

The measurement of ferroelectric thin films using piezo force microscopy

M G Cain^{*}, S. Dunn^{**} and P. Jones^{***}

^{*}National Physical Laboratory, Teddington, Middlesex, UK, markys.cain@npl.co.uk

^{**}Cranfield University, Cranfield, UK, S.C.DUNN@cranfield.ac.uk

^{***}Cranfield University, Cranfield, UK, pjones4981@yahoo.com

ABSTRACT

The use of Atomic Force Microscopy to evaluate the properties of ferroelectric thin films is often associated with poor contrast images and quantitative analysis is often not possible. In this paper elements of the metrology associated with this technique are explored, and results comparing different materials types and surface cleanliness are described.

Keywords: piezo force microscopy, ferroelectric, thin films, AFM, characterisation

1 INTRODUCTION

Ferroelectric materials in bulk or thin film form are used in a large variety of applications and with the emergence of Micro-Electro-Mechanical-Systems (MEMS) have driven the reduction of scale for devices that utilise them. The piezoelectric effect (for which ferroelectrics are a sub-set of) is used in such devices to convert motion or stress into electrical signals whilst the converse piezoelectric effect is used to enable motion in structures. More recently, ferroelectric thin films have been used in the development of non-volatile memory devices, such as the Sony Playstation 2. In order to understand and characterise the thin films used for these devices it is necessary to investigate the domain structure and polarisation of the material at the nanometre length scale. At present, one of the best techniques to undertake these investigations is Piezo Force Microscopy (PFM). Using an electrically conductive tip the Atomic Force Microscope (AFM) can detect the piezoresponse induced vibrations of the film when an alternating current (ac) electric field is applied across the film thickness.

PFM is based on a uniquely configured Atomic Force Microscope and makes use of the converse piezoelectric effect in piezo-materials [1][2][3]. The conductive tip of the AFM is used as the top electrode on a ferroelectric thin film sample which has a grounded base electrode. When an ac signal is passed through the tip, with zero dc offset, an alternating electric, E , field is generated between the two electrodes. This E -field causes the generation of strain in the film by way of the converse piezoelectric effect. The value of this strain is $\epsilon = d_{33}E$, where ϵ is the strain, d_{33}

is the *out-of-plane* piezoelectric coefficient and E the applied E -field.

As well as the out-of-plane strain there can also be an *in-plane* strain where the material will expand or contract parallel to the surface. The magnitude of the in-plane strains is dependent on $\epsilon = d_{13}E$ and $\epsilon = d_{23}E$, where d_{13} is the piezoelectric coefficient in the x-axis and d_{23} the piezoelectric coefficient in the y-axis (In many ferroelectric perovskites, these two tensor components are equivalent because of the symmetry of the crystalline system). The resulting strain causes the film to deform in a periodic manner with respect to the driving frequency, which is detected by the AFM optics. By adding a dc offset to the driving ac voltage, in excess of the materials coercive field, it is possible to pole (electrically orient) individual grains of the ceramic thin film [4]; the poling orientation being controlled by the polarity of the dc offset.

Some of the more commonly used ferroelectric materials used in MEMS are based on lead zirconium titanate (PZT) due in part to their high mechanical strain under an applied E -field [5]. Other materials such as gallium nitride also find use in opto-electronic systems [6]. Most macroscale measurements of these materials ferro/piezoelectric response give information only about its bulk properties. It has been observed that thin films possess a reduced *effective* piezoelectric coefficient compared to their bulk equivalents. In order to understand and characterise ferroelectric thin films for use at the nanometre scale, in devices like memory, piezoelectric micro-actuators and pyroelectric detectors [7], it is necessary to observe the dynamics of domains within the material at the nanometre scale [8]. Piezo-Force Microscopy is ideally suited to the investigation of the individual domains within these materials [6]. Though other techniques have been used to investigate ferroelectric films [9] such as scanning/transmission electron microscopy, they do not have the flexibility that is offered by PFM in both resolution and sensitivity [10].

It has been found that the PFM technique can be used to give greater information about the domain structure in ferroelectric materials, but the actual interactions that take place between the SPM cantilever and sample are not fully understood. A review of the literature reveals that images obtained by PFM are not always repeatable even when the

same settings are used for each scan. A thorough investigation into the nature of the interaction between the AFM tip and sample has not yet been carried out. Our research will investigate the nanoscale interactions between tip and sample surface including effects of contamination and environment, and modelling of the E-fields generated around the tip and in the ferroelectric samples. This short paper describes some early results showing the effect of surface contamination on PFM image quality.

