron Microscopy (TEM) observations show that dislocations exert a pinning force on the domain wall motion in a $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin film under an applied electric field.¹⁴ High resolution TEM observations and piezoresponse force microscopy illustrate that dislocations induce the polarization instability and thus suppress electromechanical response of epitaxial $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ islands.¹² Misfit dislocations at the interface between a ferroelectric thin film and its substrate can relax the misfit strain and affect the ferroelectric response.¹³ Theoretically, the Landau theory and phase field simulations have been employed to study the effect of misfit dislocations on the domain configuration and polarization switching behavior of ferroelectric films,^{3,4,15} indicating that the hysteresis loops are strongly dependent on the type and density of misfit dislocations. Dislocations generated at an elevated temperature higher than the Curie temperature affect the ferroelectric domain structure, because the domain structure forms at a temperature lower than the Curie temperature. The dislocation-dependent domain structure has a great influence on the

polarization switching behavior. In this Letter, we investigated the effect of pre-existing dislocation walls on the domain configuration and polarization switching by phase field simulations.

In the present study, two dimensional (2D) phase field simulations were conducted under the plane strain condition. The supplementary material of Ref. 19 describes the used phase field model. Fig. 1(a) is a schematic drawing of the used simulated cell of 64×64 discrete grids with a normalized cell size of $\Delta x_1^* = \Delta x_2^* = 0.8$, where the x_1 and x_2 axes are set along the pseudo cubic crystallographic [100] and [010] directions, respectively. A dislocation wall composed of periodically distributed dislocations with the same Burgers vector of $\frac{\Delta x_1^*}{2}[100]$ is allocated at the middle height of the simulated cell. The dislocation spacing and the simulated cell dimension are denoted by D and L , respectively, giving the Dislocation Linear Density (DLD) of L/D . For the maximum DLD, the dislocation spacing is 2.4 nm, which is close to the experimentally observed value of 2.7 nm.¹¹ The periodic boundary condition is adopted in both x_1 and x_2 directions, implying that the simulated cell is within an infinitely large 2D single crystal with periodically distributed dislocations walls. The used normalized variable formula and the material constants of PbTiO_3 single crystal at room temperature are all listed in Ref. 19. A random distribution of initial polarizations with the maximum magnitude less than 0.0005 is assigned to the simulated system to trig the polarization evolution, which leads to the initial domain structure after 20 000-steps-evolution with a dimensionless time step of $\Delta t^* = 0.04$. Then, a dimensionless external electric field of $E_2^{ex,*} = E_0^* \sin(2.5\pi i/100\,000)$ is applied along the x_2 direction, where i denotes the time step. At each time step, the simulated system evolves once and 100 000 step-electric loading is applied to complete one and a quarter cycle of the switching. The average polarization along the electric field direction is taken as the macroscopic response of the simulated ferroelectric single crystal.

When there is no dislocation at all, the polarizations in the periodic ferroelectrics form a twin domain structure with 90° domain walls, which is shown in Fig. 1(b), due to the

^{a)}Author to whom correspondence should be addressed. Electronic mail: mezhangt@ust.hk. Tel: +852 2358 7192. Fax: +852 2358-1543.

FIG. 1. Schematic drawing of the simulated cell with a dislocation wall along the middle line of a periodic ferroelectric (a), and the simulated domain structures from a random initial state in the ferroelectric with different DLD; (b) DLD = 0; (c) DLD = 3; (d) DLD = 7; (e) DLD = 13; (f) DLD = 21. Unusual 90° domain walls are formed along the dislocation walls in (e) and (f).

clamped mechanical boundary condition. To visualize the domain structure clearly, the polarizations are represented by arrows and the arrows are plotted alternatively. The formation of the 90° domain structure indicates that the elastic energy dominates in the periodic ferroelectric, which is consistent with the previous study.^{16,17} The dislocation wall generates a DLD-dependent stress field^{18,19} and changes the twin domain structure to a multi-domain structure with both types of the 90° and 180° domain walls, as shown in Figs. 1(c)–1(f). Most 90° domain walls still incline at $\pm 45^\circ$ angles with respect to the coordinate axes and the polarizations have a head-to-tail arrangement at the 90° domain walls, which are similar to the case without dislocations. When the DLD is higher than 9, an unusual 90° domain wall along the dislocation wall appears, parallel to the crystallographic axis, as shown in Figs. 1(e) and 1(f), and the domain structure is separated into two major regions by the unusual 90° dislocation wall. In the upper region above the dislocation wall, there is a multi-domain structure with 180° domain walls all along the x_2 axis and the number of the 180° domain walls increases with the DLD, while in the lower region below the dislocation wall, a single domain is formed along the x_1 axis in Fig. 1(e), and a bi-domain structure with one 180° domain wall appears in Fig. 1(f). Due to the strain mismatch between the vertical and horizontal domains, the unusual 90° domain wall is unstable when there is no dislocation or the DLD is low, as shown in Figs. 1(b)–1(d). When the DLD increases, the unusual 90° domain wall becomes more energetically compatible because the dislocations release the misfit strain between the vertical and horizontal domains and reduce the strain energy. The higher the DLD is, the more the misfit strain will be released. Therefore, the horizontal 90° domain wall with a higher DLD = 21 in Fig. 1(f) is more close to a straight line than that with a lower DLD = 13 in Fig. 1(e).

