

Effects of preferred orientation on the piezoelectric properties of Pt/Pb(Zr_{0.3}Ti_{0.7})O₃/Pt thin films grown by sol–gel process

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Abstract Tetragonal lead zirconate titanate (PZT) films with different orientations and 200 nm film thicknesses were prepared on platinized silicon substrates. Types of substrate and control of thermal processes, such as layer-by-layer and one-crystallization heat treatments, result in highly (111) or (100)-oriented PZT films. The piezoelectric, dielectric, and ferroelectric properties of polycrystalline PZT films have been investigated as a function of preferred orientation. The property difference between (111) and (100)-oriented films appears to be induced by the effect of ferroelastic domain existence (90° domain in tetragonal composition). From a modified phenomenological equation, the higher electrostrictive coefficient value of $5.6 \times 10^{-2} \text{ m}^4/\text{C}^2$ for (100)-oriented PZT may be responsible for the larger piezoelectric coefficients in (100)-oriented polycrystalline PZT films of 44 pm/V in comparison to (111)-oriented PZT films with about $3.1 \times 10^{-2} \text{ m}^4/\text{C}^2$ of Q_{33} and 40 pm/V of $d_{33,f}$. It was also observed that two (100)-oriented films prepared by different heat treatments showed

different values in piezoelectric, dielectric, and ferroelectric properties even though only (100) orientation was characterized for both cases. This process-induced difference may also play an important role in determining both intrinsic and extrinsic contribution to the properties, even though these parameters seem to be more responsible for extrinsic components, such as domain wall motion.

1 Introduction

Due to the large anisotropy of ferroelectric PZT crystals, all physical and electrical properties of PZT films are strongly dependent upon crystallographic orientation [1]. Since PZT films have the same crystallographic orientation in the high temperature paraelectric phase, the different orientation will imply the different domain structures formed in the films during the phase transition. Such different domain structures are believed to determine not only intrinsic properties but also extrinsic ones on the piezoelectric and ferroelectric properties. Although considerable research relating to the orientation dependence of ferroelectric properties has been devoted to PZT thin films, driven predominantly by FeRAM effort, a comparatively small effort has been given to investigation of piezoelectric properties of PZT thin films. With increasing interest in ferroelectric-based MEMS for microsensors and microactuator applications, information on the orientation dependence of piezoelectric properties has begun to be published [2–6].

Du et al. [2, 3] calculated the intrinsic values of the piezoelectric and dielectric properties of PZT crystals along the (100) and (111) directions by projecting the values along the principal axis based on the phenomenological theory. Their

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calculations showed that the dielectric constant monotonically increases with the angle from the spontaneous polarization direction for both tetragonal and rhombohedral PZT. The minimum and maximum values are found in the directions that are parallel and perpendicular to the polarization direction, respectively. Similarly the piezoelectric constant d_{33} is found to have a maximum value along the polarization direction and decreases as the crystal is rotated away from that axis for tetragonal PZT. Hiboux and Murali [4] investigated the orientation dependence of tetragonal and polycrystalline PZT (45/55) on the piezoelectric properties. The maximum d_{33} of (100)-oriented PZT was 85 pm/V and that of (111) was 55 pm/V. However, no clear explanation was addressed regarding different piezoelectric responses as a function of film orientation. Taylor and Damjanovic reported the piezoelectric properties of rhombohedral PZT (60/40) films with 0.9 μm thickness [5]. A slightly higher d_{33} in (100) orientation was achieved than that of (111) orientation. From the nonlinear response of d_{33} , it was found that strong domain wall contribution in the (111) direction lead to a small difference of d_{33} between the (111) and (100)-oriented PZT films. Recently, the orientation dependence of epitaxial PZT films on the properties was also reported [6]. However, limited study has been reported about the orientation dependence on piezoelectric properties of polycrystalline PZT thin films deposited on silicon-based substrates, which contains more practical implications for microsensor and actuator applications.

In this study, $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ films with (111) and (100) orientations were obtained on platinized silicon substrates by a sol–gel process. The dependence on orientation of piezoelectric, ferroelectric, and dielectric properties was systematically investigated. In addition, the predominant factors for piezoelectric properties are discussed in terms of a quantitative evaluation of the intrinsic and extrinsic contribution to the observed properties.

2 Experimental

The $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ (PZT) films were prepared by a sol–gel process. The precursors are on lead acetate trihydrate [$\text{Pb}(\text{O}_2\text{C}_2\text{H}_3)_2 \cdot 3\text{H}_2\text{O}$], titanium isopropoxide [$\text{Ti}(\text{OC}_3\text{H}_7)_4$], and zirconium *n*-propoxide [$\text{Zr}(\text{OC}_3\text{H}_7)_4$]. Methanol was used as a solvent for all precursors, and alkanolamine was used as a chelating agent [7]. Each PZT layer was spin coated onto platinized silicon substrates at 3000 rpm for 30 s. The platinized silicon substrates used in this study were (111)-oriented Pt/Ti/SiO₂/Si, (111)-oriented Pt/TiO_x/SiO₂/Si, and (200)-oriented Pt/SiO₂/Si. For the controlling heat treatments, two methods were employed. One is layer-by-layer heat treatment and the other is one-crystallization heat treatment. By the first method, PZT films were prepared by

pyrolysis at 450 °C for 8 min and, subsequently, crystallization at 700 °C for 2 min per each layer. Final annealing was performed at 700 °C for 15 min to ensure perovskite phase formation. The other method involved repeated pyrolysis followed by final crystallization (450 °C for 8 min only until getting the desired thickness and then final crystallization at 700 °C for 20 min). The film thickness of all PZT films for this study was 200 nm.

