

Domain switching in $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ thin films

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Switching behavior of $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (PZT) thin films, which have various domain configurations, were investigated by comparing their remanent polarization charges evaluated from P - E hysteresis measurements and their domain structures characterized by X-ray diffraction reciprocal space mapping. The domain structures of the PZT films were controlled by changing the orientation of the bottom electrodes. We fabricated films that includes domain that polarization vector laying perpendicular to the applied electric field and that do not include such a domain. The ratios of obtained remanent polarizations were well explained by their domain configurations if we assume that the domain is pinned during electric field cycling. The result of the present study indicates the possibility of strong domain pinning in the thin PZT film.

Key words: Lead zirconate titanate, XRD, remanent polarization, domain, domain switching

1. INTRODUCTION

$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) is a well known material to have a excellent properties in, for example, remanent polarization and piezoelectric response. Due to the reason, this material has a great attention for the application to such as ferroelectric random access memories (FeRAMs)¹ and microelectromechanical systems (MEMS).² However, there exists important problems should be overcome, especially in the devices employing this material in the form of the thin film.

The problem in the FeRAM application is the reduction of remanent polarization in lower temperature ($< 400^\circ\text{C}$) grown film. Lower temperature growth of the PZT film is highly desired to minimize the process damage for

another stacked layer. On the other hand, the problem in the MEMS application is the smaller piezoelectric response than that expected from the bulk PZT crystal. Especially, the latter problem is believed due to the non- 180° domain pinning in the form of the thin film (typically, thinner than a micrometer).

Non- 180° domain switching has been widely studied with various ways. Xu et al.³ and Kholkin⁴ confirmed the 90° domain pinning by nonlinearities of piezoelectric and dielectric constants on an ac driving electric field and Roelofs⁵ showed it by using piezoelectric force microscopy. However, very few papers described the relation between crystal orientation, domain switching and electrical property.

In the present study, we tried to control the domain structure by selecting the orientation of the bottom electrodes and fabricated the films include and do not include the domain oriented perpendicular to the applied electric field direction. And the remanent polarizations obtained from P - E hysteresis measurements were compared to the domain structures characterized by XRD reciprocal space mappings.

2. EXPERIMENTAL

2.1 Thin film growth and electrical characterization

PZT thin films were grown on three differently oriented substrates, namely, (001), (110) and (111) oriented conductive perovskite $SrRuO_3$ (SRO) bottom electrodes grown on $SrTiO_3$ (STO) single crystal substrates by pulsed MOCVD from $Pb(C_{11}H_{19}O_2)$, $Zr(O \cdot t-C_4H_9)_4$, $Ti(O \cdot i-C_3H_7)_4$ and O_2 as starting materials (pseudo-cubic indexes were used for SRO). The deposition temperatures of PZT thin films growths were 620°C and the film thicknesses were 200nm each. Growth conditions for SRO bottom electrodes were reported previously.^{6,7} Film compositions were $Pb/(Zr+Ti+Pb)=0.5$ and $Zr/(Zr+Ti)=0.65$, which were characterized by an X-ray fluorescence spectrometer (Philips PW-2404, Eindhoven, Netherlands). Electrical characterization was carried out using RT-6000 ferroelectric tester by placing platinum top electrode of $100\mu\text{m}$ ϕ .

2.2 Characterization of domain structure using XRD

Domain structures of the PZT films were characterized using a high-resolution X-ray diffraction reciprocal space mapping (HRXRD-RSM, Philips X'Pert-MRD, Eindhoven, Netherlands). Detail description about HRXRD-RSM can be found in our previous reports.^{8,9}

Relative volume fraction of the domain was calculated from the diffraction intensity integrated over a mapped area by HRXRD-RSM with following formula.

$$\text{Volume}\%_{hkl} = \frac{(I_{\text{int},hkl}/|F_{hkl}|^2 \cdot LP_{hkl} \cdot A_{hkl})}{\sum_{hkl} (I_{\text{int},hkl}/|F_{hkl}|^2 \cdot LP_{hkl} \cdot A_{hkl})} \quad (1)$$

, where $I_{\text{int},hkl}$, F_{hkl} , LP_{hkl} and A_{hkl} are integrated intensity, structure factor, Lorentz and polarization factor and absorption factor for hkl diffraction, respectively.