The pre-existing dislocation walls yield the dislocation density-dependent initial domain structure, which plays a crucial role in the polarization switching behavior. For clarity, Fig. 2 shows the simulated hysteresis loops of average

polarization (P_2^*) versus applied electric field ($E_2^{ex,*}$) for DLDs 0, 7, 13, and 21. The P-E loop is the biggest without any dislocations and becomes smaller as the DLD increases from 0 to 13. When the DLD increases further from 13 to 21, the P-E loop becomes bigger again. Based on the hysteresis loops, the normalized coercive field and remanent polarization versus the DLD are plotted in Fig. 3. Both normalized remanent polarization and coercive field decrease to their minimal values when the DLD increases from zero to 13. Then, the normalized remanent polarization increases to 1.15 with a normalized coercive field of 0.56 as the DLD increases further to 21. The best ferroelectric properties for memory applications are a high remanent polarization and a low coercive field. Therefore, the simulation results suggest that one can improve the ferroelectric properties by introducing pre-existing dislocations at high temperature. For example, with DLD = 16, the coercive field is reduced to only one third as that without dislocations, whereas the remanent polarization is enhanced to 111% as that without dislocations. How do the dislocation walls affect the polarization switching behavior? The simulations exhibit the mechanism.

Supplementary materials of Ref. 19 are movies of the temporal evolution of the polarization switching process. Figs. 4(a1–a4), (b1–b4), and (c1–c4) show the polarization distributions at polarization switching stages ai, bi, and ci ($i = 1, 2, 3, 4$) marked in Fig. 2 in the simulated ferroelectrics with DLDs of 0, 13, and 21, respectively, where a1–c1 and a2–c2 denote the polarization stages at the maximum and zero applied fields, respectively, a3–c3 and a4–c4 are the stages between which the mean applied field is the coercive field. Although the magnitude of the averaged polarization along the applied field is about the same for the three ferroelectrics at the maximum applied electric field, their domain structures are different. There is the typical twin domain structure with 90° domain walls in the dislocation-free ferroelectric and the volume ratio of the domains with polarizations parallel to the applied field over these polarizations perpendicular to the applied field is about 2.05. The volume

FIG. 2. Hysteresis loops between the average polarization and applied electric field in the x_2 direction for the ferroelectrics with different DLDs.

ratio is reduced to about one when the applied field decreases from the maximum to zero, meaning that only a half of the polarizations contribute to the remanent polarization, as shown by Fig. 4(a2). The polarization switching process in the dislocation-free ferroelectric is achieved by homogeneous new domain nucleation and domain wall motion, as illustrated in detail in Ref. 19.

Figs. 4(b1) and 4(c1) show that the unusual 90° domain wall along the dislocation wall is very stable at the maximum applied field. For the ferroelectric with $\text{DLD} = 13$, the stress field induced by the dislocation wall is not high enough to pin all polarizations, especially at the maximum applied field. Since the stress field in the upper region above the unusual 90° domain wall assists the applied field to align the polarizations, the polarizations in the upper region are almost align themselves along the maximum applied electric field, as shown in Fig. 4(b1), except of a triangle domain of horizontal polarizations bounded with conventional 90° domain walls. Considering the periodic boundary conditions, we find that there are only two types of polarization domains between two adjacent dislocation walls, the vertical domains and the horizontal domains. Each of the horizontal domains looks approximately like a triangle. There is only one vertical domain between two adjacent dislocation walls under the maximum applied electric field. The residual horizontal domains embedded inside the vertical domain are attributed to the strain

FIG. 3. The dependence of normalized coercive field (E_c/E_c^0) and normalized remanent polarization (P_s/P_s^0) on the DLD, where E_c^0 and P_s^0 are the coercive field and remanent polarization corresponding to the case $\text{DLD} = 0$, respectively.