1.1 Effects of surface contamination

Surface contamination comes from a variety of sources including initial film formation, absorbed water from the surrounding environment, and even conductive layers deposited by contact with other objects and oxidation. Often it is stated that there is no surface preparation required before PFM is carried out [11], with most experiments being undertaken at atmospheric pressures and humidity.

Desheng et al [12] proposed that one of the reasons why the measured piezo coefficients, using PFM, were so low was because an ultra-thin air gap could exist between the tip and the sample. At nanometre scales this could have a noticeable affect on the E-field. An alternative explanation is that, as most of these experiments are operated in atmospheric conditions, absorbed water fills any space between tip and sample creating a meniscus on the tip, introducing a thin dielectric layer between tip and sample.

PFM is ideally suited to explore these issues because; by changing the tip force interaction (via changing the bias voltage on the AFM cantilever and scanning the tip) we are able to 'wipe' successive layers of contaminant material from the surface of the ferroelectric thin film.

2 EXPERIMENTAL PROCEDURE

All the samples were manufactured using the sol-gel fabrication method and were deposited on two substrate types:

- ITO/Glass, coated with PZT (30,70) at 210nm thickness, which formed a rosette like structure surrounded by an amorphous matrix on the surface [13].

- Pt/Ti/SiO₂/Si, coated with PZT (30,70) at 200nm thickness and formed a very fine grain structure [14].

On each sample, one corner of the PZT was carefully scraped off using a scalpel and fine wire anchored in place with conductive epoxy resin. This enabled the bottom electrode to be grounded during experimentation. In the experiments described in this paper, no separate top electrodes were deposited onto the ferroelectric thin film.

The AFM was configured for PFM operation, utilising a digital lock-in amplifier and signal generator. Details may be found in references [1][2]. The grounding wire of the sample was connected to the ground of the signal generator output. The output from the signal generator was set to a frequency of 18kHz and amplitude of 4V_{pk-pk}. For all the samples used, an initial scan of 25µm x 25µm at 0V deflection set-point was undertaken. On completion of the initial scan an area of interest was selected, and a series of scans then followed, using an initial deflection set point of 0V and ending with 6V, in increments of 1V. This had the effect of increasing the force between the Si-AFM tip and the ferroelectric thin film. Two sets of materials were investigated. One set was several years old that had been stored in a normal laboratory environment. The second set was the same material type but had been cleaned using a standardized si-wafer cleaning process. The effect of removal of surface contamination on PFM image contrast was then established.

3 EXPERIMENTAL RESULTS

3.1 Un-cleaned (aged) samples

The first scans at 0V deflection set point (low tip force) resulted in poor PFM image contrast. Increasing the tip force resulted in an improvement in image contrast up to a certain level beyond which the contrast did not improve noticeably. The difference between the contained area and the scrubbed area can be seen clearly in Figure 1. The image on the left of the figure is a topographic AFM image and the image on the right is the PFM image, where bright regions indicate a high degree of piezoelectric induced strain.

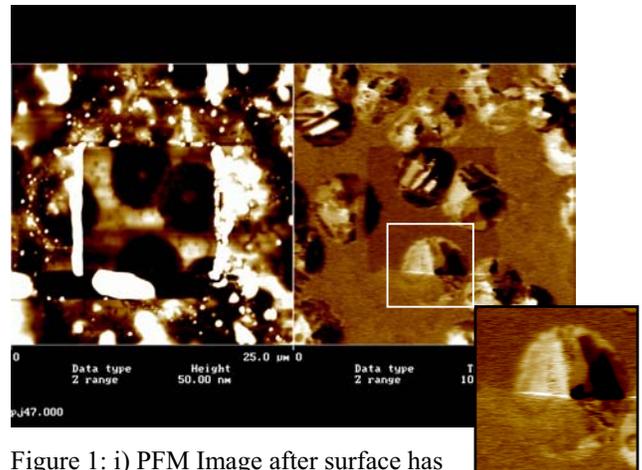


Figure 1: i) PFM Image after surface has been scrubbed clean by tip & inset ii) zoomed in area across the scrubbed un-scrubbed interface.

The magnified rosette in Figure 1ii shows how the demarcation between the scrubbed and un-scrubbed areas

affects the contrast. The top half of the rosette is in the scrubbed and the bottom in the un-scrubbed areas.

