

Quantification of Properties of Ferroelectric Thin Film Using Piezoresponse Force Microscopy

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ABSTRACT

Piezoresponse force microscopy has been employed to monitor the effects of surface contamination and tip-sample contact on the piezoelectric coefficients of PZT thin films. Calibration has been achieved through the use of an interferometer, offering sub-picometer resolution. Surface contamination leads to the piezoelectric properties being reduced by an order of magnitude. Cleaning can remove the surface contamination leading to a restoration of the piezoelectric properties. In addition, modelling of the tip-sample interaction has been performed using finite difference methods. Incorporating non-ferroelectric layers between tip and sample leads to large variations in the electric field across the ferroelectric film. The use of such models provides a better understanding of the tip-sample interactions, allowing for more robust measurements of piezoelectric properties using PFM.

Keywords: piezoresponse force microscopy, lead zirconate titanate, ferroelectric, thin films, characterisation

1 INTRODUCTION

Ferroelectric thin films represent an important class of materials for use in applications such as non-volatile memories [1] and micro-electro-mechanical (MEMS) devices [2]. At these reduced dimensions, device performance may be reduced due to effects such as residual stresses during the growth process [3], although island patterning can reduce clamping [4]. Such factors may result in a degradation of the piezoelectric coefficients, namely d_{33} and d_{31} , or changes to the remnant polarisation and coercive voltage of the ferroelectric material. In order to monitor these effects, experimental techniques are necessary which can offer nanometer resolution and below. Piezoresponse force microscopy (PFM) has been developed as a variation of the atomic force microscopy [5], which can provide both quantitative and qualitative information. Ferroelectric domains can be observed with a resolution below 10 nm [6], whilst on application of a known voltage, sample motion can be detected down in the picometer range. Despite the range of work performed using PFM, quantification is still limited due to a lack of complete understanding of the tip-sample contact. Various theoretical work has been performed to address this [7,8]. However, as

most PFM work is performed under ambient conditions, a surface contaminant layer must be accounted for. Previous work has speculated the presence of atmospheric oxide and carbonate layers at PZT surfaces [9]. Thermodynamic analysis using MTDATA software from NPL show that lead carbonate may form in the presence of trace amounts of carbon dioxide [10]. In this work, a quantitative PFM study has been performed to provide a better understanding of the tip-sample interactions. In order to provide a comparison with PFM experiments, finite difference (FD) modelling has been performed. In addition, results have been compared with a compact differential interferometer system, designed at NPL, which offers sub-picometer resolution through the use of lock-in techniques.

2 EXPERIMENTAL PROCEDURE

PFM experiments were performed using a modified Dimension 3000 AFM. Two tip types were used in this work. For quantitative work, Pt-coated and Pt/Ir-coated Si tips ($f_0 \sim 75$ kHz, $k \sim 3$ N/m) were employed, whilst for domain imaging, softer Pt/Ir-coated Si tips ($f_0 \sim 13$ kHz, $k \sim 0.1$ N/m) were utilised to reduce the possibility of damage to the thin films. Imaging was achieved using a frequency close to the resonant tip frequency and a sinusoidal voltage (1 V amplitude). Quantitative measurements were obtained at a tip frequency of approximately 20 kHz, well below the resonant frequency. Measurements were obtained using two methods, either by applying the voltage directly to the tip (PFM mode) or to a top electrode (AFM mode). In each case, the bottom electrode was grounded.

The NPL interferometer, shown in figure 1, was used for calibrating PFM measurements. The system makes use of common path optics to direct a measuring and reference laser beam onto the sample under investigation. A differential set up is utilised to remove errors due to sample bending or external vibrations. Through the use of lock-in techniques, a voltage is applied to the sample, giving rise to displacements that may be measured with sub-picometer accuracy. In order to model the tip-surface interactions, finite difference modelling was employed. A 2-D static model was employed, with the AFM tip represented by a trapezium with semi-circular apex held at a voltage of 1 V. The bottom edge of the PZT film was clamped and fixed at 0 V. Successive overrelaxation (SOR) and conjugate gradient (CG) solutions were utilised in the modelling.