For electrical characterization, circular platinum top electrodes were deposited at room temperature on the PZT films through a shadow mask, using DC magnetron sputtering, and then annealed at 600 °C for 10 min. The typical thickness of Pt top electrodes was 100 nm. The electrode diameter for electrical characterization was 250 μm , while a diameter between 500 and 2000 μm was used for piezoelectric measurements. A sensitive double beam laser interferometer was used to measure electrically induced strains in the PZT films. The effective longitudinal piezoelectric coefficient, $d_{33,f}$, was measured using a low AC oscillation superimposed on a DC bias. Stepping the DC bias between positive and negative polarity resulted in a piezoelectric hysteresis loop, which is the $d_{33,f}$ coefficient as a function of DC electric field. An RT66A ferroelectric tester (Radiant Technology, Albuquerque, NM) was used for the measurement of field-induced polarization. The polarization hysteresis loops were measured with a 30 Hz triangular signal. The dielectric properties were measured using a HP 4192A impedance analyzer. The oscillation signal used was typically 1 kHz in frequency and 0.1 V_{rms} in amplitude. In addition, these measurements were also performed as a function of temperature between 80 and 300 K, using an MMR Technology Inc. cryogenic stage. For low-temperature measurement, the samples were maintained in a vacuum. The heating and cooling rate was approximately 18 K/min. The nonlinear dielectric measurements were performed with sweeping AC voltage from 0 to 1.1 V_{rms} . Frequency was kept at 1 kHz. Phase identification and texture analysis were performed using an X-ray diffraction system equipped with an area detector (Bruker AXS, Cu K α radiation). Field emission scanning electron microscopy (JEOL JSM-7000F) was used to examine surface morphology.

3 Results and discussion

3.1 Orientation development

Table 1 summarizes the observed crystallographic orientation of polycrystalline $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ (PZT) films grown on platinized silicon substrates as a function of substrate and heat treatment process. Strongly (111)-oriented PZT films were obtained on Pt/Ti/SiO₂/Si substrates with layer-by-

Table 1 List of PZT films controlled by types of substrate and thermal process parameters

Substrate	Layer-by-layer [450 °C (8 min) + 700 °C (2 min)] × 4 + 700 °C (15 min)	One-crystallization [450 °C (8 min)] × 4 + 700 °C (20 min)
(111) Pt/Ti/SiO ₂ /Si	(111)	(111)/(100)
(200) Pt/SiO ₂ /Si	(100)	(100)/(110)
(111) Pt/TiO _x /SiO ₂ /Si	(111)/(100)	(100)

layer heat treatment. (100) orientation of PZT films was characterized on Pt/TiO_x/SiO₂/Si by one-crystallization heat treatment and on Pt/SiO₂/Si by layer-by-layer heat treatment. Other combinations resulted in mixed orientations. In the evolution of (111) orientation, Ti underneath Pt is considered to play an important role. Among the proposed factors from the literature, the formation of TiO₂ on Pt [8] or Pt–Ti intermetallic compounds [9] would be more plausible compared with direct nucleation of (111) PZT on Pt [10] or Pb–Pt compound formation [11] in these films. For the one-crystallization method, it appears that the effect of the (111)-oriented Pt substrate is quite reduced. Since the growth planes of PZT with the lowest activation energy are the (100)-planes, (100)-oriented nuclei will tend to grow more rapidly if the formation of (111) nuclei is not a rate determining step. From the observed results, (111) orientation was maximized when (111) nuclei at the substrate are the most energetically favorable and growth of PZT film is controlled by nucleation. When the energy barrier for (111) nucleation is not effectively lowered, (100) nuclei become dominant. In the intermediate case, the orientation appears to be random. Three samples are chosen for investigating the orientation dependence on the properties, which are (111)-oriented PZT grown on (111)Pt/Ti/SiO₂/Si substrate by layer-by-layer process, (100)-oriented PZT on (200)Pt/SiO₂/Si by layer-by-layer process, and (100)-oriented PZT on (111)Pt/TiO_x/SiO₂/Si with one-crystallization heat treatment.

The XRD patterns and SEM images of three samples were shown in Figs. 1 and 2, respectively. All three samples show dense and uniform grain distribution. (100)-Oriented PZT films show a bit larger grain size than films with (111) orientation. A growth dominant condition can be the reason for bigger grain size observed in (100) PZT compared to (111) PZT.