3. RESULTS AND DISCUSSION

Figures 1 (a) to (c) show conventional surface normal θ - 2θ scans for the film grown on (001), (110) and (111) SRO/STO substrates (hereafter, we denote these films as film A, B and C), respectively. It can be seen that the film A and B have orientation of (001) and (110), respectively, and the film C has mixed (111) and $(11\bar{1})$ orientation. To figure out the domain structure three-dimensionally, we applied cross sectional and plan view HRXRD-RSM measurement on these films and the results were presented in Fig. 2 and Fig. 3. Figures 2 (a)-(c) show cross sectional and Fig. 3 (a)-(d) show plan view HRXRD-RSM results of the films A, B and C, respectively. The diffraction spot of PZT 004 shown in Fig. 3 (a) was split into four spots as it was indicated by dotted circles. This indicates that the (001) of PZT are tilted from the substrate normal direction and the tilt angles were 0.27° . The tilt angle is equal to the distortion angle of the rhombohedral PZT crystal. Therefore, it seemed that the (001) oriented PZT grow with 'back to

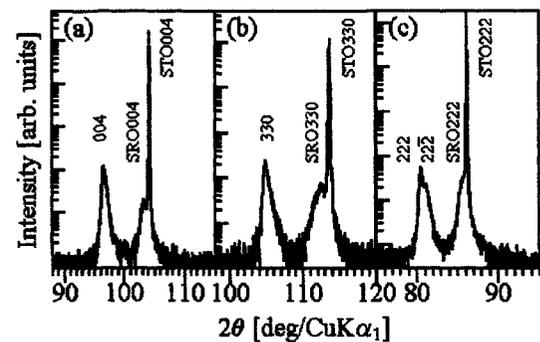


Fig.1 Conventional θ - 2θ scans of film A; (a), film B; (b), and film C; (c).

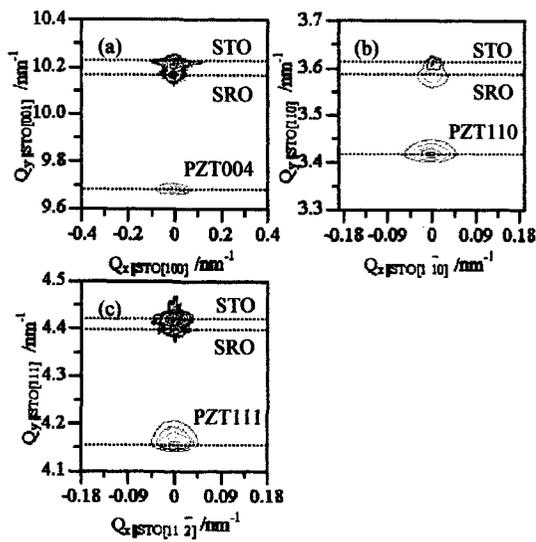


Fig.2 Cross sectional HRXRD-RSM results of film A; (a), film B; (b), and film C; (c).

back' configuration of that (100) and (010). On the other hand, the diffraction spots of PZT of the film B and C are vertically aligned parallel to those of SRO/STO, meaning that there are no tilt between the substrate and the PZT crystal. Moreover, the diffraction spots of PZT 110 and 111 in Fig. 2 (b) and (c), respectively, are tailed to + Q_y direction. This is possibly attributed to the existence of different orientation, such as $(10\bar{1})$ for the film B and $(11\bar{1})$ for the film C. In the case of the film C, this is verified by conventional θ - 2θ scan as it is shown in Fig. 1 (c). In the case of the film B, however, both of PZT 110 in Fig. 2 (b) and PZT 330 in Fig. 1 (b) show just longer tailed diffractions to smaller d-value direction. The reason for the consideration of the existence of $(10\bar{1})$ orientation in the film B is that we confirmed previously these two orientations are coexist in the epitaxially grown $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ film grown on (110) STO single crystal substrate.¹⁰ Therefore, in the calculation of the relative volume fractions of the orientation, we applied peak deconvolution algorithm using pseudo-Voigt function, which is the mixed function of Gauss and Lorentz functions.