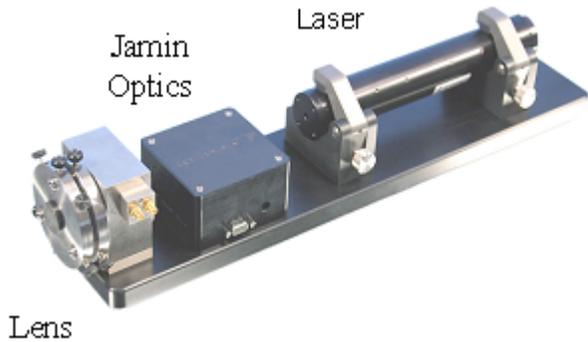


Figure 1: A photograph of one arm of the NPL interferometer, showing the major features.

3 EXPERIMENTAL RESULTS

In order to provide calibration for the PFM, d_{33} was determined for a bulk quartz sample, which should yield a value of 2.3 pm/V [11]. In addition, this was compared with that obtained by the interferometer. Figure 2, shows the results of the calibration process. Using the interferometer yielded a value for d_{33} of 2.07 pm/V, whilst PFM gave 2.06 pm/V. Both of these numbers agree with each other but fall below the expected value by approximately 10 %. This is believed to be due to the sample mounting in each case, with sample motion reduced by the holding adhesive.

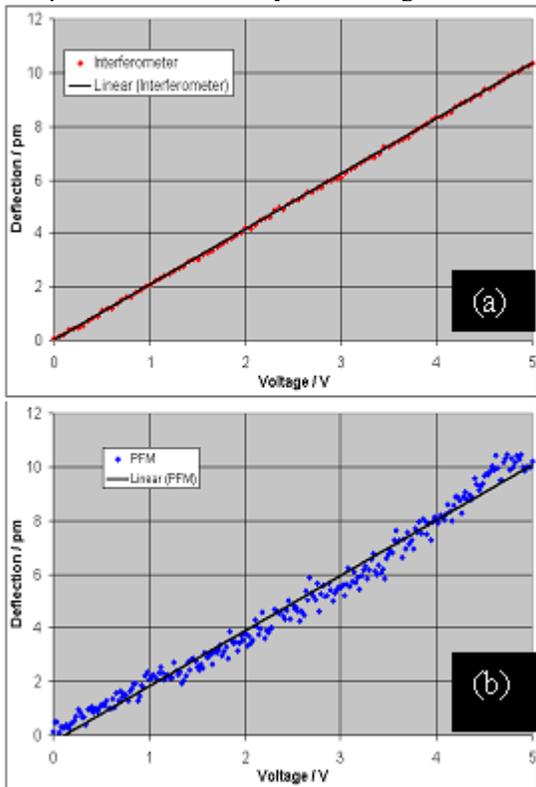


Figure 2: Plots of deflection against voltage for a quartz calibration sample using (a) NPL interferometer; and (b) PFM.

On performing the calibration procedure, results were then obtained from a variety of PZT samples. An early test was to measure d_{33} from a bulk PZT cubed sample using PFM and compare with the value found using the interferometer. For these measurements, the top surface of the PZT cube was electroded, but the experiment was performed in PFM mode. Results, not shown here, indicate good linearity and agreement between the two measurement techniques. Interferometry yielded a value of 263 pm/V, whilst in PFM mode, a value of 259 pm/V was achieved. The slight discrepancy in these results may be put down to the use of a reflector on the top electrode surface of the cube to enhance the laser signal.

Despite the good agreement shown between the two experimental techniques when using bulk samples, when attention was turned to thin films, discrepancies arose which could be explained by poor tip-sample contact and the presence of a non-ferroelectric surface layer. Initial studies were performed on a 500 nm PZT(30/70) thin film. On application of an increasing ac voltage to the film, a value for d_{zz} of 19.0 pm/V was measured. However, when measurements were attempted using PFM, d_{zz} was much smaller than expected. Figure 3 shows a frequency sweep against deflection when measurements were attempted in both AFM and PFM mode. In AFM mode, the deflection corresponds to a value for d_{zz} of approximately 22 pm/V, whereas in PFM mode, the value was reduced to below 5 pm/V. It should be noted that these experiments were recorded from the same region of the sample.