3.2 Characterization of polarization and permittivity

It is well known that the piezoelectric response of ferroelectrics originates from both intrinsic and extrinsic sources [12, 13]. The intrinsic contribution refers to the lattice contribution from the displacements of the

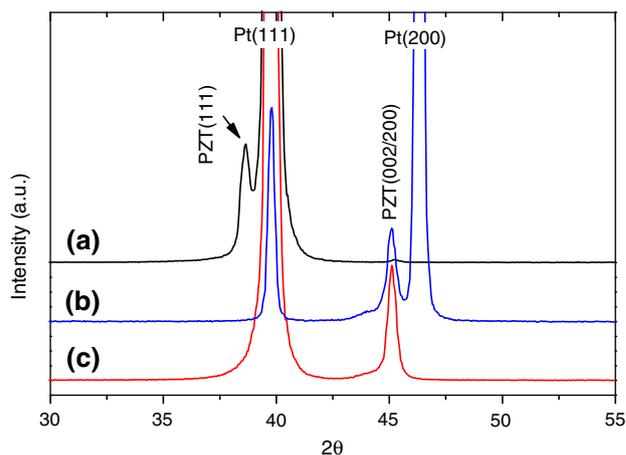


Fig. 1 XRD patterns of PZT films with different preferred orientations; (a) (111)-oriented PZT grown on (111)Pt/Ti/SiO₂/Si by layer-by-layer heat treatment, (b) (100)-oriented PZT grown on (200)Pt/SiO₂/Si by layer-by-layer heat treatment, and (c) (100)-oriented PZT grown on (111)Pt/TiO_x/SiO₂/Si by one-crystallization

individual ions. This corresponds to the response observed in a single-domain single crystal. On the other hand, the piezoelectric response that originates from sources other than the intrinsic contribution is defined as extrinsic. The extrinsic contributions to the piezoelectric response in ferroelectric materials are mainly due to ferroelastic domain wall motion.

The piezoelectric coefficient (d_{ijk}) can be expressed as a function of polarization (P_k), relative permittivity (ϵ_{kl}), ϵ_0 the permittivity of free space, and electrostrictive coefficient (Q_{ijkl}) according to the following equation:

$$d_{ijk} = 2\epsilon_0\epsilon_{kl}Q_{ijkl}P_k, \quad (i, j, k = 1, 2, 3) \quad (1)$$

The analysis of the piezoelectric properties in these PZT films was performed by comparing the measured and calculated piezoelectric response from the constituent parameters.

The P – E loops for different orientations were measured as shown in Fig. 3. The (111)-oriented PZT film exhibits a square P – E hysteresis loop with very abrupt switching. While (100)-oriented PZT films prepared by (200)-oriented Pt substrate and by the one-crystallization process show slanted loops. When compared with two (100)-oriented PZT films, the P_r of PZT film prepared on (100)-oriented Pt shows slightly higher than that of PZT film prepared by the one-crystallization process. It is considered that better crystallinity and probably less defect density when employing the layer-by-layer process may be the reason for slightly better polarization behavior than (100)-oriented PZT grown on (200)-oriented Pt. When comparing (111) and (100)-oriented PZT films, the higher P_r and larger E_c in (111) tetragonal PZT films were observed, as shown in Fig. 3, and are consistent with the previous reports [12]. Fox has

