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## CONTRIBUTED PAPERS

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# MICRODIFFRACTION USED TO STUDY DOMAIN SWITCHING OF FERROELECTRIC THIN FILMS\*

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Since the advent of the microdiffractometer a new world of analysis possibilities have opened. In this paper we will discuss a novel use of the Rigaku microdiffractometer (MDG).  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) thin films are being developed for use in optical and electronic memory devices. These types of memories utilize the movement of beta site atoms in the perovskite structure to accomplish ferroelectric switching. To study ferroelectric switching behavior, we have produced relatively untextured PZT thin films on Si substrates. We have developed a method for using x-ray diffraction to observe domain switching *in situ*. Our study involved the use of a Rigaku MDG to monitor the switching behavior in relatively small (0.7 mm diameter) electroded areas on the surface of the thin films. Diffraction analyses were done while DC voltages were applied and removed, representing several places in the ferroelectric hysteresis loop. In particular, we were looking for relative intensity changes in the  $[h00]$ ,  $[00l]$  diffraction peaks as a function of position in the hysteresis loop. Our study shows that the type of switching behavior exhibited by ferroelectric films produced through various processing conditions can be monitored using the MDG.

## Introduction

Ferroelectric thin films are being developed for the next generation of electronic devices, in particular nonvolatile RAM, optical memories, and micro-switches. Domain formation and therefore switching behavior is influenced by processing conditions, especially the stresses which occur as the material is cooled through the Curie point [1, 2]. Understanding which processing conditions influence switching behavior is of paramount concern because  $90^\circ$  domain switching is needed to obtain the field induced change in birefringence required for optoelectronic devices. Recent theories postulate that  $90^\circ$  domain formation and, therefore,  $90^\circ$  domain switching is severely limited in films when the grain size is less than about  $1\ \mu\text{m}$  [2]. To study this behavior we investigated the  $90^\circ$  switching behavior of several films deposited on Si.

To study switching in thin film we developed a method for using micro x-ray diffraction ( $\mu\text{XRD}$ )

techniques to observe domain switching *in situ*.  $\mu\text{XRD}$  is a nontraditional x-ray diffraction technique which has recently attracted much attention [3]. The MDG is capable of obtaining a diffraction pattern from  $0$ - $150^\circ$   $2\theta$  simultaneously from regions as small as  $30\ \mu\text{m}$  in diameter. The purpose of this study was to determine if ferroelectric switching of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) thin films can be observed using micro-diffraction. This method will be extremely valuable as we target the necessary processing parameters to achieve the desired switching behaviors and to monitor switching in micron-sized devices.

We have previously shown that processing conditions influence grain size and therefore domain formation [2]. Also the stresses that develop during cooling through the curie point greatly effects how the crystallites are oriented along their  $[h00]$  and  $[00l]$  crystallographic directions normal to the plane of the film [1]. For example, if the in-plane stress is compressive during cooling through Curie point then the  $[00l]$  orientations will tend to develop normal to the plane of the film. This occurs because the slightly smaller  $a$ -axis will more easily develop in the plane of the film. It also has been shown that  $90^\circ$  domain

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formation does not readily occur in films with grain sizes less than about 1  $\mu\text{m}$  [4, 5]. If 90° domain formation does not occur, despite the strong elastic forces generated by transformation strain, then 90° switching may be severely limited. Therefore, we postulate that 90° domain switching should be diminished in films where the grain size is smaller than one or two microns and that we should be able to monitor this behavior using the MDG.

