

Ferroelectric characteristics of oriented $\text{Pb}(\text{Zr } 1x \text{ Ti } x) \text{O}_3$ films

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Ferroelectric characteristics of oriented $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ films

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$\text{Pb}_{1.2}\text{Zr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) films with a variety of compositions were prepared by spin coating on Pt/Ti/SiO₂/Si substrate with sol-gel processing. The roles of composition (phase) and orientation in ferroelectric properties of PZT films have been determined. The Zr-rich PZT films with (111)-oriented PZT films have a higher remanent polarization but also show a higher fatigue rate as compared to (100)-oriented films in both Zr-rich(65/35) and Ti-rich(35/65) PZT compositions. The lower fatigue rate of (100)-oriented film can be attributed to its easier reversible domain-wall motions compared to (111)-oriented PZT films due to the absence of internal field stress and less dependence on electrical field. A mode based on domain-wall contribution instead of film-electrode interface is favored to elucidate the role of orientation in fatigue characteristics of PZT films.

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I. INTRODUCTION

Lead zirconate titanate $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) thin films for nonvolatile memory applications have attracted great attention in view of their potential application in memory and micromechanical devices.¹⁻³ Electrical properties of PZT films are strongly dependent on many parameters, including composition, crystallographic structure, microstructure, orientation, and properties of the substrate. Although the role of these parameters in ferroelectric properties has been well investigated, ferroelectric fatigue is a major obstacle in the practical application of the films for nonvolatile memory applications. Ferroelectric fatigue is the loss of switchable polarization with repeated polarization reversals, which is due to pinning of domain walls, inhibiting switching of the domains. Many interpretations of fatigue mechanisms based on the domain-wall pinning have been studied and proposed.⁴⁻⁷

Several studies on the control of PZT crystal alignment on various substrates and the analysis of electrical properties of PZT films have been reported.⁸⁻¹² However, the effect of crystallographic orientation on fatigue characteristics of PZT films has been not definitely reported.¹³ Recently, fatigue anisotropy was observed in pseudocubic/rhombohedral relaxor ferroelectric-PbTiO₃ thin films.¹⁴ They revealed that fatigue characteristics of $\text{Pb}[\text{Yb}_{1/2}\text{Nb}_{1/2}]\text{O}_3\text{-PbTiO}_3$ (PYbN-PT)/SrRuO₃ (SRO) films are strongly dependent on their crystalline orientation. (001)-oriented PYbN-PT/SRO/LAO heteroepitaxial thin films result in fatigue-free capacitors up to 10¹¹ cycles, while (111)-oriented PYbN-PT/SRO/STO heterostructures exhibit a marked degradation of the switchable polarization by a voltage cycling. A model based on oxygen-vacancy planes was proposed to elucidate the pinning of domain walls preferentially along certain crystallographic direction.¹⁵ However, the role of preferred orientation in fatigue properties of PZT thin films for both Ti-rich and Zr-rich PZT compositions with different orientation on one same

substrate, especially on Pt/Ti/SiO₂/Si, has been not systematically studied and compared. Therefore, in the present work, a detailed comparison of fatigue characteristics for oriented PZT films is investigated. The relationships among composition, orientation, and fatigue characteristics of PZT thin films on Pt/Ti/SiO₂/Si substrate are also discussed.

II. EXPERIMENTAL PROCEDURE

A. Preparation of stock solution and fabrication of thin film

Following the sol-gel method proposed by Budd *et al.*,¹⁶ PZT films were prepared with zirconium *n* propoxide, titanium isopropoxide, and lead acetate precursors. The 20 mol % excess Pb solution was used to overcompensate for any Pb loss during high temperature annealing. Thin films were fabricated on Pt(111)/Ti/SiO₂/Si substrates by spin coating. A detailed description of the (111)- and (100)-oriented film process used is described elsewhere.¹⁷ [111] orientation was obtained by fast heating film at 700 °C for 0.5 h. [100] orientation can be obtained by first pyrolysis at 400 °C for 0.5 h and then by annealing at 700 °C for 0.5 h in air. A single coating generally gave a 0.11–0.13 μm crack-free film after firing. After first-layer seeding, up to three additional layers were subsequently coated onto the film. Between each coating, the film was rapidly annealed at 700 °C for 0.1 h.