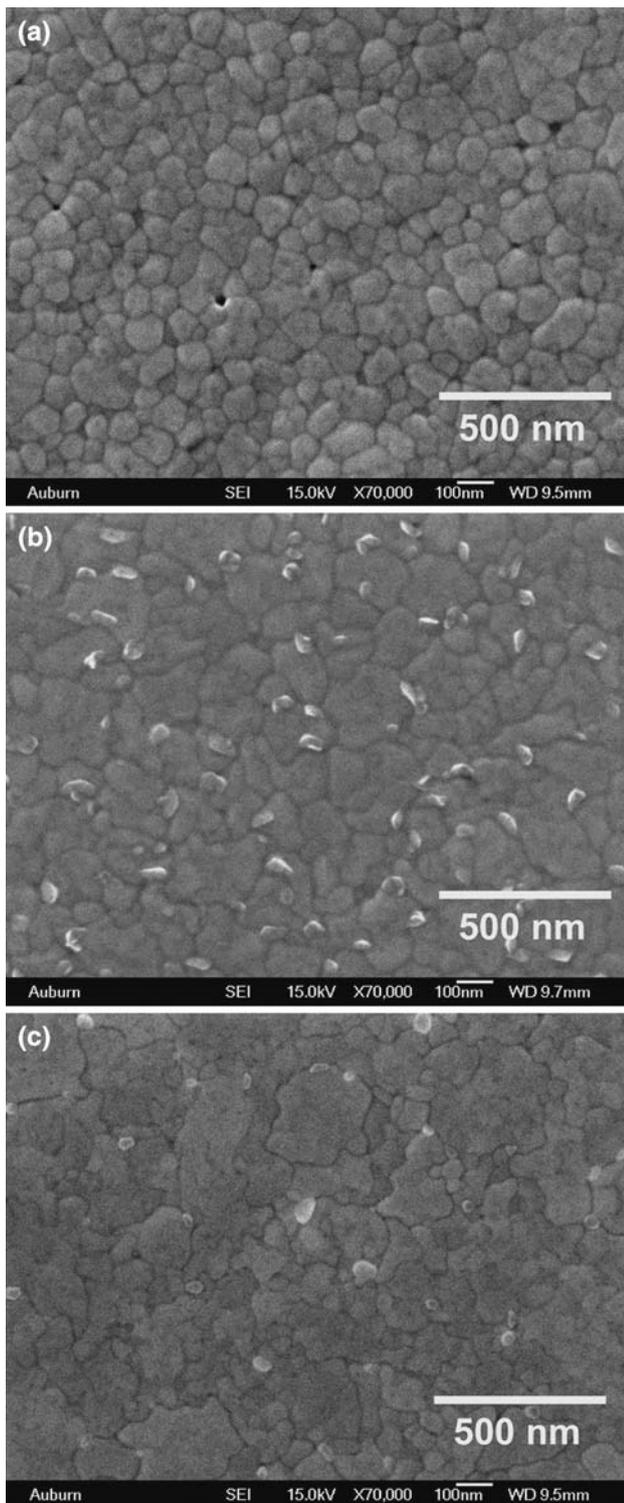


Fig. 2 SEM images of PZT films grown on platinumized silicon substrates; **(a)** (111)-oriented PZT grown on (111)Pt/Ti/SiO₂/Si by layer-by-layer heat treatment, **(b)** (100)-oriented PZT grown on (200)Pt/SiO₂/Si by layer-by-layer heat treatment, and **(c)** (100)-oriented PZT grown on (111)Pt/TiO_x/SiO₂/Si by one-crystallization

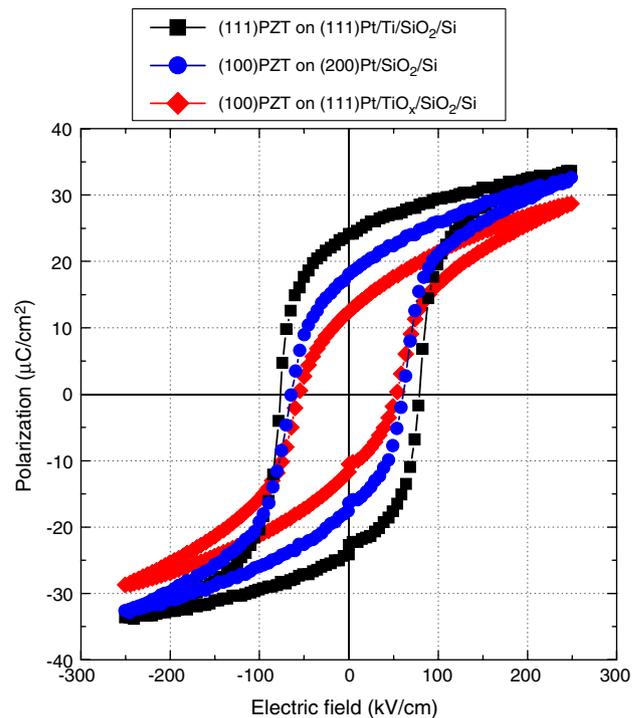


Fig. 3 The polarization hysteresis loops for tetragonal PZT films with different orientations

quantitatively demonstrated that higher volume fraction of (100) orientation is proportional with smaller switching charge density in tetragonal PZT films [13]. It is likely that this phenomenon is mainly due to non-activity of non-180° domain wall motions in thin polycrystalline films. It is believed that the electrical switching (domain reversal) of 90° domain is severely limited in thin tetragonal PZT films since it requires a collaborative atom displacement with much higher energy and therefore has very low probability. Moreover, for externally clamped boundary conditions in the thin film case, an additional energy barrier exists because 90° domain switching would induce very large mechanical stresses, which strongly affect the *P*–*E* hysteresis characteristics [14].

In addition, (100)-oriented tetragonal PZT film is believed to have a larger amount of ferroelastic domain (90° domain) than (111)-oriented film, thereby causing a lower *P_r* and smaller *E_c* in (100)-oriented PZT, which results from the 90° domain existence. The spontaneous polarization direction of tetragonal phase is (001) direction and its value for PZT (30/70) single crystal is calculated around 64 μC/cm² [15]. When PZT (30/70) is oriented to the (111) direction, expected spontaneous polarization can be $64/\sqrt{3} \sim 37 \mu\text{C}/\text{cm}^2$. Therefore, the lower *P_r* in (100)-oriented PZT films may indicate a significant amount of 90° domain and a quite limited motion in this polycrystalline film. It has been reported that

epitaxially grown tetragonal PZT films with around a 200–300 nm thickness shows a higher P_r in (100)-oriented film than that of (111)-oriented film. This would be due to the different domain activities between polycrystalline and epitaxial film that might result from the difference in the local built-in fields and the misorientation of the domains with respect to the sample reference's measurement axis [6, 16].

The field dependence of the dielectric constant was measured for (111) and (100)-oriented PZT films as shown in Fig. 4a. The typical symmetric “butterfly” curves were observed for all samples. The abrupt drop of the dielectric constant in (111) orientation may be indicative of the characteristic of 180° domain wall motion, and the less abrupt curve in (100)-oriented films seems to be the effect

