Domain Pinning Behavior of Ferroelectric $Pb_{1-x}Sr_xTiO_3$ Ceramics

Chen-Chia Chou, Chun-Shu Hou and Tsung-Her Yeh

Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, R.O.C.

Transmission electron microscopy (TEM) was employed to investigate 90° domain nucleation, growth and interactions of ferroelectric **$(Pb_{1-x}Sr_x)TiO_3$** (PSrT) ceramics under electrical loading in the present work. Experimental results imply that as-sintered specimens exhibit simple domain arrangements. Domain boundaries multiply quickly by nucleating from grain-boundaries and/or defective regions under electrical loading. A conventional 90° domain boundary may dissociate into a set of zigzag domain boundaries with unconventional polarization arrangements under alternate electrical stimulation. If the zigzag domains grew and were impeded by one or a set of boundaries, leading to domain pinning, another sets of zigzag domains may nucleate from a 90° domain boundary again. Nucleation, growth and pinning of domain boundaries repeated and finally highly strained grains with polarization degradation and defects appear during electric polarization cycles.

Keywords: Electron microscopy, Ferroelectric, Fatigue, Domain boundary, Perovskite.

Introduction

Ferroelectrics have emerged as an important class of materials due to their incredibly wide diversity of exhibited phenomena, such as piezoelectricity, pyroelectricity, ferroelectricity, electro-optical and acoustic-optic phenomena. The properties of ferroelectrics and piezoelectrics are closely related to dynamical behavior of their domain structures due to polarization variation under working conditions.

The problem of fatigue frequently limits the application of ferroelectric ceramics, since it may markedly degrade the switching polarization. Polarization fatigue has been extensively investigated in many previous works using various models. [1-10] Domain pinning was reported and has been thought to be an important cause of the fatigue of ferroelectric materials, and the major mechanisms of domain pinning proposed can be classified into two categories: firstly, the defects with charges,[1] such as oxygen vacancies, electronic or ionic charges etc.[2-4] and secondly, the mechanical fatigue.[5-8]

Most of works, using the model of space charges and electronic properties to interpret the phenomenon of ferroelectric fatigue, suggest that electronic or ionic charges are trapped at domain boundaries[5-7], Such as Warren [5] suggests that fatigue is associated with the trapping of electronic charge and atomic-scale distortions in the perovskite oxygen octahedron.

Recently, the mechanism of mechanical fatigue was considered for ferroelectrics. Most of researchers believe that 90° domain arrangements follow "tail-to-head" or "head-to-tail" rules to reduce electrical energy. However, some peculiar domain arrangements have been reported to arise after an electric field and thermal treatment were applied. [9-14] Tsun and Chou[9] reported microstructural evolution of ferroelectric tin-modified lead zirconate titanate ceramics, indicating that polarization degradation is closely related to domain boundary interactions during polarization switching. Chou and Chen.,[10] using $PbTiO_3$ single crystals, demonstrated that various high energy polarization configurations may exist in the specimens if strain field is large, indicating that mechanical strain energy may play more important role than electrostatic energy in polarization fatigue of ferroelectrics. Khachaturyan[6] proposed that the degradation of the ferroelectric properties is a direct consequence of the mechanical fatigue. Demczyk[15] has also claimed that domain pinning occurred at grain boundaries.

This paper seeks to understand the mechanism of domain pinning. The roles played by the nucleation and growth of 90°domains during polarization switching is considered. Secondly, dynamic behavior of domain boundaries after applying external fields induced by electric polarization. Domain wall motions under electric and mechanical stress loading were simulated and microstructural evolution was investigated using transmission electron microscopy.

Experimental procedures

The polycrystalline ceramic materials $Pb_{1-x}Sr_xTiO_3$ (x=0.01~0.9) was prepared by solid-state reaction, using powders of PbO (99.99%), $SrCO_3$ (99.5%) and TiO_2 (99.9%). The mixed powders were calcined at 700□ for 2 h in air. After wet ball-milling, the powders were compacted with a cold-isostatic press at 40000 Psi and sintered at 1250 □ for 4 h in an atmosphere of oxygen. The structure of the bulk was elucidated using an X-ray diffractometer with a copper target. During sintering, the lead-containing materials were completely covered with powders of the same composition, using a double-crucible method in an oxygen atmosphere, to prevent possible loss of PbO.

