

Ultra high resolution of PZT 30/70 domains as imaged by PFM

S. Dunn, C P Shaw, Z Huang and R. W. Whatmore

Building 70 (Nanotechnology) Cranfield University, Cranfield, MK43 0AL, UK.

Abstract

PiezoForce Microscopy (PFM) has been used to determine the domain structure of lead zirconate titanate (PZT) (30/70) on an Indium Tin Oxide (ITO)/Glass substrate with a TiO_2 boundary layer. The PZT nucleates into the perovskite form in a random crystallographic manner, which leads to a random domain structure in the final film. Using PFM it has been possible to visualise the domain structure of the PZT and determine that the domain structure has features as fine as 8nm herringbone patterns. The possible impact of these structures for future devices utilising nanoscale features of PZT and especially FeRAM developments is highlighted.

Here we report the use of an SPM (scanning probe microscope), modified to perform PFM (piezoresponse force microscopy), to visualise the domain structure in PZT 30/70 (lead zirconate titanate 30/70) thin films with nanometric resolution and the possible impacts for ferroelectric memories. The use of ferroelectric thin film materials as the storage medium in memory devices is not a new phenomenon [1-4] The potential advantages of using the ferroelectric layer to store data was first highlighted during the 1950's with work continuing up to the present day [5, 6]. Further development of non-

volatile memory devices for use in information technology applications is becoming increasingly reliant on the ability to produce high quality ferroelectric thin films [7, 8]. A thorough understanding of their behaviour at the nanoscopic level is essential if we are to understand the problems of retention and fatigue associated with many ferroelectric materials when applied to memory devices. The use of PFM to study and manipulate the domain structure of a ferroelectric materials at nanometric resolution has been widely reported [9-12]. Here we show that it is possible to image features as fine as 8nm in the domain structure of PZT 30/70 films deposited on ITO (indium tin oxide) coated glass and that the domain structure in the PZT is not homogeneously distributed.

Using the polarisation state of a ferroelectric material it was proposed that a device with a very fast access time and low power consumption, could be manufactured [13]. However, when such devices were produced they suffered from excessive fatigue[2, 14], i.e. reduced ability to store charge upon subsequent cycling. Two broad solutions have been investigated to reduce the fatigue demonstrated by the device. These are the use of oxygen donating electrodes[15-18] such as ITO or RuO₂ or substituting the ferroelectric layer for a so-called 'fatigue free' ferroelectric material[19-21]. Fatigue free materials have proved difficult to grow in an orientation suitable for use as the capacitor layer in Fe-RAM devices [21]. It is possible to produce ferroelectric material, such as PZT, on oxygen donating electrodes such as iridium/iridium oxide or ruthenium oxide. The resulting ferroelectric layer can be too 'leaky' (the charge stored leaks away rather than remaining in the memory cell) for use in non-volatile applications. However, the deposition of PZT onto ITO coated glass has been shown to increase the fatigue life of PZT [22] and has been attributed to the ability of the ITO to behave in a non-blocking

way to charged defects by conducting anions. Previous investigations have concentrated on determining the fatigue properties of the films using devices such as the Radiant Technologies RT66A and 'Fatigue' software (further information can be found at <http://www.ferrodevices.com/vision.html#mt>). These studies have derived information regarding the fatigue and ferroelectric properties of the material on a micro-meter scale. By using PFM and intermittent contact mode SPM we have determined that there are significant variations in the domain structure of the PZT below this scale and that these domains vary from region to region across the film surface.

Our films were prepared by spin coating a sol of PZT pre-cursor materials to produce a film 70nm thick. The PZT film was "dried" at 450°C and annealed at 570°C for 20 minutes producing a fully-perovskite film. A full discussion of the nature of the nucleation, the effect this has on the topography and the crystallography of the film is given by Shaw *et al* [23, 24]. A Digital Instruments Dimension 3000 SPM was modified to perform PFM, shown schematically in Figure 1. An oscillating AC signal at 17.68kHz and 1.5 V peak to peak was applied between the SPM tip and the back electrode (held at ground) across the PZT sample. This induces a converse piezoelectric effect in the PZT thin film with the resulting signal being detected by a lock-in amplifier (EG+G, 7260) and used to generate the PFM domain map. For further information regarding the technique of PFM, it's history, usefulness, physical interactions that govern the response of the cantilever and methods of data analysis the reader is directed to the following references[11, 25-33]. The SPM tips used for these experiments were Nanosensors

Electrostatic Force Microscopy tips coated in PtIr with a resonant frequency around 270 kHz. All PFM experiments were performed in contact mode.

