Crystallographic mapping of ferroelectric thin films using piezoresponse force microscopy and electron backscatter diffraction

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Abstract. Ferroelectric lead zirconate titanate (PZT) thin films have been analysed using electron backscatter diffraction (EBSD). Grain orientation mapping has been demonstrated, showing that features smaller than 100 nm may be successfully indexed. In conjunction with piezoresponse force microscopy (PFM), which was used to map and quantify the piezoelectric response from the same region of the films with a resolution of 10 nm, an analysis of the effects of grain orientation on the measured response at the nanoscale was possible. The microtexture of the film showed the presence of both mono- and multi-domains within grains exhibiting sizes of hundreds of nanometres.

1. Introduction
Ferroelectric materials have been widely used in bulk form as sensors and actuators, but are currently offering possibilities in thin film form for a variety of applications including functional MEMS devices and memory applications (FeRAM) [1,2]. As potential applications tend towards smaller sizes, there is a need for precise characterisation at these nanometre scales. Measurements of the piezoelectric properties can be achieved by using piezoresponse force microscopy (PFM) [3,4]. This technique can qualitatively yield domain orientation, as well as providing a quantitative analysis of the piezoelectric (vertical and lateral) response with a resolution of 10 nm or smaller, but is limited in its ability to divulge grain orientation information. One technique that may be used to obtain such information is electron backscatter diffraction (EBSD) [5]. Both grain orientation and ferroelectric domain structure can be quantitatively analysed. With a resolution as small as 20 nm, EBSD offers a viable technique for studying ferroelectric films, which may have grain sizes smaller than 100 nm. Used in conjunction with PFM from the same region, a quantified map of the piezoelectric response of ferroelectric thin films may be acquired.

In this work, EBSD and PFM have been used to characterise PZT(30/70) thin films, in order to relate the piezoelectric response to the grain orientation at the nanometre scale. Results indicate that both techniques are able to resolve grain structure with feature sizes of 100 nm and smaller.

2. Experimental Details
Experiments were performed on PZT thin films. PZT(30/70) thin films (Cranfield University) were produced by sol gel deposition onto a glass substrate with a thin ITO layer serving as a bottom electrode [6]. The PZT film thickness was 210 nm.
PFM experiments were performed using a Veeco Dimension 3000 AFM. Images were acquired using Pt/Ir coated silicon tips (Nanosensors PPP-EFM: $f_0 \sim 75$ kHz, $k \sim 2$ N/m) excited at a frequency of 10 kHz. Vertical and lateral piezoresponse images were acquired by using a lock-in amplifier (Stanford Research Systems SR830) to monitor the tip deflection and torsion signals respectively. The piezoresponse was quantified by using a quartz sample as a reference, and by checking the response against a differential interferometer developed in-house, with sub-picometre resolution [7]. The bias was applied to the bottom electrode, keeping the tip grounded, in order to reduce effects arising from cantilever resonances and electrostatic effects [4].

EBSD experiments were performed in a Zeiss Supra-40 field emission SEM, with a working distance of approximately 8 mm and the sample angled at 70° with respect to the electron beam. The EBSD detector (consisting of a phosphor screen and forescatter electron detector) was ~ 10 mm from the sample. Crystallographic mapping of a sample area was carried out via a raster scan of the electron beam. Depending on the step size and total area analysed, scan times ranged from tens of minutes to several hours. Indexing of the Kikuchi bands was performed automatically using the HKL computer software. In order to negate the effects of charging, a thin carbon layer was deposited onto the surface.

3. Results

Application of a 1V$_{RMS}$ ac signal to the bottom electrode of the PZT/ITO film resulted in the observation of domain contrast images (phase) or quantified piezoresponse images (magnitude) in conjunction with the topography image. Example images from a $2 \times 2 \mu m^2$ area are shown in figure 1, showing the topography, vertical piezoresponse and lateral piezoresponse. The topography image (left) showed the presence of PZT perovskite grains with lateral dimensions of the order of hundreds of nanometres (typically 200 – 400 nm). Under these growth conditions, no appreciable pyrochlore phase is expected to be present [8]. The film showed appreciable roughness, with height variations in excess of 20 nm. The vertical and lateral piezoresponse images (centre and right, respectively) showed bright regions, separated by narrow darker regions, indicating high and low piezoresponse activity respectively. The regions of low piezoactivity corresponded to both intergranular and intragranular boundaries, indicating the presence of both mono- and multi-domains across the surface. The measured features were as small as 10 nm, approaching the resolution limits of PFM in air [9,10]. A further reduction in measured feature sizes, which could aid probing the activity around domain walls, would be expected from measurements in liquid [11].