The structure of the bulks was analyzed using a Rigaku DMAX-B X-ray diffractometer (XRD). The ferroelectric properties of the ceramic samples were measured using silver electrodes. The P□E behavior was characterized using a modified Sawyer-Tower circuit. Fatigue experiments were performed at 60 Hz and 1kHz using an electric field of 35kV/cm□50kV/cm. However, the bulk of as-sintered PSrT specimens and fatigue-test specimens were hand-ground to a thickness of 20~50 μm. An ion miller was employed at 5 kV, 0.5 mA, each gun with a tilting angle of 18~20° for further thinning. After perforation, the specimens were bombarded by the ion beam with a reduced voltage (3□4kV) and titling angle (13□14°) for several minutes. The microstructure of the bulks was investigated using a Jeol 2000FXII and Jeol 4000EX microscope.

Results and Discussion

Figure 1 shows the P□E hysteresis loop for a virgin specimen and a fatigued specimen tested at a frequency of 100 kHz for up to $3x10^9$ cycles. The initial properties of the specimen are as follows; P_r=15 $\mu C/cm^2$, saturated polarization (P_s)=23 $\mu C/cm^2$, and E_c=12 kV/cm. For the specimen after fatigue testing, P_r= 12 $\mu C/cm^2$, P_s is 15 $\mu C/cm^2$, and E_c= 20 kV/cm. In this case, P_r drops 20% and the coercive field E_c increases by 83%, indicating that the specimen was fatigued, according to the commonly used P_r or E_c criterion.

To correlate electrical properties with microstructures, TEM investigations were carried out after electrical measurements. Microstructures within grains are quite simple in as-sintered specimens, as shown in Fig.2(a). The amount of domain boundaries multiplies quickly and domain structures become complicated after electric polarization switching applies. Domain boundaries may nucleate from grain boundaries where high strain accumulates due to material extension/contraction under an electric field. Intriguingly, small zigzag-shaped domain boundaries were constantly induced from a straight 90° domain wall under an A. C. field, labeled as A in Fig. 2(b). Simultaneously, the zigzag-shaped domain kept growing (including forward and lateral directions) until it intersected with other domain walls, labeled as B in Fig. 2(b). Figure 2(c), on the other hand, shows a grain with high dislocation density produced by the intersected domain after 3×10^9 switching cycles with an electric field of 55 kV/cm. The contrast of the domain boundaries is almost smeared out by defect strain fields in the present case. The intersection of domain boundaries reduces the switchability of polarization domain, and therefore the coercive field increased with the density of domains boundaries intersection.

Figure 3 is a TEM micrograph showing an intriguing domain boundary generation mechanism. A straight 90° domain boundary may dissociate into many small zigzag shaped domain boundaries under a polarization switching process. The zigzag domain boundaries nucleate and grow in both outward and lateral directions, and the domain boundaries expand till intersection with other domain boundaries. If the density of 90° domain boundaries within a grain is small, domain boundaries may keep nucleating under a stress in terms of wedge-shaped domains or zigzag-shaped domains.

When domain switching occurs, field induced polarization increases. For an as-sintered ferroelectric ceramic, remanent polarization may increase at the initial stage of polarization cycling. However, if the domain boundaries accumulate in the grains, domain intersections inhibit polarization switching, which reduces remanent polarization and increases coercive field of specimens. To elucidate the relation of domain intersection and polarization switching, a careful analysis of domain pinning using TEM was carried out. Figure 4 show two sets of a-a domain boundaries intersect with each other in a grain of a $Pb_{0.6}Sr_{0.4}TiO_3$ specimen. It is clearly observed that a strain contrast occurs at the intersections of the tips of wedge-shaped domains and the perpendicular domain boundaries. The domains were stopped and pinned due to a high distortion region occurring. The strain contrast around domain boundaries can be monitored through tilting during TEM investigation. One may observe a 180° domain boundary meandering around the 90° domain intersected region and high strain contrast regions can be seen, as shown in Fig.4 (b) Figure 4 (c) exhibits a schematic drawing of possible polarization arrangements in the structure, and one may observe that the polarization vectors at the domain tips exhibit a high-energy configuration of either head-to-head or tail-to-tail arrangement. Consequence of this is not only a high electric static energy accumulation but also a high mechanical strain happening. Therefore these intersection regions are very easily etched using a chemical solution, implying high-energy state exists. These high-energy intersection regions clearly arrest domain boundaries and impede domain boundary motion and polarization switching.