A topographic image for the region investigated is shown in Figure 2. This indicates that the PZT has not grown into a smooth layer. Individual plates have formed during crystallisation of the pyrochlore phase into the perovskite phase, resulting in the surface topography seen. Within each of the large plates (2-5 μm across) individual crystallites of PZT can be seen as small bumps on the surface of the sample. A PFM image for the same region is shown in Figure 3. The plate boundaries are easily seen as well as the large variation in the contrast in the image.

The PFM technique maps the domain structure of the material by detecting the phase shift in the converse piezoelectric effect for oppositely poled regions in the film. When a film has been deposited by a sol-gel technique it is usual and indeed thermodynamically predicted that the domain structure of the surface will have a zero net polarization. This is achieved by the surface of the film having a random orientation of domains that add to give a net neutral surface. If the film was poled in one direction, for example, with the spontaneous dipole up then the image produced would be all white. The variation in contrast across the image indicates that the domains, and hence crystal structure, in the as-deposited material are not homogeneously orientated. If the structure of the material was homogeneously orientated, i.e. a [111] or [100] pseudo-epitaxial structure, then the image would contain only regions of black and white, with no gray or grayscale areas. This finding is supported by the XRD pattern for the sample, which is similar to that of

the powder pattern for PZT [24] indicating that the crystallographic orientation in the film is not constrained to one orientation. This result means that the PZT grown on the ITO is only able to exhibit maximum spontaneous polarization, due to the perpendicular alignment of the axis of maximum polarisation in certain areas of grains at discrete regions across the surface. Some regions of the surface contain material that is aligned with the axis of maximum polarisation parallel to the surface and, as such, application of an electric field to these regions will not induce the maximum polarization for the sample. The result of this is that it is not possible to produce an image that is all black or after the application of the poling voltage. This variation of the polarisable dipole means that the material in this region is unsuitable for use as a ferroelectric memory cell. As PFM measures the displacement of the surface due to the converse piezoelectric effect, the variation in polarisation is due to the variation in effective d_{33} of the sample in the regions under the probe tip.

The scale of the regions that show a variation in the domain structure varies across the image. In region A, see Figure 3 a PFM image of the surface of the PZT, the domain structure of the PZT changes over a period of about 500nm, whereas, in region B the domain structure is varying over a period of 8nm. The PZT image shown is a raw data Digital Instruments screen capture of the SPM signal input into the AFM, no post capture data manipulation has been performed. Variations in the native polarisation direction of the ferroelectric at these dimensions are likely to have a marked effect on the performance of a FeRAM device made from PZT grown on ITO. Some memory cells could exhibit excellent retention performance due to the high polarisability with other

cells behaving less well or not at all. These variations in polarisability lie in the transformation process for perovskite development, which is directly attributed to the electrode system used. PZT grown on Pt electrodes can be produced as very highly orientated [111] but this system is not suitable for FeRAM devices[14].

It is also worth noting that the domain structure produces a herringbone like pattern along one side of the two crystallite interfaces. These structures are about 8nm in cross section, shown in Figure 4 a higher magnification image of region B shown in Figure 3. The presence of such fine domains with the associated increase in density of the domain walls is likely to have implications on the rate of fatigue for these regions. Although it is accepted that an increase in defect density, especially oxygen defects, is mainly responsible for fatigue in PZT ceramics the presence of domains walls also adds to the fatigue in the ferroelectric. This is due to the stress relaxation as orthogonal domains relax back to 180° and the resulting mechanical stresses on the film and domain wall pinning. The increase in the mechanical stress within the material reduces the polarisation of the material. Significant increases in the number of domain walls within the sample increase the local stress and therefore reduce the number of cycles required for fatigue.

The magnified section of the PFM image of Figure 4 shows that, along with the herringbone pattern present in the PZT, the surface is made up of number of discrete pits. The origin of these pits are believed to stem from noise in the system and can also be seen in Figure 3 as a speckling of the image. The speckling seen in the image can also be seen on the real time output from the lock-in amplifier and is believed to be due to

come from the vibration induced by air flow over the sample during analysis. The pits are not visible in the topographic image due to larger amplitude of z-signal when obtaining a topographic image (the topographic height variation is shown on a 50nm scale, vertical displacement of the piezoresponse signal is at best 50pm[34]). These herringbone features are therefore associated with the piezoelectric structure of the sample. A cross sectional TEM image of the sample shows features of a similar dimension to the herringbone pattern shown in the PFM image, and is shown in Figure 5. It is likely then the nanometre sized crystallites within the large plates of the PZT are responsible for the variation in the piezoelectric response found by PFM. The TEM image also shows that the origin of the plates formed in the PZT stems from the transformation mechanism of pyrochlore to perovskite PZT [24]. The mechanism of transformation from pyrochlore to perovskite PZT that was grown on ITO/Glass produces a material that has considerable variation in the piezoelectric structure.