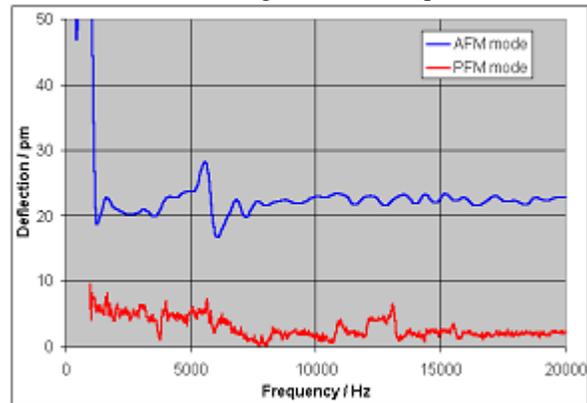


Figure 3: Plots of deflection against frequency for a 500 nm PZT(30/70) thin film when an ac voltage of 1V is applied to the film in (a) AFM mode; and (b) PFM mode.

Measurements were also obtained from two samples of similar thickness. A 210 nm PZT(30/70) film grown on an ITO/glass substrate (sample P1) gave a value for d_{zz} of 34.9 pm/V, whereas for a 200 nm PZT(30/70) film grown on a Ti/Pt/SiO₂/Si substrate (sample P2), d_{zz} was as low as 2 pm/V. This difference also shows up in PFM domain images from the two samples. Figure 4 shows PFM images from a 1×1 μm² area of each sample. Both images are shown with the same piezoresponse scales. It is apparent that the image from sample P1 yielded greater contrast,

with features as small as 15 nm being resolved. Sample P2 shows a larger minimum feature size, ascribed to the different grain size, but the image contrast is reduced due to the presence of a low permittivity surface layer producing reduced signal to noise levels.

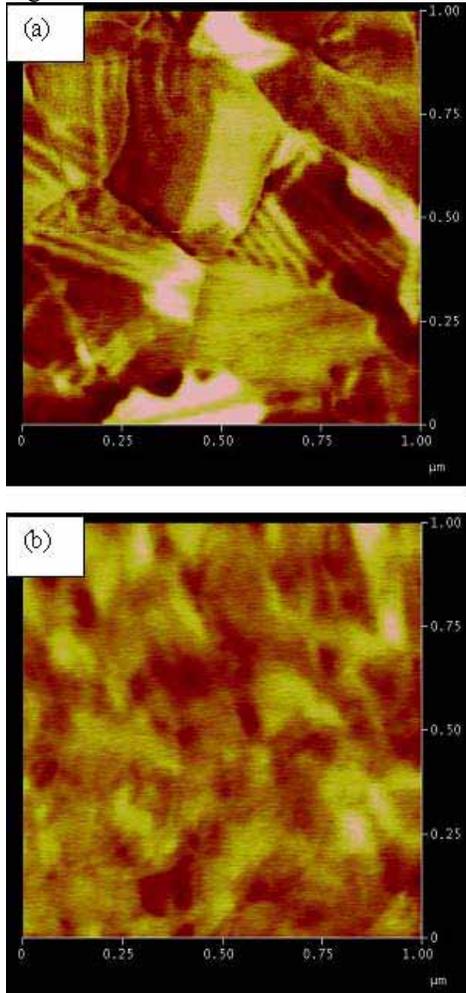


Figure 4: PFM domain images from $1 \times 1 \mu\text{m}^2$ areas of (a) sample P1; and (b) sample P2. In each case, the piezoresponse scale is the same to provide a comparison of the contrast.

To test the hypothesis of a contamination layer at the surface, attempts were made to clean the PZT thin film surfaces. For this work, a 400 nm thick PZT(30/70) film was selected. The PZT film was cleaned in a plasma barrel etcher using $\text{CF}_4 + 5\% \text{O}_2$ as the etchant. The sample film temperature was approximately 100°C during etching, with no post clean annealing being performed. Figure 5 shows deflection vs frequency plots for the sample before and after etching. It is clear that the cleaning process removes some surface contamination, although the value for d_{zz} of 14.3 pm/V is lower than would be expected for these thin films. It is believed that either some surface recontamination occurred after the cleaning process, or some contamination was unable to be removed. Further

work involving X-ray photoelectron spectroscopy is planned to resolve some of these cleaning issues.