Once high density of domain boundaries accumulated, the intersections of domain boundaries and hence the strain field spreads all around the grain, polarization switching become more difficult and therefore the observed polarization magnitude decreases. Polycrystalline materials possess many grains with various orientations within the specimen. Each grain may experience different electrical field strength and therefore each grain may display different degree of complexity of domain boundary intersection. If one grain has suffered too much strain accumulation, defects may be generated and even microcrack may appear.

Conclusions

Transmission electron microscopic investigations indicate that wedge-shaped 90° domains and zigzag-shaped 90° domains were induced under external stress at grain boundaries or domain walls and that their microstructures became more and more complicated due to domain pinning after electric polarization cycles.

Results of this study suggest that the formation of a zigzag-shaped domain and a wedge-shaped domain in ferroelectric material is important in domain pinning. Domain pinning associated with machine fatigue is more easily observed than domain pinning associated with oxygen vacancies in the microstructure. The domain pinning related to machine fatigue differs from domain pinning related to oxygen vacancies. The polarization fatigue of a ferroelectric is improved by enhancing the domain mobility and applying the optimum conditions, including frequency, electric field and interface.

Acknowledgements

The authors are grateful to National Science Council of Taiwan for financial support under contract number of NSC 92-2216-E011-029 and to Ms. Cheng and Ms. Tseng of Precision Instrument Center of National Science Council, Taiwan for helping with HRTEM and TEM investigations.

References

1. S. Triebwasser, Space charge fields in $BaTiO_3$. *Phys. Rev.*, 1960, **18**, 100-105.

2. W. L. Warren, D. Dimos, B. A. Tuttle, G. E. Pike, R. W. Schwartz, P. J. Clews, & D. C. Mclntyre, Polarization suppression in Pb(Zr,Ti)O_3 thin films. *J. Appl. Phys.*, 1995, **77(12)**, 6695-6702.

3. W. L. Warren, B. A. Tuttle & D. Dimos, Ferroelectric fatigue in perovskite oxides. *Appl. Phys. Lett.*, 1995, **67(10)**, 1426-1428.

4. J. Lee, S. Esayan, A. Safari & R. Ramesh, Effect of ultraviolet light on fatigue of lead zirconate titanate thin-film capacitors. *Appl. Phys. Lett.*, 1994, **65(2)**, 254-256.

5. W. L. Warren, D. Dimos, H. N. Al-Shareef, M. V. Raymond, B. A. Tuttle & G. E. Pike, Links between electrical and optical fatigue in Pb(Zr,Ti)O_3 thin films. *J. Am. Ceram. Soc.* 1996, **79(61)**, 1714-1716.

6. K. Khachaturyan, Mechanical fatigue in thin films induced by piezoelectric strains as a cause of ferroelectric fatigue. *J. Appl. Phys.*, 1995, **77**, 6449-6455.

7. H. M. Duiker, P. D. Beale, J. F. Scott, C.A. Pax de Araujo, B. M. Melnick, J. D. Cuchiaro & L. D. McMillan, Fatigue and switching in ferroelectric memories: Theory and experiment. *J. Appl. Phys.*, 1990, **68**, 5783-5791.

8. H. M. Duiker & P. D. Beale, Grain-size effects in ferroelectric switching. *Phys. Rev.*, 1990, **B41**, 490-495.

9. Y.F. Tsun & C. C. Chou, Microstructural evolution under polarization switching of ferroelectric tin-modified lead zirconate titanate ceramics. *Jpn. J. Appl. Phys.*, 1999, **38**, 3585-3588.

10. C. C. Chou & C. S. Chen, Banded structure and domain arrangements in $PbTiO_3$ single crystals. *Jpn. J. Appl. Phys.*, 1998, **37**, 5394-5396.

11. C. C. Chou, L. C. Yang & C. M. Wayman, Transmission Electron Microscopy Study of Domain Boundaries in $PbTiO_3$. *Mater. Chem. Phys.*, 1993, **36**, 57-63.

12. C. C. Chou, C. S. Hou & C. L. Li, Unconventional polarization arrangements in PbTiO3 single crystals. *J. Mater. Sci.: Mater. In Ele.*, 1999, **10**, 299-306.