### Experimental Process

For most of our films we used  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT) with an underlying substrate consisting of a 2500 Å electrode, a 500 Å Ti adhesion layer, and  $\text{SiO}_2$  on a Si substrate. Platinum electrodes were highly (111) oriented normal to the surface of the film. Two samples analyzed were fabricated using  $\text{RuO}_2$  electrodes. All films were fabricated using a modification [6] of the hybrid solution deposition procedure developed by Yi, Wu and Sayer. 0.4 M solutions were synthesized using an inverted mixing order process [7] for which the Zr and Ti alkoxides were blended prior to the addition of the Pb precursor. Excess Pb (5 mol%) was added to enhance perovskite formation and to improve electrical properties. The films were deposited by spin coating at 3000 rpm for 30 s. After deposition the film was heated at 300°C for 5 min. Crystallization was done at either 550° or 650°C for 30 min in air. A heating rate of 50°C/min was used. The resulting PZT was tetragonal with 4 mm symmetry. The  $c/a$  ratio ranged from about 1.02 to 1.04 for the 40/60 and 30/70 PZT films respectively. Remanent polarization values for these films were typically about 20  $\mu\text{C}/\text{cm}^2$ . These PZT films with Si substrates were in tension as they were cooled through the Curie point. Therefore though the overall film texture is relatively random, of the ( $h00$ ,  $00l$ ) types only the ( $h00$ ) planes should be normal to the sample surface. In this case a standard x-

ray diffraction scan would show a nearly random diffraction pattern, but with increased intensity of [ $h00$ ] type diffraction peaks over [ $00l$ ] types. If [ $00l$ ] are observed they could be attributed to 90° domain formation [3]. Several different films were analyzed, Table 1 shows a list of all samples discussed. All samples were analyzed using a standard diffractometer prior to analysis with the MDG.

Top Pt electrodes of 0.7 mm diameter were deposited on the PZT thin films for our measurements. We attached leads to the top and bottom electrodes by silver conductive epoxy. One mil by three mil gold foil was used as an electrical lead wire. The epoxy was cured at 160°C.

Our microdiffractometer is a Rigaku MDG on a 12 kW rotating anode with a copper target. The detector used was a 150° position sensitive proportional counter. We used total reflection capillaries to reduce the incident beam to about 100  $\mu\text{m}$ . Total reflection capillaries have about an order of magnitude less attenuation than do straight pin-hole collimators [8, 9].

DC voltages were applied to the electrodes to put the ferroelectric thin film into different polarization, electric field states. For each thin film we applied a positive and negative DC voltage to represent each of the following conditions: a non switched state; a partial switched state; and at saturation. The voltages were adjusted for each sample's particular electrical characteristics. The DC voltages were applied for an average of five minutes for each point. These times are considerably longer than the micro-second times normally used to switch PZT films. At each applied voltage, diffraction scans were made with the incident beam collimated to produce a spot size of 100  $\mu\text{m}$ . The procedure was repeated at least three times for each sample to ensure reproducibility.

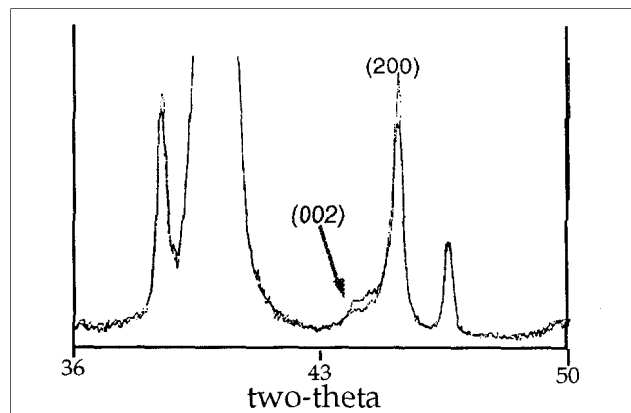
Table 1.