B. Characterization and property measurement

The orientation of the film was determined by standard θ - 2θ x-ray diffraction (XRD) method. Microstructure and thickness of films were examined using scanning electron microscopy (SEM). For the measurement of electrical properties, patterned top Au electrodes were sputter deposited through a shadow mask on an area of 8.0×10^{-4} cm² onto the PZT layers to define capacitors. Ferroelectric hysteresis loops were obtained with a Radiant Technologies RT66A ferroelectric test system, operating in the virtual ground

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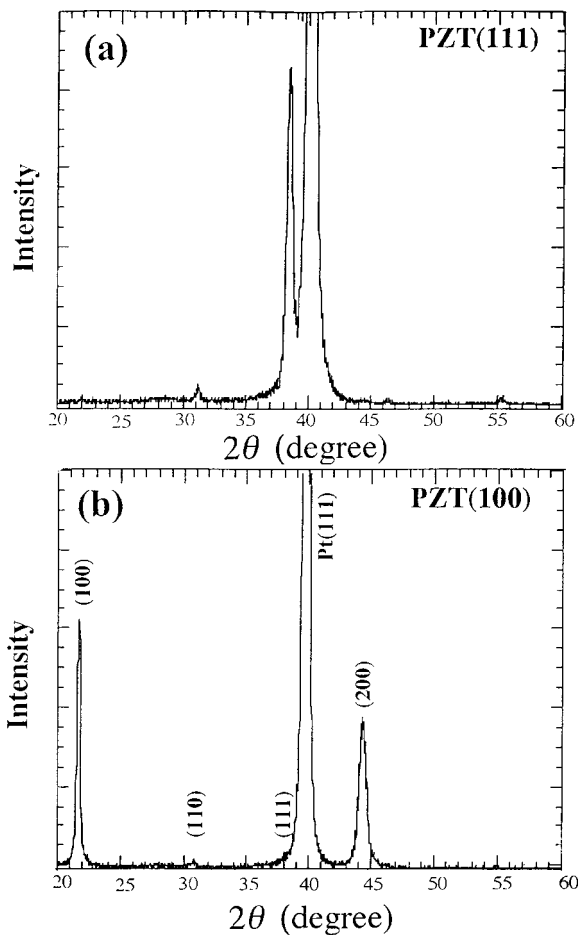


FIG. 1. XRD patterns of (a) (100)-oriented and (b) (111)-oriented PZT(65/35) films are shown.

mode with a triangular wave with a period of approximately 20 ms. A computer generated wave form consisting of alternating positive and negative pulses with a pulse width of 8.6 μs and a period of 30 μs was used to fatigue the samples with a thickness of $\sim 0.37 \mu\text{m}$ under 10 and -10 V . Most of the data reported here were checked for 3–5 samples and highly reproducible.

III. RESULTS AND DISCUSSION

A. Structure analysis

Figure 1 shows XRD patterns of the $\text{Pb}_{1.2}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ films pyrolyzed at different temperatures and then directly annealed at the same temperature of 700 °C for 0.5 h. The PZT films after first pyrolyzed at 400 °C grew with (100) preferred alignment, whereas those without pyrolysis treatment show (111)-oriented structure. Both (100) and (111) orientations can be obtained under appropriate heat-treatment control. The orientation control is possible for $\text{Pb}_{1.2}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ films with different Zr/Ti ratios. Typical SEM micrographs of (111)-oriented PZT films are presented in Fig. 2. For Ti-rich (35/65) (111)-oriented films, a fine-grained structure [Fig. 2(a)] with an average grain size about 0.1 μm was obtained. In contrast to that, a larger grain size was seen in the Zr-rich (65/35) (111)-oriented films [Fig. 2(b)]. Furthermore, it was found that for a same composition,