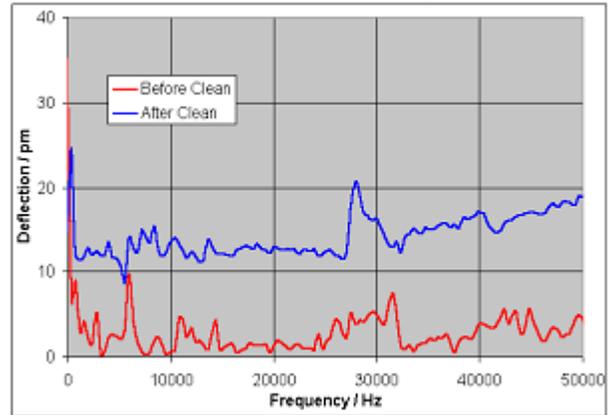


Figure 5: Plots of deflection against frequency for a 400nm thick PZT(30/70) film before and after cleaning. IT is clear that cleaning has a beneficial effect on the piezoelectric response.

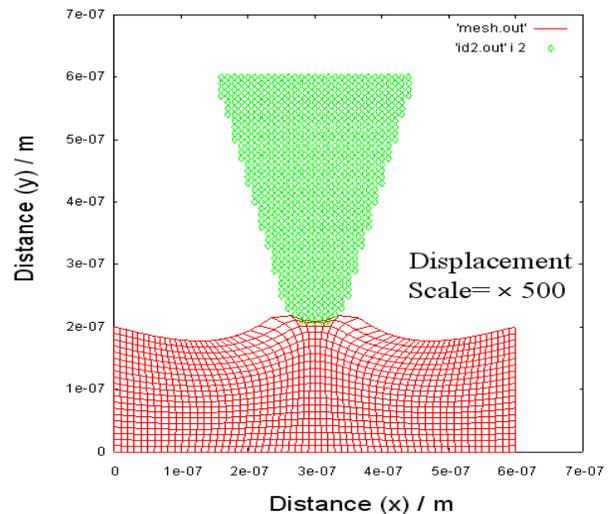


Figure 6: Result from the FD modelling, showing the film displacement from a 200 nm thick single domain PZT film. Displacements are magnified by a factor of 500 for clarity.

To investigate the tip sample interactions occurring during PFM, FD modelling was performed. The properties of the PZT layer were assumed to be as for a PZT-5H bulk sample [12]. Figure 6 shows the results of calculations on a 200 nm thick single domain PZT film when a voltage of 1V is applied to the conducting tip. The tip height of approximately 400 nm is much smaller than that used in experiments, but it is expected that this yields errors less than 5% in the film displacement. In figure 6, the film displacement, magnified by a factor of 500, is found to be approximately 50 pm. The difference between experiment and theory is put down in part to the different piezoelectric properties of the experimental system, compared to the ideal bulk PZT properties used in the FD model.

The case of a single domain can be unrealistic when studying thin films experimentally. In this way, calculations were obtained for the more realistic cases of a multi-domain PZT thin film (100 nm thick) with and without a 20 nm non-ferroelectric dead layer, exhibiting a permittivity of 80 and a stiffness equal to PZT. In both cases, domains of width 100 nm were used, exhibiting periodic up and down polarisations. Figure 7 shows the displacement plots for each sample geometry. Again for the multi-domain film with no dead layer, the film displacement is approximately 50 pm. However, when the dead layer is incorporated, the displacement was reduced by approximately an order of magnitude, which agrees with the experimental findings from the 400 nm thick PZT(30/70) film.