We have shown that a PZT film deposited by spin coating and subsequent firing onto a substrate highly suitable for FeRAM applications has a variation in domain orientation. The scale of variation in the domain orientation and changes in polarisability across the sample has implications for using the material as the storage layer in FeRAM devices. Current device design relies on homogeneity of materials properties throughout the active areas, this was not found for the PZT evaluated. The ability to image the domains of a material and show that they exist with nanometric resolution allows the further development of processes and materials suitable to produce materials for FeRAM devices.

Financial support from TDK Japan, the EPSRC and the Inamouri Foundation is gratefully acknowledged.

List of figures:

Figure 1, Schematic of apparatus used to complete PFM measurements showing modifications made to Dimension 3000 SPM system.

Figure 2, Tapping mode topographic image for PZT 30/70 grown on ITO/Glass. Individual crystallites are visible as the boundaries between them.

Figure 3, PFM domain map for region shown in Figure 2. The interfaces between crystallites are easily seen as is the variation in domain structure shown by the variation in contrast across the image. Region A indicated on the image shows a region of large scale (500nm) variation in domain structure. Region B seen on the image shows a region of small scale variation (8nm) in domain structure.

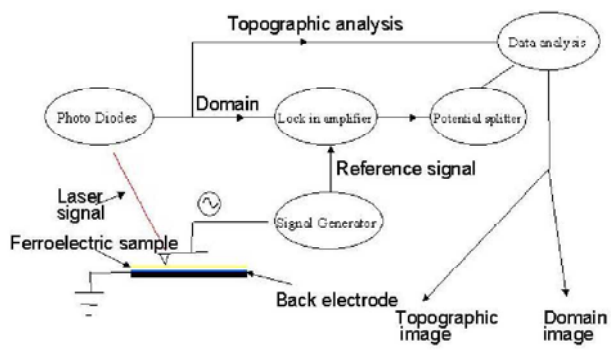
Figure 4, High resolution PFM scan of Region B indicated in Figure 3. The striations produced by the herringbone domain structure are clearly visible.

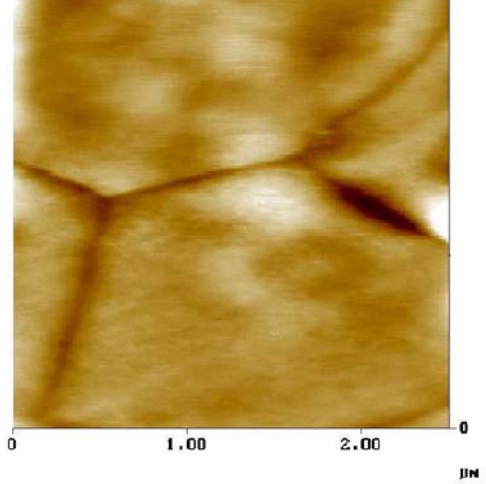
Figure 5, Cross sectional TEM image for PZT film grown on ITO/Glass