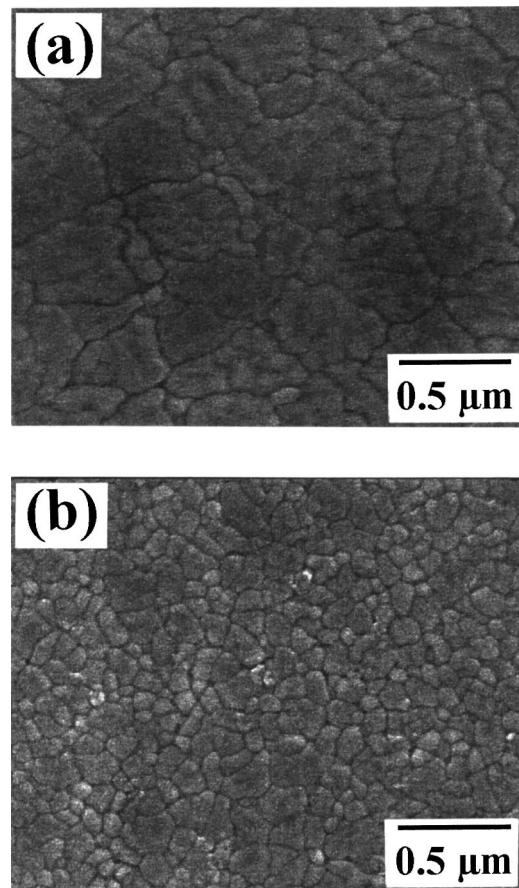


FIG. 2. SEM microstructure of (a) Ti-rich (111) and (b) Zr-rich (111) PZT(65/35) films are shown.

the microstructure morphology shows no obvious difference, independent of orientation type. Ti-rich PZT compositions have lower crystallization temperatures compared to Zr-rich PZT compositions. This is attributed to a smaller amount of perovskite nuclei in the Zr-rich PZT films that crystallize with more difficulty.¹⁸

B. Hysteresis Loop

Figure 3 shows the hysteresis loops of Zr-rich PZT(65/35) and Ti-rich PZT(35/65) films under different applied voltages. For the rhombohedral PZT(65/35), the spontaneous polarization (P_s), remanent polarization (P_r) and the coercive field (E_c) of the (111) oriented films at an applied voltage of 15 V are 55.1 $\mu\text{C}/\text{cm}^2$, 31.3 $\mu\text{C}/\text{cm}^2$, and 57.2 kV/cm, respectively. The P_s , P_r , and E_c of the (100)-oriented films are 46.7 $\mu\text{C}/\text{cm}^2$, 20.9 $\mu\text{C}/\text{cm}^2$, and 49.3 kV/cm, respectively. Since the spontaneous polar axis is along [111] direction in the rhombohedral phase, therefore, based on a same electrical field, the (111)-oriented films exhibit a higher Pr value compared to (100)-oriented film for Zr-rich PZT(65/35) films. On the other hand, for the tetragonal Ti-rich PZT(35/65) films, both P_s and P_r of (100)-oriented films are 47.3 $\mu\text{C}/\text{cm}^2$ and 25.4 $\mu\text{C}/\text{cm}^2$ which are comparable to those ($P_s=52.4 \mu\text{C}/\text{cm}^2$ and $P_r=29.1 \mu\text{C}/\text{cm}^2$) of (111)-oriented films, respectively. However, the E_c (119 kV/cm) of (111)-oriented films is higher than that (95 kV/cm) of (100)-