Sample #	Zr/Ti	Processing temp. (°C)	Film thickness	Grain size	Electrode material	Substrate
1	40/60	650/30 m	0.8 $\mu\text{m}$	0.2 $\mu\text{m}$	Pt	Si
2	30/70	550/30 m	0.4 $\mu\text{m}$	0.5 $\mu\text{m}$	$\text{RuO}_2$	Si
3	30/70	650/30 m	0.4 $\mu\text{m}$	0.4 $\mu\text{m}$	$\text{RuO}_2$	Si
4	30/70	650/30 m	2.0v	0.2 $\mu\text{m}$	Pt	Si
5	30/70	675/30 m	0.3 $\mu\text{m}$	1-2 $\mu\text{m}$	LSCO	$\text{LaAlO}_3$

In an effort to demonstrate that  $90^\circ$  domain switching would increase dramatically when grain size is increased to over a micron we deposited a  $0.3\ \mu\text{m}$  thick 30/70 PZT thin film on an LSCO electroded  $\text{LaAlO}_3$  substrate. The LSCO was deposited using pulsed laser deposition. The top electrodes were Au/Ti and were approximately  $50\ \mu\text{m}$  in diameter. This thin film corresponds to sample 5 in Table 1. For this sample a 30pm total reflection collimator was used. The electroded area was poled just prior to XRD analysis. We observed an unpoled spot and then moved to the electrode where the voltage was applied.

## Discussion

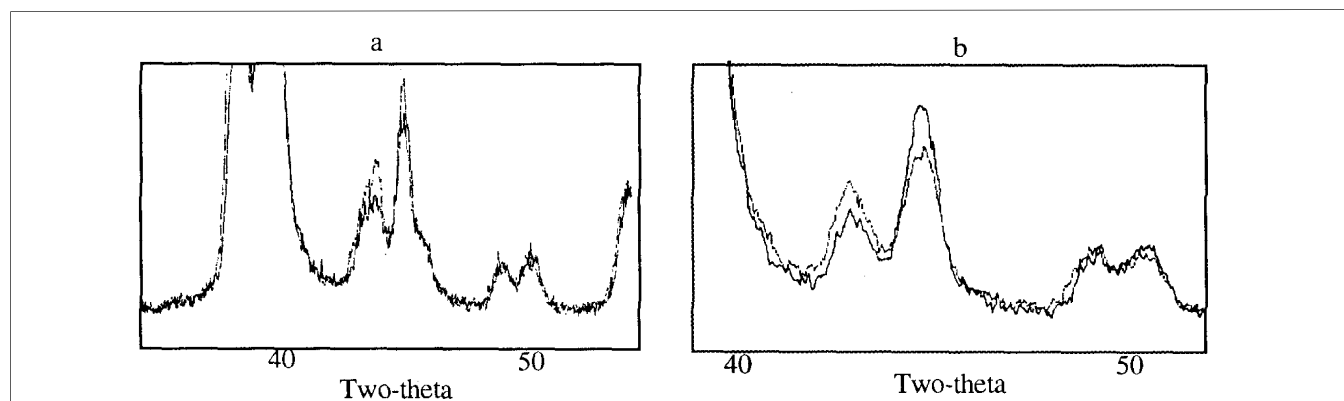
Figure 1 shows the diffraction patterns for sample 1, which is a 40/60 PZT thin film with a relatively fine grain size ( $0.2\ \mu\text{m}$ ). (200) and (002) diffraction peaks are shown. One diffraction pattern is of the unpoled