3.2 Cleaned (aged) sample

The results of the scans on the cleaned sample, Figure 2, differ from those seen when un-cleaned, in that the contrast is very clear from the first low tip force scan to the last. It is interesting to note that the contrast does not alter when different tip forces are used and so the PFM contrast results appear to be tip force independent.

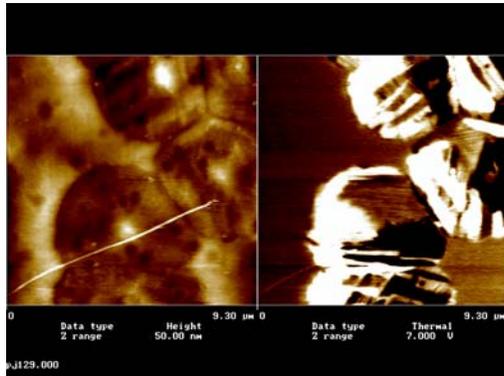


Figure 2: i) 0v Deflection set point

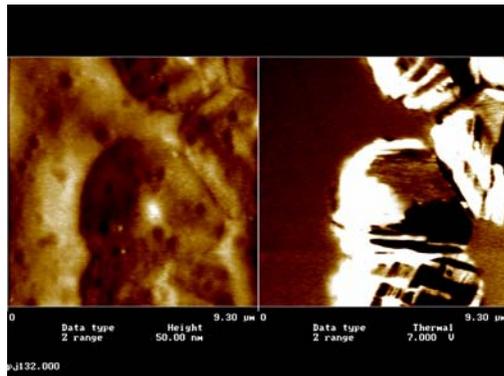


Figure 2: ii) 6v Deflection set

The images on the left of figure 2 are conventional AFM images (height) and the images on the right are PFM data.

The initial scans for the contaminated samples, Figure 1, gave an improved contrast as the tip force increased. However, the improvement with tip force reached a point of saturation beyond which no further improvements were observed. In addition, on reducing the tip force the contrast did not diminish but stayed much the same. The initial improvement in image quality was therefore due to the thick contamination layer being scrubbed from the sample surface by the scanning tip. This either allowed the tips electrical field to make better contact to the ferroelectric material and/or allowed an enhanced mechanical coupling between tip and surface (resulting in a better measurement

of resultant piezo-strain). Both improvements would result in a clearer higher contrast PFM image.

The processing of the ferroelectric thin films is known to leave a residue of a surface contamination layer of lead oxide and lead hydroxy-carbonate on all the samples. When manufacturing the thin films by the sol-gel it is normal to add excess lead to the mixture in order to guarantee that there are enough lead atoms to fill the perovskite structure (loss of volatile lead is a known challenge affecting processing of lead based perovskites). The top surface of the lead oxide film will eventually react with carbon dioxide to form a thin layer of lead carbonate, which, when exposed to water, will also form lead hydroxy-carbonate. Thermodynamic analysis carried out using NPL's MTDATA (x) software shows that only trace amounts (10^{-8} atm) of CO_2 are required for the formation of lead carbonate.

4 DISCUSSION

The lead oxide/carbonate contaminant layers are masking the piezoresponse of the thin films. The masking effect could be either electrical and/or mechanical.

Mechanically, the layer of lead carbonate can be thought of as a hard crust on top of a softer layer of lead oxide. This layer would act as a buffer allowing only a certain amount of coupling between the PFM tip and the piezoresponse of the film, reducing the effective contrast of the images obtained. The initial improvement in scan quality would be due to the PFM tip scrubbing the layers of organic contamination from the top of the lead carbonate layer. The tip would stop scrubbing at the lead carbonate layer and this would mean that the contrast obtained from scans would be the same no matter what tip pressure was applied. This theory is supported by Figure 2 showing the samples after cleaning, removing the organic and loose material from the top surface of the lead carbonate film, the images have the same contrast from the first soft scan to last hard scan.

Electrically, both the inhomogeneous E-field due to the PFM scanning tip and the dielectric properties of the lead oxide / lead carbonate layers would influence the observed piezoresponse during PFM. It has been observed that due to the shape of the PFM tip the E-field would be inhomogeneous and that the greatest flux density would be within the first few nanometres of the film [6],[15]. The thickness of the contamination layer would therefore dictate what strength of E-field the ferroelectric film would experience. If the contamination is thick then the ferroelectric will experience a greatly reduced E-field compared to that of one with a very thin contamination layer. Finite element models are being set-up to examine the effect of the PFM tips inhomogeneous E-field within

the film. The different dielectric properties of the contamination layers would also add to this variation in E-field.