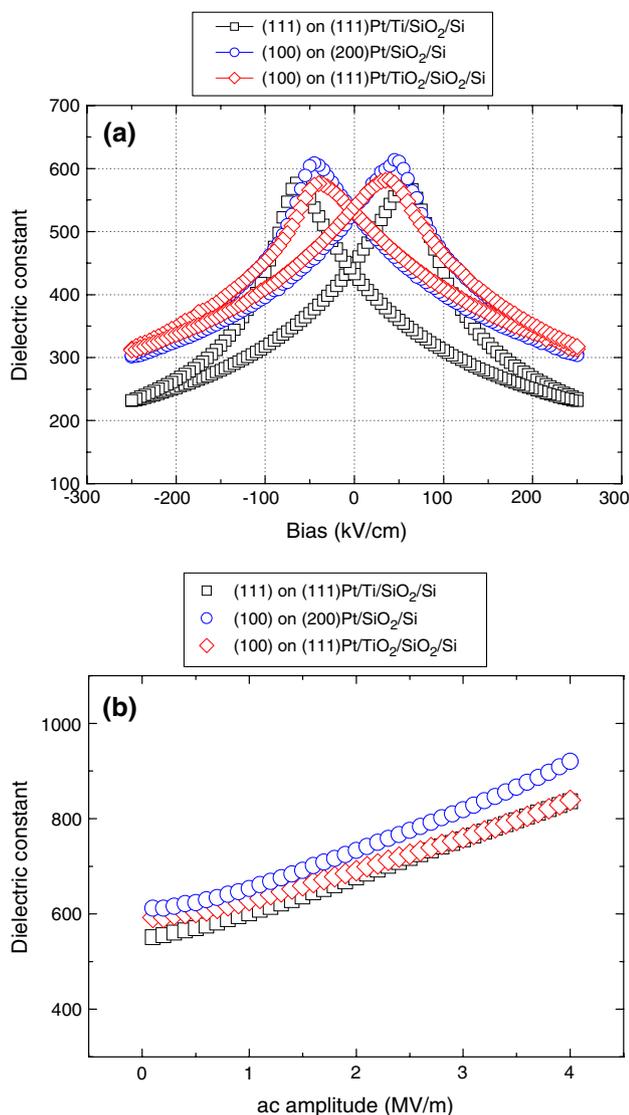


Fig. 4 (a) Field dependence of the dielectric constant with different orientations and (b) the AC field dependence of dielectric constant for different orientations

of 90° domains, which is consistent with the P – E hysteresis loop. The domain wall contribution to dielectric response of ferroelectric materials is known to be characterized by observing nonlinear behavior at subcoercive field because of the domain wall's response to weak dynamic fields [5, 17]. This nonlinear behavior can be described by the Rayleigh law, originally discovered in ferromagnetic materials. For ferroelectric materials, the Rayleigh law can be described as the following equation:

$$\varepsilon(E) = \varepsilon_0\varepsilon_{\text{init}} + \varepsilon_0\alpha E \quad (2)$$

where E denotes the applied electric field below the coercive field, ε_0 the permittivity of free space, $\varepsilon_{\text{init}}$ the initial permittivity, and α the Rayleigh constant. The Rayleigh constant can be determined by measuring the amplitude dependence of the small signal permittivity. From a linear fit to the above equation, the Rayleigh constant and the initial permittivity can be determined from the slope and intercept, respectively. Figure 4b shows the dependence of AC amplitude on the dielectric constant for three samples. The Rayleigh constants determined from the slope of this plot show relatively similar values. The Rayleigh constants were 6.7×10^{-16} F/V for (111) PZT on (111)Pt/Ti/SiO₂/Si, 5.9×10^{-16} F/V for (100) PZT on (111)Pt/TiO₂/SiO₂/Si, and 7.1×10^{-16} F/V for (100) PZT on (200)Pt/SiO₂/Si. Although the difference is not significant, the Rayleigh constant of (100) PZT films grown on (200)Pt by employing the layer-by-layer process appears to be higher than that of (100) PZT grown by one-crystallization. Since (100) PZT on (111) Pt substrate was obtained by removing high temperature annealing step per each layer, there may be the possibility of more organic residue in this film and/or more defects due to less thermal treatment, and an eventually smaller Rayleigh constant. According to theory of Bosser [18], the Rayleigh constant could have the following relationship, and this relationship can be used for the behavior of ferroelectric materials [19]:

$$\alpha \propto \frac{F_D}{L_D N} \quad (3)$$

where F_D denotes the domain wall area, L_D the average distance between domain walls, and N the defect concentration. From this equation, the existence of defects affects the domain wall and causes defect interaction, thus a reduction of domain wall mobility.

In order to quantitatively evaluate the intrinsic and extrinsic contribution to the dielectric response, the temperature dependence of the dielectric constant was performed as shown in Fig. 5. Since domain wall motion is a thermally activated process, it is possible to extract the intrinsic response by freezing out the extrinsic component of the polarization and dielectric response at low temperatures

approaching zero Kelvin [20]. Therefore the piezoelectric and dielectric properties measured near zero Kelvin could be completely from the intrinsic contribution, since the behavior of the dielectric constant with temperature shows a reasonably linear relationship. The intercept at 0 K, then, was determined as an intrinsic dielectric constant. The intrinsic dielectric constants determined by intercept of Fig. 5 are ~230 for (111) PZT on (111)Pt/Ti/SiO₂/Si, ~255 for (100) PZT on (111)Pt/TiO_x/SiO₂/Si, and ~280 for (100) PZT on (200)Pt/SiO₂/Si. In principle, the dielectric constant in tetragonal PZT is (100) > (111) > (001). Therefore, the higher dielectric constant of (100)-oriented PZT means the existence of an appreciable amount of a-domain in this polycrystalline film. In addition, the difference of two (100)-oriented PZT films indicates that the measured intrinsic dielectric constant in polycrystalline may depend on the crystallinity, domain configuration, and defects. It is important to state that the intrinsic contribution is also dependent on the materials' parameters even though its dependence is somehow weaker in comparison with extrinsic contribution.