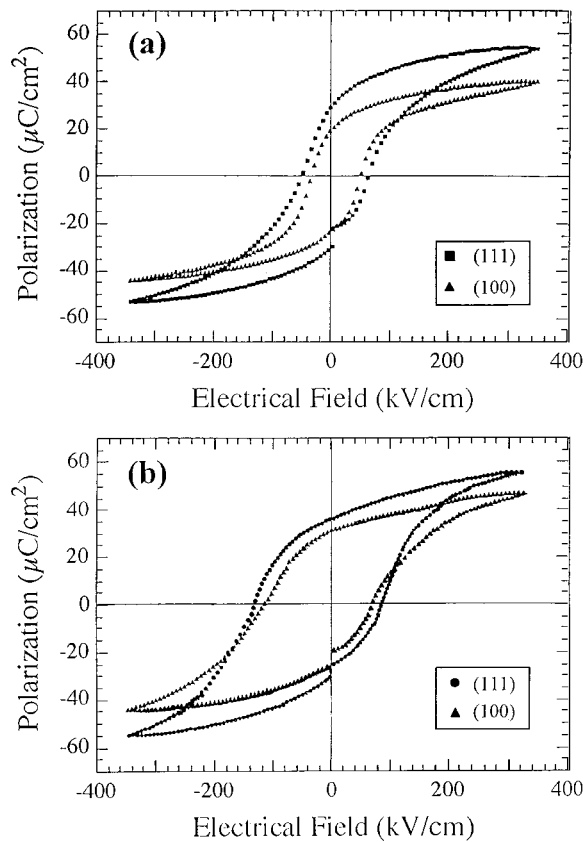


FIG. 3. Comparison of hysteresis loops for (111)- and (100)-oriented (a) $\text{Pb}_{1.2}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ and (b) $\text{Pb}_{1.2}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ films are shown.

oriented films. A nearly symmetric loop (with identical $\pm E_c$) was observed on the rhombohedral films, but asymmetric hysteresis was observed on the tetragonal films. A coercive field of $E_c = 50\text{--}60$ kV/cm was observed for the Zr-rich films. Increasing Ti concentration caused the coercive field to increase to $E_c = 90\text{--}120$ kV/cm at $x = 0.65$. This is most likely due to the large crystal strain in the tetragonal phase and small grain size as the tetragonality increases with Ti content.

It is well known that the magnitude of polarization is not only affected by the clamping of the film by the substrate, but also by domain structure as well as the mobility of the domain walls. For the rhombohedral structure, if one considers possible orientations of domains for the two crystallographic orientations shown in Fig. 4,¹⁹ two types of domains

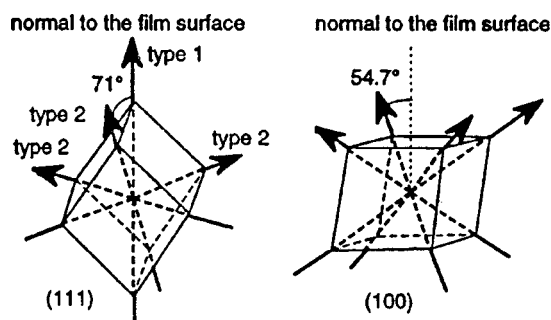


FIG. 4. Possible orientations of the polarization vector in (111)- and (100)-oriented rhombohedral film are shown (Ref. 19).

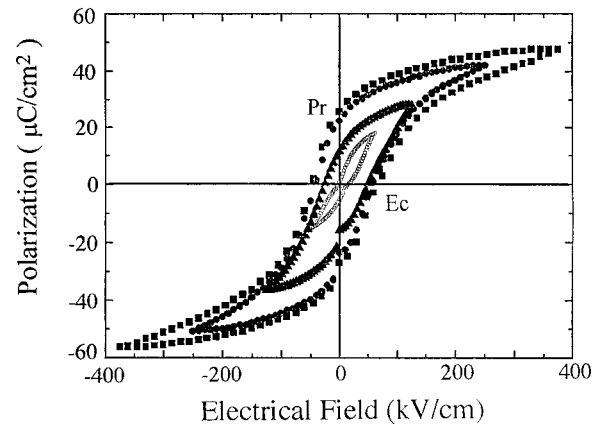


FIG. 5. Hysteresis loops of Zr-rich (111) preferred PZT films under applied voltages of 2, 5, 10, and 15 V are shown.

exist in the (111)-oriented films. There is one possible orientation (type I) normal to the film surface and three (type II) canted an angle of approximately 71° or 109° with the normal to the film. As the polarization is switched from one type to the other by an electric field, the reorientation is accompanied with strain. In contrast, the (100)-oriented films have four equal orientations to contribute to the measured polarization without induced strain. Therefore, a larger coercive electric field is required for (111)-oriented PZT films.