energy, which does not allow them to switch at the applied maximum electric field. During the decrease of the applied electric field from the maximum value to zero, the domain of horizontal polarizations grows, while the domain of polarizations parallel to the field shrinks. At $E_2^{ex,*} = 0.21$, a new domain with polarization antiparallel to the field direction is nucleated near the dislocation wall, as illustrated in the movie of Ref. 19. Clearly, the dislocation stress field assists the nucleation of the new domain. The new domain grows, by the domain wall motion, to the configuration shown in Fig. 4(b2) as the field decreases to zero. Since there is a domain with polarizations along the minus x_2 direction and the regions occupying by horizontal polarizations is larger than a half of the simulated cell, the remanent polarization is greatly reduced, as illustrated in Fig. 3. The pre-formed reversed domain above the dislocation wall makes the domain switching much easier, because no nucleation is needed any more. The reversed domain grows when the electric field increases from zero in the reversed direction, as shown in Figs. 4(b3) and 4(b4). This is the reason why the P-E hysteresis loop becomes the thinnest and the coercive field is the smallest with $\text{DLD} = 13$ in all studied cases. When the reversed electric field reaches $E_2^{ex,*} = -0.57$, the domain antiparallel to the electric field disappears and the horizontal domain shrinks more. At the maximum reversed electric field, the vertical domains with polarizations parallel to the reversed field dominate and the polarization structure pattern is similar to Fig. 4(b1) with the mirror symmetry with respect to the vertical axis.

For the ferroelectric with $\text{DLD} = 21$, the initial two domains in the lower region shown in Fig. 1(f) merge into one where the directions of the polarizations in the rows of 2, 6, 10, and 13 below the unusual 90° domain wall are respectively -0.6° , to -1.7° , -2.5° , and -179° to the x_1 direction, meaning that the polarizations rotate their directions without forming any conventional domain walls. When the applied field is reduced to zero, Fig. 4(c2), shows the evolved polarization structure, where there are only two polarization domains, penetrating into each other with the 90° domain walls. Since the polarizations in the domain below the dislocation wall are not completely horizontal and there is no reversed domain at all with polarizations along the minus x_2 direction, the remanent polarization is higher than that in the dislocation-free ferroelectric. The penetrated angles becomes slightly larger with the increase of the revised field until $E_2^{ex,*} = -0.18$, whereas the polarization structure remains almost unchanged, as shown in Fig. 4(c3). This gives the reason why the averaged polarization decreases so slow from 0.57 to 0.41 in this range of $E_2^{ex,*} = [-0.18, 0.8]$. Clearly, the dislocation walls with $\text{DLD} = 21$ stabilize the polarization structure, making it much less sensitive to the applied field in comparison with the cases of dislocation-free and low DLDs. This indicates that the stress field of dislocations does pin the polarizations. Further increasing the magnitude of the reversed field to -0.19 , a few polarizations near the upper left angle tip inside the original horizontal domain has switched clockwise about 73° , forming a nucleus of a reverse domain. The nucleus grows and the polarizations of the nucleus align themselves to the applied electric field, as the reverse field increases

FIG. 4. Polarization structures at different polarization stages ai, bi, and ci ($i = 1, 2, 3, 4$) marked in Fig. 2 for the ferroelectrics with DLD of 0, 13, and 21.

from -0.19 to -0.20 . The reverse domain reaches the dislocations when the reverse field rises to -0.21 . Then, increasing the reverse field causes the reverse domain growth laterally. These simulations exhibit clearly that the dislocation walls with the high DLD pin the polarizations tightly, which makes the new reverse domain nucleation difficult at the dislocations. Since the nucleation and growth of the reverse domain occurs quickly within a narrow range of $E_2^{ex,*} = [-0.18, -0.25]$, the average polarization drops from 0.41 to -0.08 , as shown in Fig. 2.

Figs. 4(b1)–(b4) and Figs. 4(c1)–(c4) show that the dislocation walls are the interfaces (or unusual 90° domain wall) of the horizontal and vertical domains. Due to the different lattice dimensions in the horizontal and vertical domains, there exist large misfit strains at the interface if there are no dislocations. The appearance of dislocations at the interface relaxes the misfit strain. This is very similar to the relaxation of misfit strain by interfacial dislocations between an epitaxial ferroelectric thin film and its substrate. The experimental observations show that the remanent polarizations are enhanced significantly with the relaxation of misfit strains in epitaxial ferroelectric islands¹² and thin films.¹³ The significant enhancement of remanent polarizations from DLD = 13 to DLD = 21 in Fig. 2 is due to the more relaxation of misfit

strain at the dislocation wall with the increase of DLD. This result suggests that the present phase field simulations are consistent with the experimental observations.

