

Orientation Dependence of Domain Behaviors in Tetragonal Lead Zirconate Titanate Films

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We prepared the [111]- and [001]&[100]-oriented tetragonal $\text{Pb}(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ film on Pt-coated Si substrates, and studied their polarization, dielectric, and piezoelectric responses under the application of the external fields. It is shown that the contributions of domain wall motion to these responses in the [111] film are greatly larger than those in the [001]&[100] film.

Key words: ferroelectric, dielectric, piezoelectric, domain, PZT film

1. INTRODUCTION

Ferroelectric films have great attraction in recent years because of their wide applications from nonvolatile memories to piezoelectric and pyroelectric micro-devices.[1-3] Since the ferroelectric, piezoelectric, and pyroelectric properties are essentially determined by the states of spontaneous polarization in the films, one way to improve the performance of the film device is to control the polarization orientation. With the progresses in film deposition techniques, it is now possible to grow the oriented or epitaxial tetragonal lead zirconate titanate films by various deposition technique.[4-7] However, it is extremely difficult to obtain the single domain structure, even if for the epitaxial films. The film properties are inevitably influenced by the domain behaviors.[5,8] In the previous investigations on one of the composition of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($x=30\%$, PZT30/70), we revealed that the [111]-oriented film exhibited a long time piezoelectric relaxation, in contrast, no evident relaxation was observed for the [001]-oriented film.[5] The dielectric response in these films was also shown to depend on the film orientation.[9] The different responses in different oriented films were attributed to the special domain configuration in the films.

In this work, we focused on the domain behaviors in the oriented PZT films with a different composition ($x=40\%$, PZT40/60) by studying their polarization, dielectric, and piezoelectric responses under the application of the external fields. We confirmed that the contributions of domain wall motion to these responses are significantly greater in the [111] film than those in the [001]&[100] film.

2. SAMPLES

The used PZT40/60 films were deposited on Pt/Ti/SiO₂/Si substrates by a chemical solution deposition. The film deposition and x-ray diffraction pattern have been described in detail elsewhere.[4,10] Highly [111]-

and [001]&[100]-oriented films were successfully obtained by controlling the preannealing temperature. Table I lists the relative intensities of the diffraction peaks for the obtained films. For the [001]&[100] film, over 90% of the diffractions are contributed by the [001]- and [100]-oriented grains although minor diffractions are observed for [110]- and [111]-oriented grains. The ratio of a to c domain calculated from (001) and (100) peaks is about 26.9% for the virgin film, which is quite lower than the value evaluated from (002) and (200) diffraction peaks (64.3%). A major reason might be due to the overlap of (001) and (100) peaks. The overlap of these peaks leads to the difficulty in the peak separation. The lattice constants calibrated with the (400) peak of Si substrate were determined to be 4.057Å and 4.032 Å for c and a axes, respectively. The diffraction data also show that the [111] film consists of about 93.4% of the [111]-oriented grains.

Table I Relative intensities of the (001), (100), (110), and (111) peaks for the oriented PZT40/60 films

Film	Peak intensity $I_{hkl} / \sum I_{hkl}$ (%)			
	(001)	(100)	(110)	(111)
[001]&[100]	19.2	71.5	2.0	7.3
[111]	2.0	1.7	2.9	93.4

3. RESULTS AND DISCUSSIONS

3.1 Polarization response

Figure 1 shows the orientation dependence of the hysteresis loops of the spontaneous polarization for PZT40/60 thin films. The maximum and remanent polarizations are 42 $\mu\text{C}/\text{cm}^2$ and 21 $\mu\text{C}/\text{cm}^2$ for the [111] film, 38 $\mu\text{C}/\text{cm}^2$ and 17 $\mu\text{C}/\text{cm}^2$ for the [001]&[100] film, respectively. The coercive field is about 44 kV/cm for both of the films. A significant difference in the polarization responses of these two oriented films is that the switching polarization of the [111] film is larger than

that of the [001]&[100] at the same electric field. This means that the polarization switching in the [001]&[100] film is not thorough. This is due to the existence of large amount of a -domain in the films. When a 90°-domain is switched, an elastic deformation always appears. This deformation is constrained by the substrate, leading to the difficulty in switching the a -domain to the c -domain. However, the case is different for the [111] film. Since the polarization switching can be no concern of the 90°-domain switching, it might proceed more thoroughly at high field. A geometric calculation shows that $P_s^{[111]} = P_s^{[001]} c / \sqrt{2a^2 + c^2}$. Using the above lattice constants, we can estimate that $P_s^{[001]}$ might be greater than $72 \mu\text{C}/\text{cm}^2$, which is about twice of the value $38 \mu\text{C}/\text{cm}^2$ obtained from the [001]&[100] film. Therefore, how to increase the content of the [001]-oriented grains in the film is still an important issue for the deposition technique for the future study.