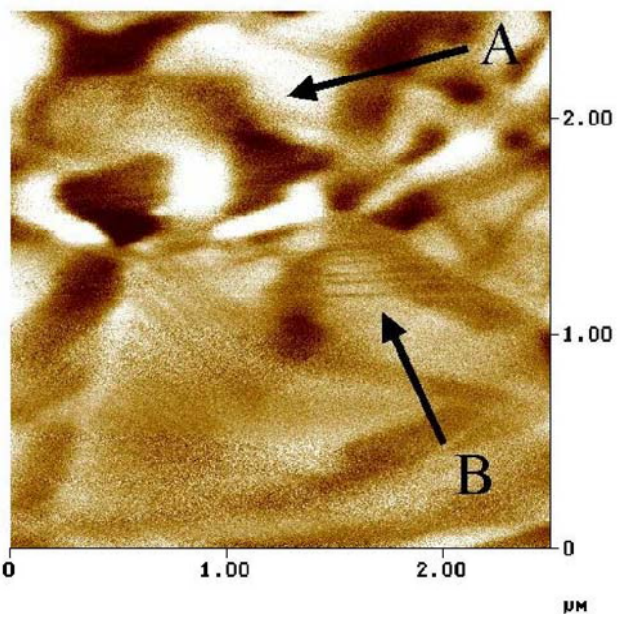
References

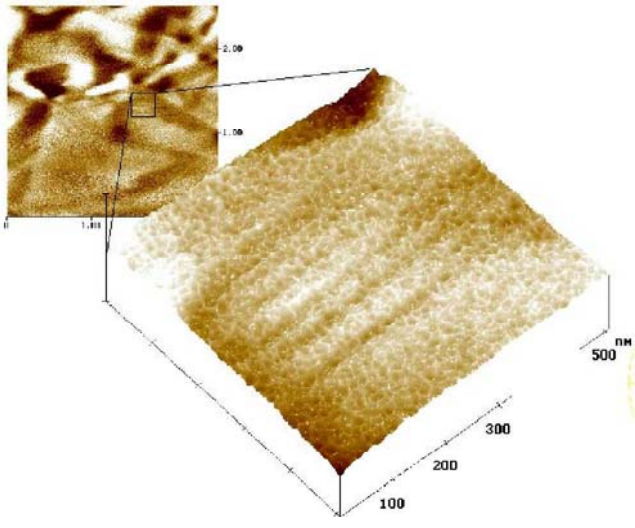
1. Sheikholeslami, A. and P.G. Gulak, *A survey of circuit innovations in Ferroelectric Random Access Memories*. IEEE- Proceedings of, 2000. 88(5): p. 667.
2. Carrano, P., et al., IEEE Transaction on Ultrasonics, Ferroelectrics and Frequency control, 1991. 38(6): p. 690.
3. Moazzami, R., et al., *Ferroelectric PZT thin films for low-voltage nonvolatile memory*. Proceedings - IEEE International Nonvolatile Memory Technology Conference, 1993: p. 44.
4. Miller, S.L., et al., Journal of Applied Physics, 1990. 68(12): p. 6463.
5. Sharma, B.S., S.F. Vogel, and P.P. I, Ferroelectrics, 1973. 5: p. 69.
6. Larsen, P.K., R. Cuppens, and G.A.C.M. Spierings, *Ferroelectric memories*. Ferroelectrics, 1992. 128: p. 265-292.
7. Scott, J.F., *Status report on ferroelectric memory materials*. Integrated Ferroelectrics, 1998. 20(1-4): p. 15-23.
8. Ramesh, R., S. Aggarwal, and O. Auciello, *Science and technology of ferroelectric films and heterostructures for non-volatile ferroelectric memories*. Materials Science and Engineering: R: Reports, 2001. 32(6): p. 191-236.
9. Alexe, M., et al., *Patterning and switching of nano-size ferroelectric memory cells*. Scripta Materialia, 2001. 44(8-9): p. 1175-1179.
10. Auciello, O., et al., *Nanoscale scanning force imaging of polarization phenomena in ferroelectric thin films*. MRS Bulletin, 1998. 23(1): p. 33-42.
11. Franke, K., et al., *Nanoscale investigations of polarisation in thin film ferroelectric films by means of scanning probe microscopy*. Ferroelectrics, 1995. 172: p. 397-404.
12. Dunn, S., A.P. De Kroon, and R.W. Whatmore, *An examination of thin film lead scandium tantalate oxide (PST) using PiezoAFM*. Journal of Materials Science Letters, 2001. 20: p. 179.
13. Scott, J.F., *Ferroelectric memories today*. Ferroelectrics, 2000. 236(1): p. 247-258.
14. Colla, E.L., et al., *Fatigued state of the Pt-PZT-Pt system*. Integrated Ferroelectrics, 1997. 18(2): p. 19-28.
15. Ramesh, R., et al., Research Society Symposium Proc., 1993. 310: p. 195.
16. Al-Sheeref, H.N., et al., Journal of Materials Research, 1994. 9: p. 2968.
17. Vijay, D.P. and S.B. Desu, Journal of Electrochemical Society, 1993. 140: p. 2640.
18. Cross, J.S., et al., *Evaluation of PZT capacitors with Pt/SrRuO₃ electrodes for FeRAM*. Integrated Ferroelectrics, 1999. 25(1): p. 265-273.
19. Harnagea, C., et al., *Quantitative ferroelectric characterization of single submicron grains in Bi-layered perovskite thin films*. Applied Physics A: Materials Science and Processing, 2000. 70(3): p. 261-267.
20. Li, T., et al., *Fatigue free ferroelectric Pb₅Ge₃O₁₁ thin films prepared by metalorganic chemical vapor deposition*. Integrated Ferroelectrics, 1999. 26(1): p. 75-83.