5 CONCLUSIONS

This work has shown that the condition of the ferroelectric sample surface has a great impact on the quality of image obtained using Piezo Force Microscopy. It was also found that some samples gave a PFM contrast that was tip to surface pressure dependent and others tip pressure independent. By testing various samples of thin film PZT on different substrates of a variety of ages it was shown that age, handling and fabrication methods has an effect on the PFM image quality.

During investigation it was found that samples that had been extensively handled since fabrication showed a distinct layer of contamination on their surfaces. This contamination had the effect of reducing the effective piezoresponse of the thin film possibly due to a masking of the applied E-field from the PFM tip. The contamination was probably organic and inorganic material from sources handled prior to the sample being touched. This layer was easily scrubbed away with the AFM tip operated at a high tip to surface pressure, the resulting PFM image becoming clearer and showing a contrast that became tip pressure independent.

The hypothesis was put forward that the pressure dependency was related to contamination layers that are native to the surfaces of all the samples, namely lead oxide and lead carbonate, not the contamination due to handling. It is thought that the contrast or effective measured piezoresponse is influenced by the degree of electrical and mechanical coupling that exists between the PFM tip and the sample surface. Future work is aimed at exploring this pressure dependence of PFM measurements on ferroelectric thin films.

REFERENCES

- [1] O.Kolosov et al., "Nanoscale Visualisation and control of ferroelectric domains by atomic force microscopy", *Physical Review letters*, Vol.74, No. 21, May 1995.
- [2] A.Gruverman, "Domain structure and polarisation reversal in ferroelectrics studied by atomic force microscopy", *Journal of Vacuum Science and Technology*, B13, Issue 3, 1995.
- [3] S.V.Kalinin et al., "Temperature dependence of polarisation and charge dynamics on the BaTiO₃ (100) surface by scanning probe microscopy", *Applied Physics Letters*, Vol 78. No.8. Feb 2001.
- [4] A.Gruverman et al., "Nanoscale imaging of domain dynamics and retention in ferroelectric thin films", *Applied Physical Letters*, 71(24), Pgs 3492-3494, Dec 1997.
- [5] A.L.Kholkin et al., "Electromechanical properties of lead based ferroelectric thin films", *Proceedings of the Materials Research Society Symposium*, Vol. 541. Pgs 623-628, 1999.
- [6] B.J.Rodriguez et al., "Piezoresponse force microscopy for piezoelectric measurements of III-nitride materials", *Journal of crystal growth*, Vol 246, pgs 252-258, 2002.
- [7] A.L.Kholkin et al, "Seeding effect on micro- and domain structures of sol-gel derived PZT thin film", *Materials Letters*. Vol. 50, pgs 219-224, 2001
- [8] C.Durkan et al., "Investigation into local ferroelectric properties by atomic force microscopy", *Ultramicroscopy* Vol. 82, pgs 141 – 148, 2000.
- [9] S.Hong et al., "High resolution study of domain nucleation and growth during polarisation switching in Pb(Zr,Ti)O₃ ferroelectric thin film capacitors", *Journal of Applied Physics*. Vol. 86, No. 1. July 1999.
- [10] S.Dunn et al., "Substrate effect on domain structures of PZT 30/70 sol-gel films via PiezoAFM", *Journal of European Ceramic Society* Vol. 22, pgs 825-833, 2002.
- [11] P.Lehnen et al., "Ferroelectric domain structures of PbTiO₃ studied by scanning force microscopy", *Journal of Applied Physics*, Vol 33, pgs 1932-1936, 2000.
- [12] Dsheng Fu et al., "Local Piezoelectric response in Bismuth-Base Ferroelectric thin films investigated by scanning force microscopy", *Japanese Journal of Applied Physics*, Vol. 41, pgs 1103-1105, 2002.
- [13] S.S.Roy 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*, Vol.29, pgs 189-213, 2000.
- [14] Q.Zhang et al., "Sol-gel PZT and Mn-doped PZT thin films for Pyroelectric applications", *Journal of Physics D: Applied Physics* (0022-3727), Vol. 34, No. 15, pgs. 2296-2307, 2001
- [15] M.Abplanalp et al., "Imaging of Ferroelectric domains with sub micrometer resolution by scanning force microscopy", *ISAF 98. Proceedings of the Eleventh IEEE International Symposium on applications of ferroelectrics*, pgs 423 –426 Aug 1998