For the tetragonal structure, the polarization dipoles will be aligned with the [100] direction. Neither [111] nor [100] directions are the polarization axis in tetragonal phase. In the case of (100)-oriented films, the switching of 90° domain from [001] to [100] is not favored by a field applied through the film thickness. Therefore, the measured remanent and saturation polarizations are smaller in the (100)-oriented than (111)-oriented Ti-rich PZT films in the tetragonal region.

The information about crystalline orientation on the polarization and domain switching behavior can be obtained from P-E hysteresis loops under different applied voltages. These loops are shown in Fig. 5. The electrical field dependence of the remanent polarization as a function of film orientation is shown in Fig. 6 for Zr-rich and Ti-rich PZT films. The Pr response to the electrical field can be considered as composed of two stages. For the Zr-rich PZT films shown in Fig. 6(a), (111)-oriented film presents a rapid increase in the initial stage and then slows toward saturation. The rapid increase in the former stage is due to 180° domain switching since the spontaneous polar axis is along [111] direction in the rhombohedral phase, but the slow increase in the latter stage is attributed to the contribution of the other three smaller polarization vectors (non- 180° domain switching). On the other hand, (100)-oriented film increases gradually with increasing electrical field and then tends toward saturation. Consequently, comparing to (100)-oriented films, the (111)-oriented PZT films always have larger remanent polarization at an identical applied field because [111] is the polarization direction of rhombohedral phase.

On the other hand, for the tetragonal Ti-rich PZT(35/65) films at an applied field below 120 kV/cm, Fig. 6(b) illustrates that the (100)-oriented film shows larger remanent polarization (Pr) than (111)-oriented film. This possibly results

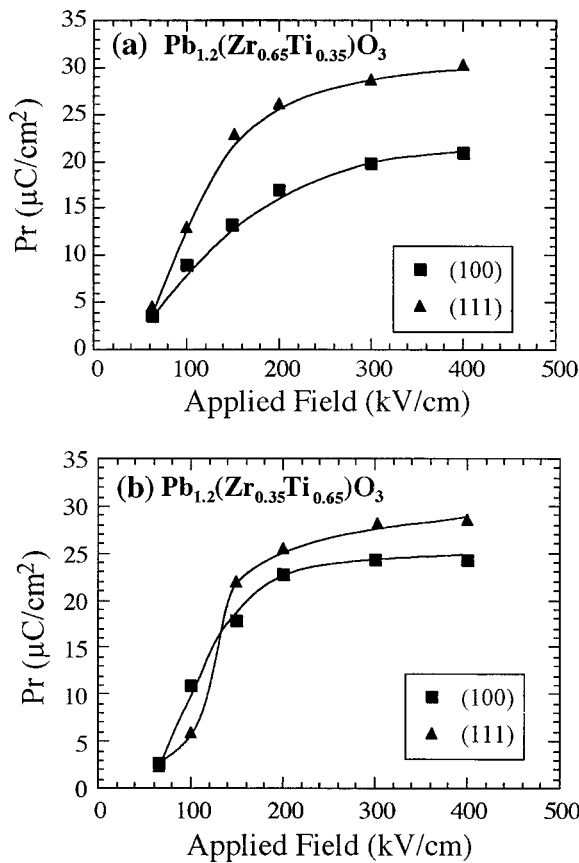


FIG. 6. Field dependence of remanent polarizations for (a) Zr-rich and (b) Ti-rich PZT films are shown.

from the contribution of smaller quantity of [001] (180°) domain switching. However, above that, comparing to the (100)-oriented film, the (111)-oriented film exhibits a rapid increase in polarization near coercive field around 120–140 kV/cm, resulting in a larger Pr. This result indicates that the (111)-oriented films have a more concentrated distribution of domains. With further increasing applied field, both Pr values of (111)- and (100)-oriented films tend toward saturation.