![Figure 1. AFM images from a $2 \times 2 \mu m^2$ region of the PZT sample, showing the (a) topography, (b) vertical PFM signal, and (c) lateral PFM signal. The colour scale for the lateral PFM image is twice that of the vertical PFM image.](image)

In order to determine the location of the region of the sample studied with PZT, a border approximately $5 \mu m \times 5 \mu m$ was scratched into the PZT surface using a nanoindentation probe (Veeco PDNISP, $k \sim 200$ N/m). It should be noted at this stage that the scratch did not penetrate completely through the PZT film, and no significant difference was observed in the average piezoresponse measured using PFM between the region inside the scratch and at a position well away from the defect. An SEM image of the scratched region is shown in figure 2 (a). From comparison with the topography image in figure 1, the location previously studied could be found and investigated further.
using EBSD. The SEM image again showed appreciable surface roughness as observed in the AFM topography image. The scratch boundary exhibited some film build up. The image of the surface showed an indication of multi-domains within each grain, but the contrast was less than for bulk samples, imaged in previous work. This may be ascribed to a lower contrast between the different grain orientations due to a smaller tetragonal splitting, as well as the smaller scale of these features.

Figure 2: (a) SEM image from the PZT surface, showing the region examined using PFM (marked by dotted line). (b) Typical Kikuchi bands from one point of the PZT surface.

An example of the quality of the Kikuchi bands obtained from the PZT film is shown in figure 2(b). The band contrast is relatively weak, due to the presence of the carbon layer to negate any sample charging and subsequent drift. Many bands were required for analysis in order to minimise any mis-indexing from examining the tetragonal film structure with c/a ~ 1. For mapping an area across a surface, this resulted in long scan times. An orientation contrast map including the region imaged using PFM is shown in figure 3. The image has been corrected for the small drift during acquisition. The orientation contrast map shows the microtexture using a grey scale based on one of the three Euler angles, used to describe the crystallographic orientation at a point. More details on orientation contrast maps may be found elsewhere [12]. In this work, the Euler angle, $\phi$, was used, which represents an anticlockwise rotation about the x-axis of the system. Despite indexing many bands, it was still not possible to achieved 100% indexing – regions not indexed are shown as white in the image. For this image, a 20 nm step size was used. Features smaller than 100 nm can be observed in figure 3. Some grains show regions of differing greyscale, indicating multi-domains, as also observed with PFM.

Figure 3: 3 × 2 $\mu$m$^2$ orientation contrast map, showing the grain orientations as a function of Euler angle, $\phi$. Differing shades of grey represent varying domain orientation.

In order to quantify the microtexture within the scanned area, the data is plotted in figure 4 as pole figure plots. In this figure the data points with either (100)-, (110)-, (111)- or (001)-orientation are plotted as a stereographic image against the Cartesian axes describing the sample. The x- and y-axes represent in-plane orthogonal directions, with the z-axis aligned along the sample normal direction. The pole figures clearly show that there is no texture within the scanned area. This differs from that observed for PZT deposited on a conventional Pt/Ti/SiO$_2$/Si substrate, where a predominantly (111)- or (001)-oriented film can be grown depending on factors such as annealing time and temperature. However, this random orientation is expected for PZT deposited onto an ITO/glass substrate [6,8].
4. Conclusions
The microtexture of a PZT thin film has been successfully characterised using PFM and EBSD from the same region. Both techniques are able to gather information with a resolution approaching 10 nm. PFM shows the appearance of multi-domains, with features resolved to 10 nm. EBSD has been used to determine the grain orientation, with the piezoresponse being related to the polar axis. Features smaller than 100 nm could be observed using EBSD. Further work will involve prediction of the vertical and lateral piezoresponse measured using PFM from the EBSD data.

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