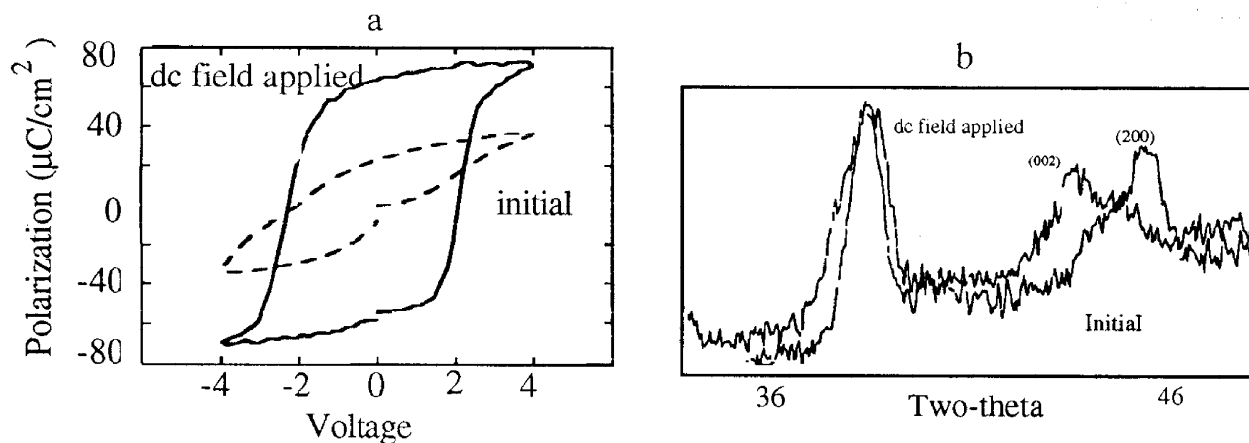
**Fig. 1** Superimposed diffraction patterns of 40/60 PZT taken with a microdiffractometer with no field applied and with a +12V DC field applied. Note the limited intensity of the (002) reflection and the very slight increase when the field is applied.

state and the other is at saturation. Note that very little (002) is present. With a field applied, very limited  $90^\circ$  switching occurs as shown by the slight increase in intensity of the (002) peak coupled with a slight decrease in intensity of the (200) peak. Figures 2a and 2b representing samples 2 and 3 show that with a slightly coarser grain size approaching about  $0.5\ \mu\text{m}$ ,  $90^\circ$  domain formation is increased slightly as evidenced by the slightly larger (002) peak in the unpoled state.  $90^\circ$  domain switching at saturation is increased when compared to the previous fine grained sample, but is still quite limited.

For the thin film deposited on  $\text{LaAlO}_3$ , Field emission scanning electron microscopy indicated that the grain size of this film was between 1 and  $2\ \mu\text{m}$ . Preliminary data on this film indicates that  $90^\circ$  domain switching was quite remarkable. The initial remanent polarization was  $38\ \mu\text{C}/\text{cm}^2$  indicating that the material contained predominantly ( $h00$ ) domains. When a DC field was applied the remanent polarization increased to  $65\text{--}70\ \mu\text{C}/\text{cm}^2$ . This value approaches that for single crystal [2] indicating that domain switching had occurred and the predominant domains were switched to (00l). Figure 3b shows the diffraction pattern for this sample at  $-\text{Pr}$  corresponding to the two hysteresis loops in Fig. 3a. The orientation clearly changes from being predominantly (200) initially to being predominantly (002) after applying the DC bias. Although these diffraction patterns demonstrate that  $90^\circ$  domain switching did occur in this relatively large grained film, *in situ* diffraction studies have been unsuccessful to date due to shorting of the film under bias for extended times.



**Fig. 2** a and b are superimposed diffraction patterns with no field applied and at saturation for two PZT 30/70 thin films with grain sizes approaching  $0.5\ \mu\text{m}$ . Both films have  $\text{RuO}_2$  electrodes. Note that  $90^\circ$  domain formation and switching is slightly increased in these samples when compared to the fine grained sample in Fig. 1, but is still quite limited.



**Fig. 3** 30/70 Pzt on LaAlO<sub>3</sub> with a grain size exceeding 1 μm. The hysteresis loop and diffraction patterns suggest that 90° domain switching has occurred.

## Conclusion

We have shown that we can monitor 90° domain switching *in situ*, using microdiffraction techniques. We can also observe the switched state. Our study clearly shows that for PZT films deposited on silicon substrates, where the grain size is less than about 0.5 μm, 90° domain formation as well as 90° domain switching is severely limited.

Our preliminary results also indicate that 90° domain switching can occur in PZT films deposited on LaAlO<sub>3</sub> when the grain size exceeds 1 μm. We are continuing to develop the microdiffraction techniques to monitor smaller devices.

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