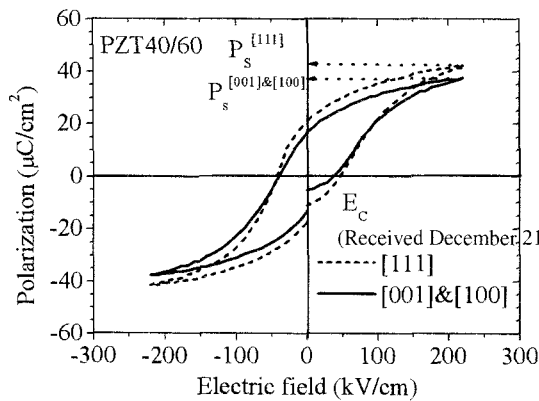


Fig. 1 Orientation dependence of spontaneous polarization for PZT40/60 films.

3.2 Dielectric response

The dielectric response also provides abundant information about the domain behaviors in the films. Figure 2 shows the frequency response of dielectric

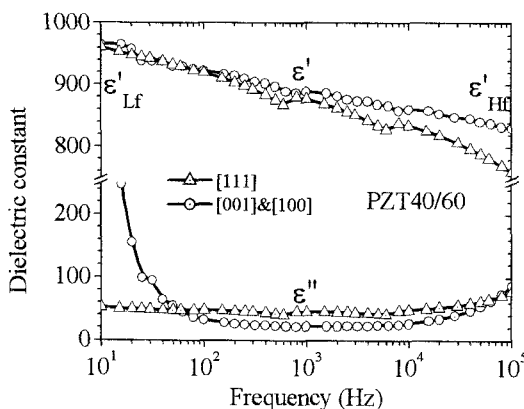


Fig. 2 Frequency dependence of dielectric constant for the [111]- and [001][100]-oriented PZT40/60 films.

constant in the films. It is obvious that the dielectric response in the [001]&[100] film is less frequency-dependent in comparison with the [111] film. For frequencies lower than 1000 Hz, the dielectric responses in both of the films coincide with each other. However, when the frequency increases to high frequency, the dielectric constant of the [111] film drops more rapidly. The variations in dielectric constant $(\epsilon'_{Lf} - \epsilon'_{Hf}) / \epsilon'_{Hf}$ are 26.3% and 16.3% for the [111] and [001]&[100] films, respectively, in the observed frequency range. This fact clearly indicates that the domain wall motion is significantly active in the [111] film in comparison with the [001]&[100] film.

This conclusion is also confirmed from the measurements of field-dependence of dielectric constant. As shown in Fig. 3, a butterfly of the dielectric response was observed. This is due to the domain reversal in the ferroelectric materials. When the polarization is switched to the opposite state at the coercive field, the variation in polarization is the largest, leading to a maximum ϵ'_{max} of the dielectric response. At high field, since the switchable domains have been reversed, the contribution of domain wall motion to the dielectric response is minor. The dielectric constants at the saturated polarization state ϵ'_{Ps} were estimated to be 530 and 440 for the [001]&[100] and [111] films, respectively. The relative variation in dielectric constant $(\epsilon'_{max} - \epsilon'_{Ps}) / \epsilon'_{Ps}$ for the [111] film was evaluated to be 118%, which was also greater than the value of the [001]&[100] film (89%). It is thus concluded that the contribution of domain wall motion to the dielectric response is greater in the [111] film than that in the [001]&[100] films.