3.3 Piezoelectric properties

Figure 6a shows the DC field dependence of effective $d_{33,f}$ for PZT films with different orientations. It was found that the effective remanent piezoelectric coefficients ($d_{33,f}$) are ~40 pm/V for (111) PZT on (111)Pt/Ti/SiO₂/Si, ~35 pm/V for (100) PZT on (111)Pt/TiO_x/SiO₂/Si, and ~44 pm/V for (100) PZT on (200)Pt/SiO₂/Si.

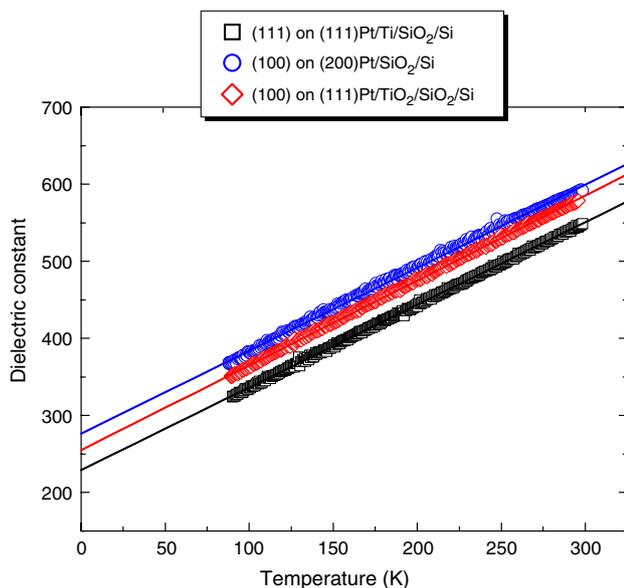


Fig. 5 Temperature dependence of dielectric constant of PZT films with different crystallographic orientations

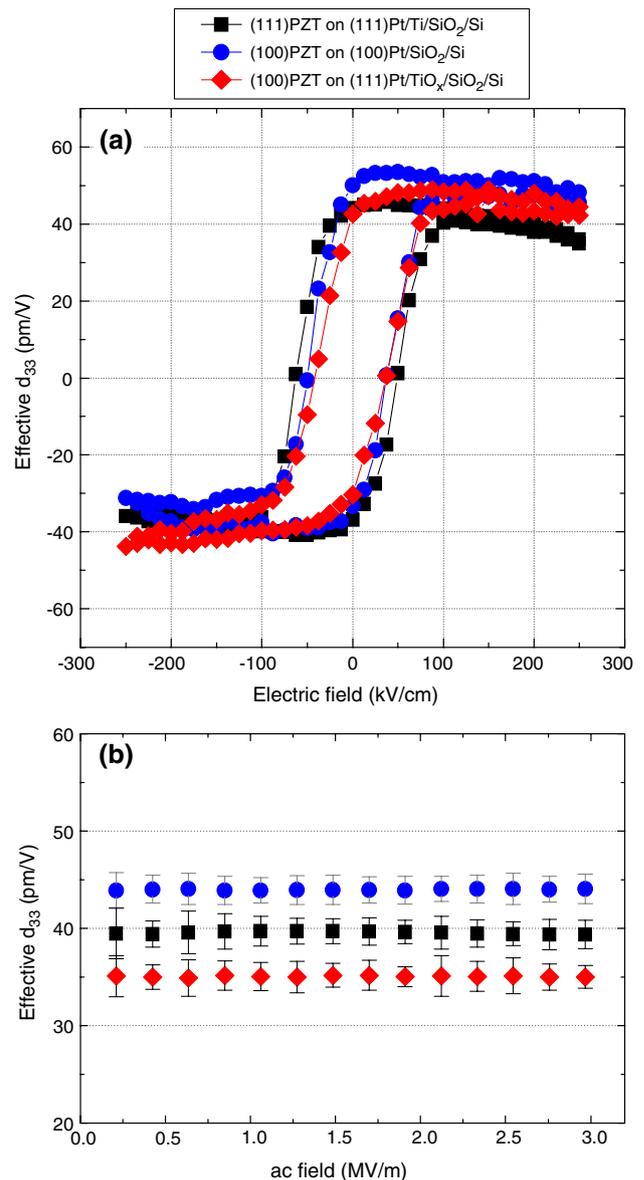


Fig. 6 (a) The piezoelectric hysteresis loops and (b) nonlinear response of effective $d_{33,f}$ for PZT films with different orientations measured by laser interferometry

Due to difficulty in separating the intrinsic and extrinsic contributions to $d_{33,f}$ in thin films, an investigation of nonlinearity has been suggested to evaluate the domain wall, which is the main source for extrinsic contribution to $d_{33,f}$. When non-180° domain walls move, the consequence of an irreversible component of this movement is that a nonlinear and hysteretic piezoelectric response is induced, even at relatively low external electric fields and pressure [21]. Therefore, nonlinear behavior is observed when non-180° domain wall motion contributes to the piezoelectric response. Figure 6b shows the piezoelectric coefficient $d_{33,f}$ measured as a function of the amplitude of AC field for PZT thin films with different orientations. These films did