In summary, the phase field simulations exhibit that dislocation walls, introduced at high temperature, play a crucial role in the initial polarization structure and hence the polarization switching behavior. The unusual 90° domain walls formed along the dislocation walls with a DLD higher than 9 are stable under the applied electric field range of $[-0.8, 0.8]$. In the dislocation-free ferroelectric, there is the typical twin domain structure with 90° domain walls and the polarization switching is homogeneous domain nucleation and domain wall motion. When the DLD = 13, the reverse domain nucleates near the dislocations even when the applied electric field has not been reduced to zero, thereby leading to the lowest values of the coercive field and remanent polarization. The simulations illustrate a unique polarization structure when the dislocation walls with DLD = 21, where the polarizations rotate their polarization directions as they get far away from the dislocation walls and thus do not form any conventional domain walls. Due to the strong polarization pinning, the polarization switching becomes difficult and the reverse domain has to be nucleated far away from the dislocations, which enhances the coercive field.

This work was financially supported by Hong Kong Research Grants Council (Grant No. 622610). J. Wang was partially supported by the Natural Science Foundation of China under Grants (11002123, 11090333), Zhejiang Provincial Natural Science Foundation under Grant R6110115. H. H. Wu was partially supported by the Nanotechnology Program at HKUST.

¹J. F. Scott and C. A. Paz De Araujo, *Science* **246**, 1400 (1989).

²V. Garcia and M. Bibes, *Nature* **483**, 279 (2012).

³Y. L. Li, S. Y. Hu, S. Choudhury, M. I. Baskes, A. Saxena, T. Lookman, Q. X. Jia, D. G. Schlom, and L. Q. Chen, *J. Appl. Phys.* **104**, 104110 (2008).

⁴Y. Zheng, B. Wang, and C. H. Woo, *J. Mech. Phys. Solids* **55**, 1661 (2007).

⁵Z. Feng and X. Ren, *Appl. Phys. Lett.* **91**, 032904 (2007).

⁶Y. H. Zhang, J. Y. Li, and D. N. Fang, *Phys. Rev. B* **82**, 064103 (2010).

⁷S. Choudhury, Y. L. Li, C. E. Krill III, and L. Q. Chen, *Acta Mater.* **55**, 1415 (2007).

⁸W. Shu, J. Wang, and T. Y. Zhang, *J. Appl. Phys.* **112**, 064108 (2012).

⁹C. A. Randall, N. Kim, J. P. Kucera, W. Cao, and T. R. Shrout, *J. Am. Ceram. Soc.* **81**, 677 (1998).

¹⁰I. B. Misirlioglu, A. L. Vasiliev, S. P. Alpay, M. Aindow, and R. Ramesh, *J. Mater. Sci.* **41**, 697 (2006).

¹¹X. Zhu, J. Zhu, S. Zhou, Q. Li, Z. Liu, and N. Ming, *Appl. Phys. Lett.* **79**, 1345 (2001).

¹²M. W. Chu, I. Szafraniak, R. Scholz, C. Harnagea, D. Hesse, M. Alexe, and U. Gösele, *Nature Mater.* **3**, 87 (2004).

¹³V. Nagarajan, C. L. Jia, H. Kohlstedt, R. Waser, I. B. Misirlioglu, S. P. Alpay, and R. Ramesh, *Appl. Phys. Lett.* **86**, 192910 (2005).

¹⁴P. Gao, C. T. Nelson, J. R. Jokisaari, S. H. Baek, C. W. Bark, Y. Zhang, E. Wang, D. G. Schlom, C. B. Eom, and X. Pan, *Nat. Commun.* **2**, 591 (2011).

¹⁵S. Y. Hu, Y. L. Li, and L. Q. Chen, *J. Appl. Phys.* **94**, 2542 (2003).

¹⁶Y. L. Li, S. Y. Hu, Z. K. Liu, and L. Q. Chen, *Acta Mater.* **50**, 395 (2002).

¹⁷J. Wang, S. Q. Shi, L. Q. Chen, Y. Li, and T. Y. Zhang, *Acta Mater.* **52**, 749 (2004).

¹⁸Y. Li, S. Li, and T. Y. Zhang, *J. Nucl. Mater.* **395**, 120 (2009).

¹⁹See supplementary material at <http://dx.doi.org/10.1063/1.4809945> for the phase field model and the anisotropic analytical solution of a dislocation wall in one simulated cell, the domain evolution with $DLD=0$, for the domain evolution with $DLD=13$, and for the domain evolution with $DLD=21$.