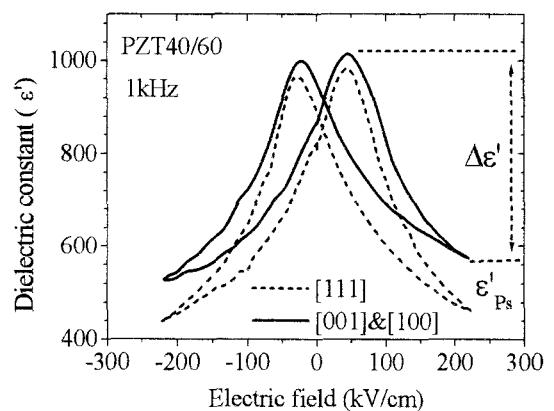


Fig. 3 Dependence of dielectric constant on the bias electric field for the [111]- and [001][100]-oriented PZT40/60 films. Measurements were performed at 1 kHz.

3.3 Piezoelectric response

Piezoelectric responses in the films were studied by measuring the stress-induced charge with a continuous charge integration.[5,8,10] Briefly, a step stress is applied

to the sample, and the time dependence of the induced charges due to the direct piezoelectric is observed by an integration circuit with ultra-low bias-current. The piezoresponse function $f(t)$ can be derived from the charge response. The advantage of this time-domain technique is that we are able to estimate the contribution of domain wall motion to the total piezoresponse quantitatively. We found that the response function of the PZT can be described very well by the following formula,[3,5,8,10]

$$d_{33}(t) = d_{33}^{\text{intri}} + d_{33}^{\text{relax}} (1 - \exp(-(t/\tau)^n)), t > 0. \quad (1)$$

Here, the first term d_{33}^{intri} represents the contribution from the intrinsic response due to the rapid coupling of polarization to the unit cell distortion, and the second term d_{33}^{relax} originates from the relaxation effect due to the slow domain wall motion in a multidomain materials. Table II lists the values of d_{33}^{intri} and d_{33}^{relax} for the PZT40/70 films. We want to emphasize again that the contribution of the domain wall motion to the total response in the [111] film (27.4%) is significantly greater than that in the [001]&[100] film (13.4%). This result is in agreement with the dielectric responses described above, and also with the previous report for the PZT30/70 films.[5]

Table II Contribution of intrinsic and relaxation effects to the piezoelectric responses in the [001]&[100] and [111] PZT40/60 films.

Film	d_{33}^{intri} (pC/N)	d_{33}^{relax} (pC/N)	$d_{33}^{\text{relax}}/(d_{33}^{\text{relax}} + d_{33}^{\text{intri}})$ (%)
[001]&[100]	175	26.9	13.4
[111]	186	70.1	27.4

4. SUMMARY

In summary, we have studied the effects of orientation on the polarization, dielectric, and piezoelectric responses of the PZT40/60 films. We clearly show that different crystallographic orientations lead to different responses in the films. The contributions of domain wall motion to the dielectric and piezoelectric responses in the [111] film are significantly greater than those in the [001]&[100] film. These results are of great significance for the practical application since the film orientation will determine the response speed and the stability of the device.

5. REFERENCES

- [1] J. F. Scott and C. A. Paz deAraujo, *Science*, **246**, 1400-05 (1989).
- [2] P. Muralt, *J. Micromech. Microeng.*, **10**, 136-46 (2000).
- [3] D. S. Fu, H. Suzuki, T. Ogawa, and K. Ishikawa, *Appl. Phys. Lett.*, **80**, 3572-74 (2002).
- [4] H. Suzuki, Y. Kondo, S. Kaneko, and T. Hayashi, *Mater. Res. Soc.Sym. Proc.*, **596**, 241-246 (2000).
- [5] D. S. Fu, K. Ishikawa, Y. Yoshimi, and H. Suzuki, *Jpn. J. Appl. Phys.*, **41**, L580-82 (2002).
- [6] D. V. Taylor and D. Damjanovic, *Appl. Phys. Lett.*, **76**, 1615-17 (2000).

- [7] C. M. Foster, G. -R. Bai, R. Csencsits, J. Vetrone, R. Jammy, L. A. Wills, E. Carr, and Jun Amano, *J. Appl. Phys.*, **81**, 2349-57 (1997).
- [8] D. S. Fu, K. Ishikawa, M. Minakata, and H. Suzuki, *Jpn. J. Appl. Phys.*, **40**, 5683-86 (2001).
- [9] D. S. Fu, Y. Yoshimi, H. Suzuki, and K. Ishikawa, *Key Engineering Materials*, **228-229**, 63-68 (2002).
- [10] D. S. Fu, K. Kato, K. Ishikawa, Y. Yoshimi, and H. Suzuki, *Ferroelectrics*, (2003)(In press).

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