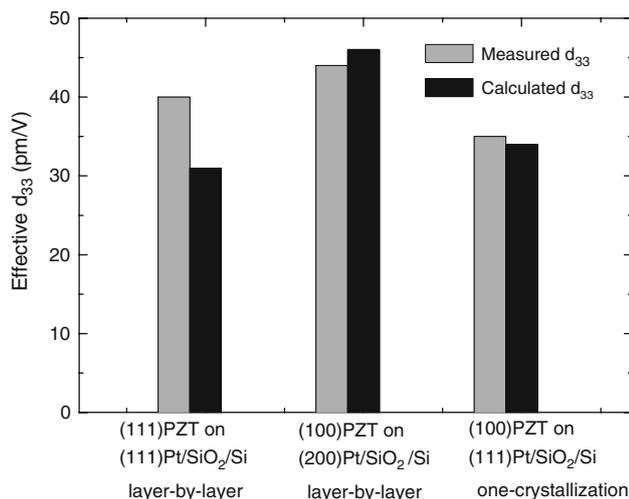


Fig. 7 The comparison of effective $d_{33,f}$ determined from measurement and estimated from calculation based on a modified phenomenological equation

not show increases in the $d_{33,f}$ with an increase of AC amplitude. This result suggests that non-180° domain wall motion in response to the applied field is negligible or at least significantly clamped under this measurement condition in these polycrystalline films, irrespective of orientation.

Since extrinsic contribution appears to be negligible in these films, the longitudinal piezoelectric coefficient d_{33} , can be described after modifying Eq. 1 as [22]

$$d_{33} = 2\varepsilon_0\varepsilon_{\text{int}}Q_{33}P(E) \quad (4)$$

Since (100)-oriented PZT film has a different mechanical boundary condition, the effective electrostrictive coefficient for (100)-oriented PZT film is calculated. The electrostrictive coefficient for (100)-oriented PZT(30/70) is calculated to have $\sim 5.6 \times 10^{-2} \text{ m}^4/\text{C}^2$, while (111)-oriented PZT(30/70) has $\sim 3.1 \times 10^{-2} \text{ m}^4/\text{C}^2$ [23]. When considering the polarization value and the intrinsic constant, the piezoelectric response is expected to be smaller in (100)-oriented film. Therefore, the higher electrostrictive coefficient value for (100)-oriented PZT may be responsible for the larger piezoelectric coefficients in (100)-oriented PZT films when domain wall motion is limited. Figure 7 shows the comparison of the effective $d_{33,f}$ determined from piezoelectric hysteresis loop with calculated $d_{33,f}$ from a modified phenomenological equation. (100)-oriented films show similar values between measured and calculated d_{33} , while (111)-oriented film shows deviation. Such deviation might result from the error in estimating intrinsic permittivity due to the experimental limit of approaching 0 K and/or due to the AC electric field-induced movement of 180° domain walls that contribute to $d_{33,f}$ [24]. Again, the difference of piezoelectric coefficient in two (100)-oriented PZT films may be

attributed to possibly different crystallinity, domain configuration and defects derived by different process conditions.

4 Conclusions

Tetragonal PZT films with different orientations were obtained on platinized silicon substrates. By choosing appropriate substrates and controlling the thermal process, (111) and (100)-oriented PZT films were successfully grown. The strongest (111)-oriented PZT films were grown on (111)-oriented Pt/Ti/SiO₂/Si substrates. The substrates without Ti-interlayer show less degree of (111) orientation, which implies that platinum may not be sufficient enough to provide (111) nucleation sites. (111) orientation in PZT films was maximized when (111) nuclei at the substrate are the most energetically favorable and growth of PZT film is controlled by nucleation. When the energy barrier for (111) nucleation is not effectively lowered, (100) nuclei of PZT films become dominant, which leads to bigger grain size in microstructure.

The dependence of orientation on piezoelectric, ferroelectric, and dielectric properties was investigated. The property difference between (111) and (100)-oriented films appears to be induced by the effect of ferroelastic domain existence (90° domain in tetragonal composition), which results in lower polarization, higher dielectric constant, and piezoelectric response. From a modified phenomenological equation, the higher electrostrictive coefficient value for (100)-oriented PZT may be responsible for the larger piezoelectric coefficients in (100)-oriented PZT films. It was also observed that two (100)-oriented films prepared by different heat treatment methods have different values in piezoelectric, dielectric and ferroelectric properties even though only (100) orientation exists for both cases. Therefore, the process-induced difference, such as crystallinity, poly-domain configuration, and defects concentration, may also play an important role in determining both intrinsic and extrinsic contribution to the properties, even though these parameters seem to be more influential on extrinsic components such as domain wall motion.