13. M. Tanaka & G. Honjo, Electron optical studies of barium titanate single crystal films. *Jpn. J. Phys. Soc.*, 1964, **19(6)**, 954-970.

14. C. A. Randall, D. J. Barrer & R. W. Whatmore, Ferroelectric domain configurations in a modified-PZT ceramic. *J. Mater. Sci.*, 1987, **22**, 925-931.

15. B. G. Demczyk, A. G. Khachaturyan & G. Thomas, On a minimum grain size for domain formation in Lanthanum-moddifid lead titanate ferroelectric ceramics. *Scripta Metall.*, 1987, **21**, 967-969.

Captions

Figure 1 The P-E curves of $Pb_{0.6}Sr_{0.4}TiO_3$ ceramics under an a. c. field at a working frequency of 1 kHz implying the difference of remanent polarization and coercive field at the initial and fatigue (after 10^9 cycles) states.

Figure 2 TEM micrographs showing microstructural evolution of $Pb_{0.6}Sr_{0.4}TiO_3$ ceramics under polarization switching at a working frequency of 1 kHz and 55 kV/cm. (a) as-sintered state; (b) polarization switching for 10^5 cycles; (c) 3×10^9 switching cycles.

Figure 3 Domain boundary dissociation under a polarization switching cycles of $Pb_{0.6}Sr_{0.4}TiO_3$ ceramics, suggesting an intriguing strain energy absorbing mechanism.

Figure 4 Two sets of a-a domain boundaries intersect to form an immobile variant boundary. (a) A bright field image close to (100) zone; (b) a bright field image near the (110) zone; (c) schematic drawing and polarization arrangements among the intersected domain boundaries.

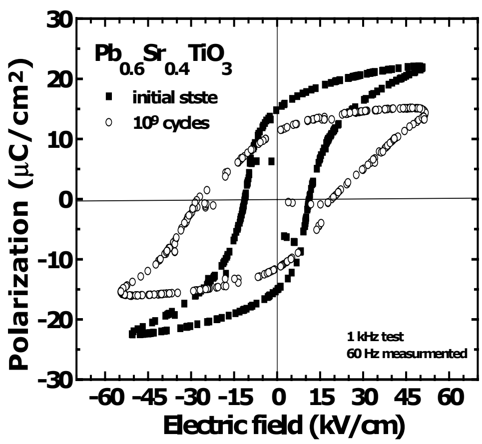

Figure 1 The P-E curves of $Pb_{0.6}Sr_{0.4}TiO_3$ ceramics under an a. c. field at a working frequency of 1 kHz implying the difference of remanent polarization and coercive

field at the initial and fatigue (after 10^9 cycles) states.

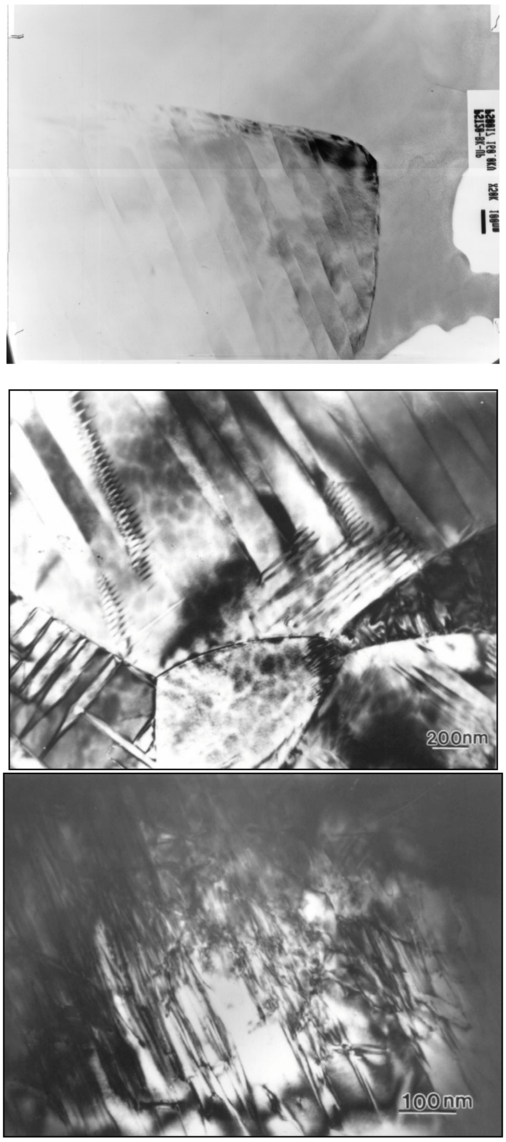

Figure 2 TEM micrographs showing microstructural evolution of $Pb_{0.6}Sr_{0.4}TiO_3$ ceramics under polarization switching at a working frequency of 1 kHz and 55 kV/cm. (a) as-sintered state; (b) polarization switching for 10^5 cycles; (c) 3×10^9 switching cycles.