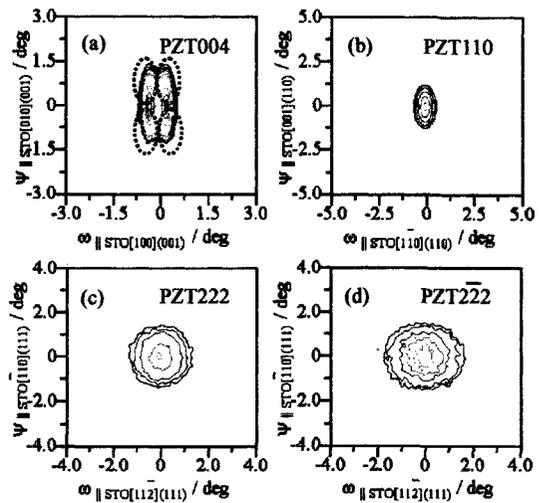


Fig.3 Plan view HRXRD-RSM results of film A; (a), film B; (b), film C; (c) and (d).

The relative volume fractions of the orientations were calculated from the integrated intensities of the diffractions shown in Fig. 3 (a)-(d) and we obtained those numbers as 100% of (001) orientation for the film A, 78% and 22% of (110) and $(10\bar{1})$ orientation for the film B, and 54% and 46% of (111) and $(11\bar{1})$ orientation.

Figure 4 shows P - E hysteresis curves of the film A, B and C. All of the films showed highly square shaped and well saturated hysteresis curves. The remanent polarizations (P_r) were as high as 42, 47 and 52 $\mu\text{C}/\text{cm}^2$ for the film A, B and C, respectively. The obtained P_r values as well as relative volume fractions of the orientations were summarized in Table 1.

The spontaneous polarization of rhombohedral PZT crystal exists along [111]. Therefore, if we assume that 71° and 109° domains do not switch during electric filed cycling, 57%, 81%, 0%, 100% and 33% of spontaneous polarizations are simply expected for (001), (110), $(10\bar{1})$, (111) and $(11\bar{1})$ oriented crystals. Relative expected polarizations for the film A and B against for the film C calculated assuming that the domains do not switch are simple summation of the volume and these are

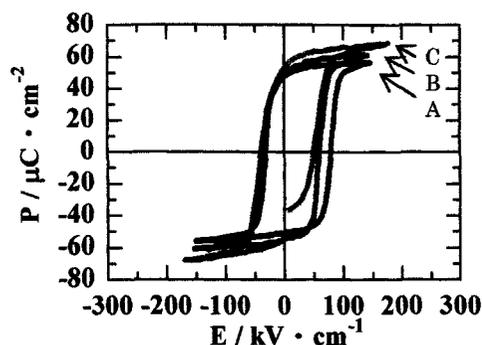


Fig.4 P - E hysteresis curves of the film A, B and C.

83% and 91% for the film A and B, respectively. The numbers are well agreed with the ratio of the obtained P_r values of 81% and 90% for the film A and B against for the film C. This indicates that the domain in such a thin PZT film is not switching by applied electric field cycling.

Table.1 Relative volume fractions of differently oriented domains and their remanent polarizations.

Film	A	B	C		
Orientation	(001)	(110)	(10 $\bar{1}$)	(111)	(11 $\bar{1}$)
Volume %	100	78	22	54	46
P_r , $\mu C/cm^2$	42	47	52		

4. CONCLUSION

We succeeded to grow 200nm thick epitaxial $Pb(Zr_{0.65},Ti_{0.35})O_3$ thin films with three different domain configurations by changing the orientation of the substrate using pulse MOCVD method. The HRXRD-RSM revealed that the (001) oriented PZT film showed pure (001) orientation but tilted growth to $\langle 110 \rangle$ -(001) $SrRuO_3/SrTiO_3$ substrate due to the rhombohedral distortion. Moreover, it revealed that the (110) and (111) oriented films consist of mixed domain orientation with (10 $\bar{1}$) and (11 $\bar{1}$), respectively. The

relative volume fractions of these domains were 22% and 46%, respectively.

Assuming that the domain does not switch during electric field cycling, the remanent polarizations obtained from P - E hysteresis measurement of three films were well explained by the relative volumes of the domains and their effective polarization. These results gave an aspect of domain switching behavior in the thin PZT film by externally applied electric field cycling.

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(Received December 21, 2001; Accepted January 31, 2002)