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References

1. J.F. Nye, *Physical Properties of Crystals: Their Representation by Tensors and Matrices* (Oxford University Press, Oxford, 1985)
2. X.-H. Du, J. Zheng, U. Belegundu, K. Unchino, *Appl. Phys. Lett.* **72**, 2421 (1998). doi:10.1063/1.121373

3. X.-H. Du, U. Belegundu, K. Uchino, *Jpn. J. Appl. Phys.* **36**, 5580 (1997). doi:[10.1143/JJAP.36.5580](https://doi.org/10.1143/JJAP.36.5580)
4. S. Hiboux, P. Muralt, *Ferroelectrics* **224**, 315 (1999). doi:[10.1080/00150199908210582](https://doi.org/10.1080/00150199908210582)
5. D.V. Taylor, D. Damjanovic, *J. Appl. Phys.* **82**, 1973 (1997). doi:[10.1063/1.366006](https://doi.org/10.1063/1.366006)
6. T. Oikawa, M. Aratani, H. Funakubo, K. Saito, M. Mizuhira, *J. Appl. Phys.* **95**, 3111 (2004). doi:[10.1063/1.1645646](https://doi.org/10.1063/1.1645646)
7. S.-H. Kim, D.-J. Kim, S.K. Streiffer, A.I. Kingon, *J. Mater. Res.* **14**, 2476 (1999). doi:[10.1557/JMR.1999.0332](https://doi.org/10.1557/JMR.1999.0332)
8. P. Muralt, T. Maeder, L. Sagalowicz, S. Hiboux, S. Scalese, D. Naumovic, R.G. Agostino, N. Xanthopoulos, H.J. Mathieu, L. Patthey, E.L. Bullock, *J. Appl. Phys.* **83**, 3835 (1998). doi:[10.1063/1.366614](https://doi.org/10.1063/1.366614)
9. T. Tani, Z. Xu, D.A. Payne, in *Materials Research Society Symposium*, ed. by E.R. Myers, B.A. Tuttle, S.B. Desu, P.K. Larsen (Materials Research Society, Boston, MA, 1993), p. 269
10. K.G. Brooks, I.M. Reaney, R. Klissurska, Y. Huang, L. Bursill, N. Setter, *J. Mater. Res.* **9**, 2540 (1994). doi:[10.1557/JMR.1994.2540](https://doi.org/10.1557/JMR.1994.2540)
11. S.-Y. Chen, I.-W. Chen, *J. Am. Ceram. Soc.* **77**, 2332 (1994). doi:[10.1111/j.1151-2916.1994.tb04602.x](https://doi.org/10.1111/j.1151-2916.1994.tb04602.x)
12. D.J. Wouters, G. Willems, E.-U. Lee, H.E. Maes, *Integr. Ferroelectr.* **15**, 79 (1997). doi:[10.1080/10584589708015698](https://doi.org/10.1080/10584589708015698)
13. G.R. Fox, in *Materials Research Society Symposium*, ed. by R.W. Schwartz, P.C. McIntyre, Y. Miyasaka, S.R. Summerfelt, D. Wouters (Materials Research Society, Boston, MA, 2000), p. 205
14. S.-H. Kim, D.-Y. Park, H.-J. Woo, D.-S. Lee, J. Ha, C.S. Hwang, I.-B. Shim, A.I. Kingon, *Thin Solid Films* **416**, 264 (2002). doi:[10.1016/S0040-6090\(02\)00726-5](https://doi.org/10.1016/S0040-6090(02)00726-5)
15. M.J. Haun, *Thermodynamic Theory of the Lead Zirconate–Titanate Solid Solution System* (The Pennsylvania State University, University Park, PA, 1998)
16. R.E. Garcia, B.D. Huey, J.E. Blendell, *J. Appl. Phys.* **100**, 064105 (2006). doi:[10.1063/1.2336073](https://doi.org/10.1063/1.2336073)
17. D. Damjanovic, *J. Appl. Phys.* **82**, 1788 (1997). doi:[10.1063/1.365981](https://doi.org/10.1063/1.365981)
18. O. Boser, *J. Appl. Phys.* **62**, 1344 (1987). doi:[10.1063/1.339636](https://doi.org/10.1063/1.339636)
19. D. Bolten, U. Boettger, T. Schneller, M. Grossmann, O. Lohse, R. Waser, *Appl. Phys. Lett.* **77**, 3830 (2000). doi:[10.1063/1.1331353](https://doi.org/10.1063/1.1331353)
20. Q.M. Zhang, H. Wang, N. Kim, L.E. Cross, *J. Appl. Phys.* **75**, 454 (1994). doi:[10.1063/1.355874](https://doi.org/10.1063/1.355874)
21. A. Kholkin, *Ferroelectrics* **238**, 799 (2000). doi:[10.1080/00150190008008789](https://doi.org/10.1080/00150190008008789)
22. D.-J. Kim, J.-P. Maria, A.I. Kingon, S.K. Streiffer, *J. Appl. Phys.* **93**, 5568 (2003). doi:[10.1063/1.1566478](https://doi.org/10.1063/1.1566478)
23. D.-J. Kim, *Piezoelectric and Ferroelectric Properties of Lead Zirconate Titanate Thin Films* (North Carolina State University, Raleigh, NC, 2001)
24. S. Trolrier-McKinstry, N.B. Gharb, D. Damjanovic, *Appl. Phys. Lett.* **88**, 202901 (2006). doi:[10.1063/1.2203750](https://doi.org/10.1063/1.2203750)