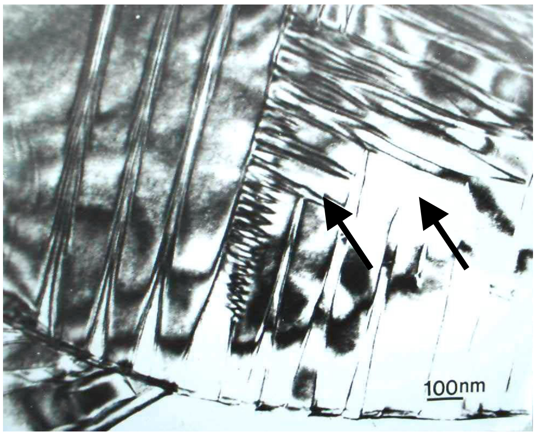

Figure 3 Domain boundary dissociation under a polarization switching cycles of $Pb_{0.6}Sr_{0.4}TiO_3$ ceramics, suggesting an intriguing strain energy absorbing mechanism.

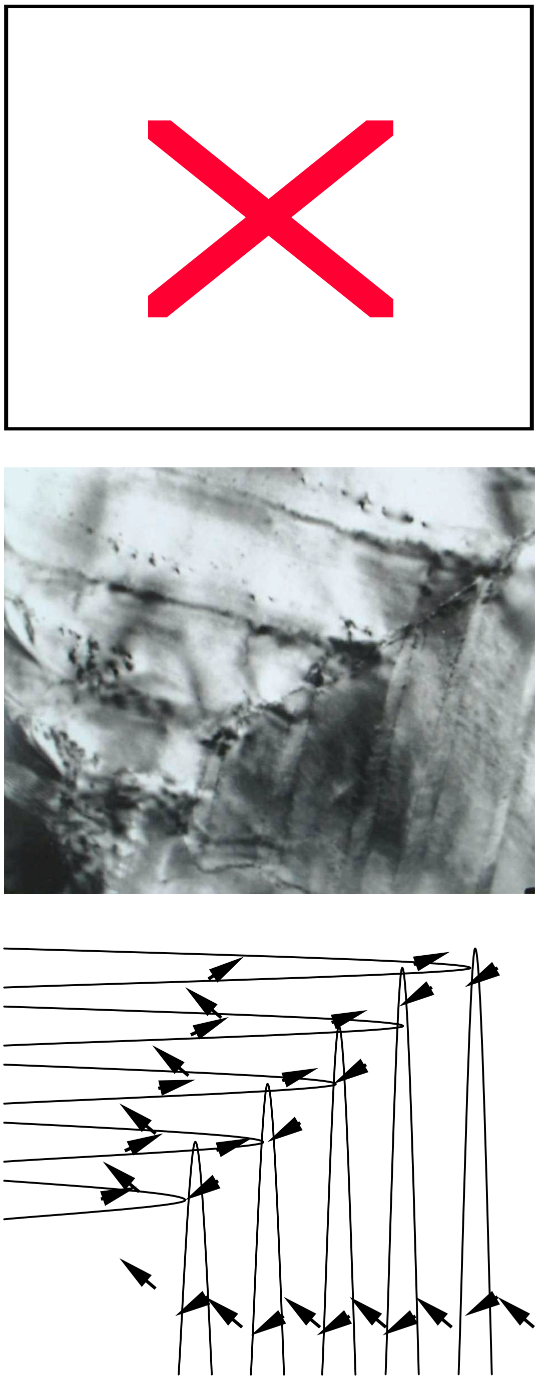

Figure 4 Two sets of a-a domain boundaries intersect to form an immobile variant boundary. (a) A bright field image close to (100) zone; (b) a bright field image near the (110) zone; (c) schematic drawing and polarization arrangements among the intersected domain boundaries.