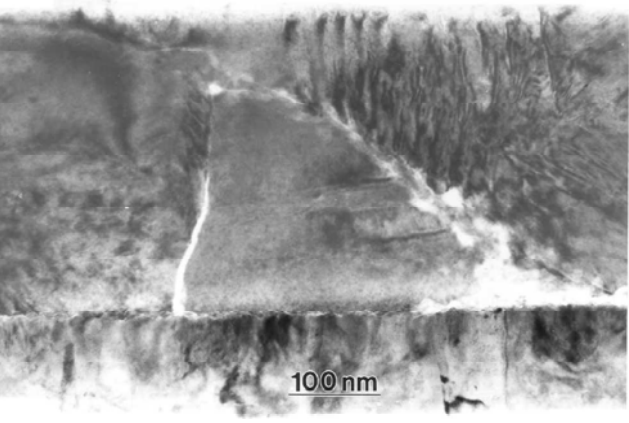
21. Yang, H.-M., J.-S. L'uo, and W.-T. Lin, *In situ growth of fatigue-free SrBi₂Ta₂O₉ films by pulsed laser ablation*. *Journal of Materials Research*, 1997. 12(4): p. 1145-1151.
22. Rao, A., V, S.A. Mansour, and A.L. Bement, *Fabrication of ferroelectric thin film capacitors with indium tin oxide (ITO) electrodes*. *Materials Letters*, 1996. 29(December 1996): p. 4.
23. Shaw, C.P., et al., *Growth and characterisation of lead zirconate titanate (30/70) thin film using TiO₂ seeding for oxide ferroelectric-liquid crystal display application*. *Integrated Ferroelectrics*, 2001. 256: p. 159.
24. Shaw, C.P., et al., *Growth and characterisation of lead zirconate titanate (30/70) on indium tin oxide coated glass for oxide ferroelectric-liquid crystal display application*. *Integrated Ferroelectrics*, 2000. 29: p. 189-213.
25. Guthner, P. and K. Dransfeld, *Local poling of ferroelectric polymers by scanning probe microscopy*. *Applied Physics Letters*, 1992. 9(31): p. 61.
26. Franke, K., et al., *Modification and detection of domains on ferroelectric PZT films by scanning force microscopy*. *Surface Science Letters*, 1994. 302(L283).
27. Hidaka, T., et al., *Formation and observation of 50nm polarized domains in PbZr_{1-x}Ti_xO₃ thin film using scanning probe microscope*. *Applied Physics Letters*, 1996. 68(17): p. 2358.
28. Hidaka, T., et al., *Characteristics of PZT thin films as Ultra-High density recording media*. *Integrated Ferroelectrics*, 1997. 17: p. 319-327.
29. Gruverman, A., et al., *Nanoscale investigation of polarization retention loss in ferroelectric thin films via scanning force microscopy*. *Ferroelectric Thin Films VI; Materials Research Society Symposium Proceedings*, 1998. 493: p. 53-58.
30. Durkan, C. and M.E. Welland, *Investigations into local ferroelectric properties by atomic force microscopy*. *Ultramicroscopy*, 2000. 82(1-4): p. 141-148.
31. Odagawa, H. and Y. Cho, *Simultaneous observation of nano-sized ferroelectric domains and surface morphology using scanning nonlinear dielectric microscopy*. *Surface Science*, 2000. 463(1): p. L621-L625.
32. Harnagea, C., et al., *Piezoresponse scanning force microscopy: What quantitative information can we really get out of piezoresponse measurements on ferroelectric thin films*. *ISIF 2001, Integrated Ferroelectrics*, 2001. *Proceedings Of ISIF 2001*.
33. Zavala, G., J. Fendler, and S. Trolier-McKinstry, *Characterization of ferroelectric lead zirconate titanate films by scanning force microscopy*. *Journal of Applied Physics*, 1997. 81(11): p. 7480.
34. Dunn, S. and R.W. Whatmore, *Substrate effects on domain structure of PZT 30/70 sol-gel films via PiezoAFM*. *Journal of the European Ceramic Society*, 2002. 22: p. 825.











Ultrahigh resolution of lead zirconate titanate 30/70 domains as imaged by piezoforce microscopy.

Dunn, Steve

2006-11-14T15:31:35Z

Dunn S, Shaw CP, Huang Z, Whatmore RW. (2002) Ultrahigh resolution of lead zirconate titanate 30/70 domains as imaged by piezoforce microscopy. *Nanotechnology*, Volume 13, Issue 4, 2002, pp. 456-459

<http://hdl.handle.net/1826/1228>

Downloaded from CERES Research Repository, Cranfield University