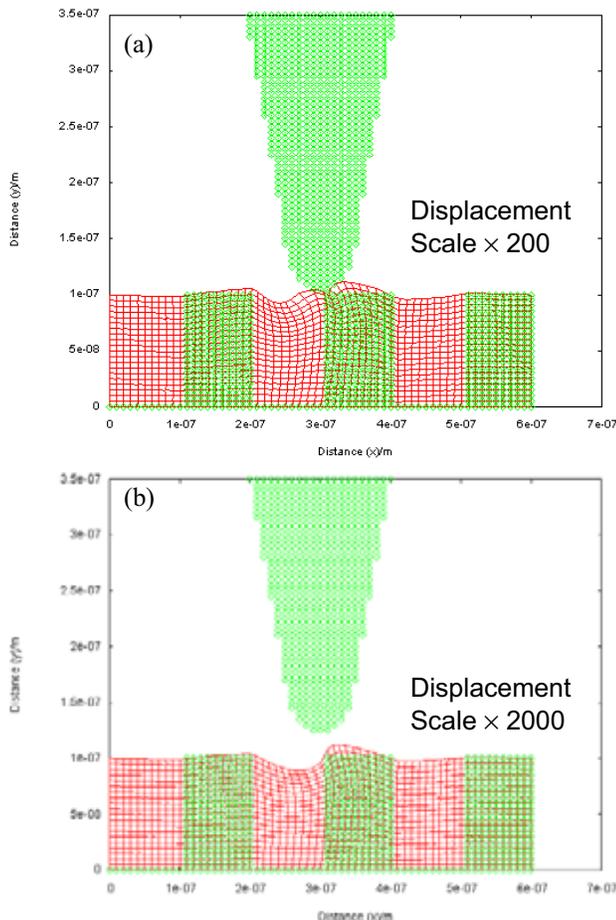


Figure 7: Result from the FD modelling, showing the film displacement from a 100 nm thick multi domain PZT film (a) without; and (b) with a non-ferroelectric dead layer. Displacements are magnified for clarity. Green symbols show undisplaced locations of $-y$ oriented PZT domains.

The presence of the dead layer at the surface leads to a drop in the electric field across the ferroelectric thin film by an order of magnitude. This produces an effect which is similar to that found if an air gap exists between the tip and sample, but the magnitudes of the separations differ due to the difference in permittivity of the two insulating layers. A similar effect has also been found for BaTiO₃ using Green's

functions and incorporating a variable thickness water layer [7]. At present further experimental work is necessary to characterize the chemical state of the PZT surface, although some work is now becoming available [13].

4 CONCLUSIONS

PFM studies have been conducted on various PZT sample and compared with an interferometer system which offers traceable calibration. It is shown that for good tip-sample contact, results obtained using PFM agree with those from the interferometer. However, good tip-sample contact is essential for quantitative PFM. Cleaning the thin films can remove some contaminants and yield piezoelectric properties that agree with expectations. Finite difference modelling shows that the presence of a non-ferroelectric dead layer can result in the voltage dropped across the thin film being reduced, leading to reduced piezoelectric properties. It is therefore essential that ferroelectric surfaces are free from contamination to enable accurate determination of the piezoelectric coefficients of such materials.

REFERENCES

- 1 O. Auciello, J. F. Scott and R. Ramesh, *Phys. Today* **51**, 22 – 27, 1998.
- 2 P. Murali, *J. Micromech. Microeng.* **10**, 136 – 146, 2000.
- 3 T. M. Shaw, Z. Suo, M. Huang, E. Liniger, R. B. Laibowitz and J. D. Baniecki, *Appl. Phys. Lett.* **75**, 2129 – 2131, 1999.
- 4 V. Nagarajan, A. Roytburd, A. Sanishevsky, S. Prasertchoung, T. Zhao, L. Chen, J. Melngailis, O. Auciello and R. Ramesh, *Nature Materials* **2**, 43 – 47, 2003.
- 5 A. Gruverman, O. Auciello and H. Tokumoto, *Annu. Rev. Mater. Sci.* **28**, 101 – 123, 1998.
- 6 S. Dunn, C. P. Shaw, Z. Huang and R. W. Whatmore, *Nanotechnology* **13**, 456 – 459, 2002.
- 7 F. Felten, G. A. Scheider, J. Munoz Saldana and S. V. Kalinin, *J. Appl. Phys.* **96** 563 – 568, 2004.
- 8 S. V. Kalinin and D. A. Bonnell, *Phys. Rev. B* **65** 125408-1 – 125408-11, 2002.
- 9 M. G. Cain, S. Dunn and P. Jones, *Technical Proceedings of the 2004 Nanotechnology Conference and Trade Show*, Volume **3**, 362 – 365, 2004.
- 10 Analysis using MTDATA: software copywrite NPL.
- 11 V. E. Bottom, *J. Appl. Phys.* **41**, 3941 – 3944, 1970.
- 12 Vernitron Bulletin, "Five Modern Piezoelectric Ceramics", Bulletin 66011/F, Jan 1976.
- 13 F. Peter, K. Szot, R. Waser, B. Reichenberg, S. Tiedke and J. Szade, *Appl. Phys. Lett.* **85**, 2896 – 2898, 2004.