C. Fatigue property

The switching cycles in terms of logarithm on the x axis are generally used to evaluate the fatigue characteristic. Following the method of Mihara *et al.*,²⁰ the fatigue properties of both (100)- and (111)-oriented Zr-rich (65/35) and Ti-rich (35/65) PZT films are shown in Figs. 7 and 8, respectively. Three stages are found in the cumulative switching cycles as follows. (1) Slow fatigue state: this stage corresponds to the cumulative switching cycles ranging from 10 to 1 × 10⁴ cycles. No trace of obvious difference in 2Pr versus the log scale of switching cycles for different oriented and structural PZT films was observed. (2) Logarithmic fatigue stage: this stage ranges from 1 × 10⁴ to 1 × 10⁸ cycles and was commonly recognized by many researchers.^{20–22} As the cycling number increases above 10⁴ cycles, 2Pr decreases continuously with different rates depending on the orientation and initial polarization. For the rhombohedral Zr-rich PZT(65/35) films although the initial 2Pr value of (111)-oriented film is larger, the fatigue rate [defined as Δ(2Pr)/Δ cycles] in this

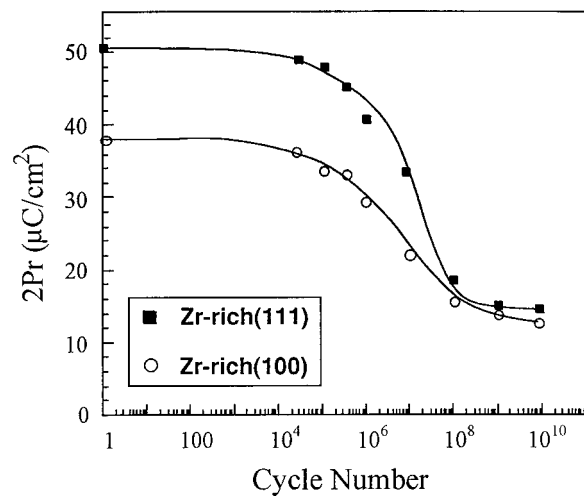


FIG. 7. Remanent polarization as function of cumulative polarization switching cycles for (111)- and (100)-oriented Zr-rich PZT films is shown.

stage is much larger for (111)- than (100)-oriented PZT films. On the other hand, for the tetragonal Ti-rich PZT(35/65) films, the 2Pr value of the (111)-oriented film was found slightly larger than that of the (100)-oriented film but the former still decays in a larger rate. (3) Saturated stage: this stage corresponds to at switching cycles above 10⁸. The 2Pr tends toward a saturated value.

Different fatigue mechanisms which include the models of conducting dendrites,²² microcracking,²³ space charge defects along grain boundaries,²⁴ domain walls at the surfaces and interfaces,²⁵ and oxygen defects at the film electrode²⁶ have been proposed to explain the polarization degradation. However, (111)- and (100)-oriented PZT films display very different fatigue behavior. This leads us to believe that the other mechanism besides interface and film–electrode effects is responsible for the fatigue, which probably involves domain switching and domain-wall pinning due to the crystal orientation. As reported by Bornand *et al.*¹⁴ for relaxor ferroelectric-PbTiO₃ films, the orientation of these ferroelectric films plays a critical role in determining fatigue characteristics. (001)-heteroepitaxial films result in a fatigue-free

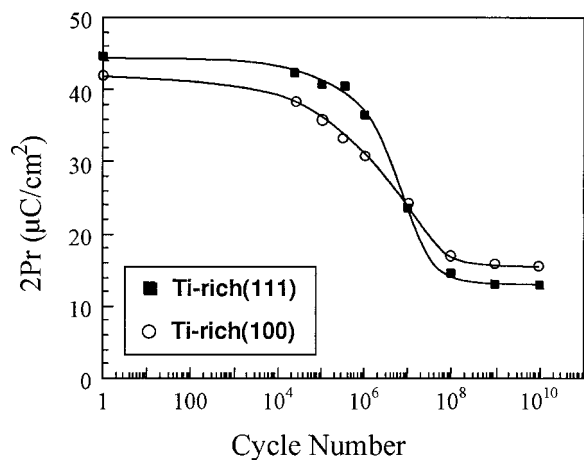


FIG. 8. Remanent polarization as function of cumulative polarization switching cycles for (111)- and (100)-oriented Ti-rich PZT films.

capacitor up to 10^{11} cycles, while $\langle 111 \rangle$ -oriented heterostructures exhibit a marked degradation of the switchable polarization by an ac voltage cycling. Obviously, the observed fatigue difference due to the orientation is strongly related to the displacements of domain walls, which in turn was controlled by the domain structure. This could be elucidated by considering the possible orientations of domains for the two crystallographic orientations as depicted in Fig. 4. In the case of (100)-oriented films, as proposed by Taylor and Damjanovic,¹² all polarization directions are tilted away by the same angle ($\sim 55^\circ$) from the normal to the film surface and contribute equally to the measured polarization. Therefore, the switching of these domains does not change the dimension of the (100)-oriented film along the direction normal to the film surface. On the other hand, for (111)-oriented films, switching of polarization from one type to the other will change the dimension of the film and induce internal field stress, thus limiting their contribution to the film response. The fact that the displacement of non- 180° domain walls induces the internal field stress in (111)-oriented films but does not make induction in (100)-oriented film is reflected in the difference of domain switching behavior. This implies that there exists a stronger relationship between domain-wall motion and applied field in the (111)- than (100)-oriented films, which is consistent with literature report for the piezoelectric properties.²⁷ Therefore, the absence of internal field stress leads to a smaller fatigue rate in (100)-oriented than (111)-oriented PZT(65/35) films at an applied voltage of 10 V.

On the other hand, for the tetragonal Ti-rich PZT films, the polarization dipole was along the [001] direction. In the case of (100)-oriented films, two types of domains are observed. The first type (100), normal to the film surface, 180° domain is the primary contribution to the polarization. The other type (001), parallel to the film surface, consists of 90° domains that are hard to reorient the domains and contribute to the polarization except under a larger applied field. Therefore, when the films were measured at pulse amplitude of 150 kV/cm [Fig. 6(b)], the obtained polarization in (100)-oriented films mostly results from 180° domain switching; the contribution from 90° domain switching is scarce. In the other case of (111)-oriented films, the three $\langle 100 \rangle$ components are canted an angle of approximately 55° with the normal to the film surface and the measured polarization is strongly dependent on the applied field. This indicates that the reversible domain-wall motions in (100)-oriented films are expected to be easier than (111)-oriented films, which is attributed to the fast switching of 180° domains and are less dependent on electrical field in the PZT tetragonal regions. Consequently, after being cycled at an applied voltage of 10 V, the (100)-oriented films decay in a smaller rate at the logarithmic fatigue stage compared to (111)-oriented films.

IV. CONCLUSIONS

Zr-rich and Ti-rich PZT films with (100) and (111) preferred orientations were prepared on Pt/Ti/SiO₂/Si substrates using a sol-gel method. The (111)-oriented films have a larger remanent polarization and coercive field than the (100)-oriented films for both Zr-rich PZT(65/35) and Ti-rich PZT(35/65) compositions. It has been demonstrated that the preferred orientation indeed makes a significant contribution on the fatigue characteristics, which is correlated with the motions of domain walls. The easier reversible motion in (100)-oriented than (111)-oriented PZT films reflects a smaller fatigue rate, which is attributed to the absence of internal field stress and less dependence on electrical field in rhombohedral and tetragonal regions, respectively.

ACKNOWLEDGMENT

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