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Thickness dependence of submicron thick $Pb(Zr_{0.3}Ti_{0.7})O_3$ films on piezoelectric properties

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Abstract

The effects of thickness on the piezoelectric and electric properties of tetragonal composition, polycrystalline, (1 1 1)-textured $Pb(Zr_{0.3}Ti_{0.7})O_3$ films are investigated. The effective piezoelectric coefficient d_{33} is characterized by a double-beam laser interferometer and is measured to increase with film thickness although extrinsic contribution such as 90° domain wall motion is negligible from the nonlinearity of piezoelectric coefficient. Constituent parameters to affect piezoelectric coefficient such as polarization and dielectric properties were analyzed based on the semiempirical phenomenological equation. The effectiveness of poling was also evaluated as a function of film thickness. These results present that the increase of effective d_{33} in these tetragonal PZT films can be mainly due to enhanced intrinsic contributions.

Keywords: A. Sol–gel processes; C. Piezoelectric properties; D. PZT

1. Introduction

The development of microelectromechanical systems (MEMS) such as microsensors and microactuators with Si-based circuitry in small-size devices has recently become an important area in microelectronics. Ferroelectric $Pb(Zr_xTi_{1-x})O_3$ (PZT) films can offer an attractive option for MEMS technology due to superior piezoelectric and pyroelectric properties. In order to use these materials to their full potential, thorough and systematic research of their properties is needed.

In case of piezoelectric properties of PZT films, the piezoelectric coefficients have been measured to be smaller than those of bulk PZT. It has been proposed that the reduced piezoelectric effect in thin films can be attributed to limited extrinsic contribution and the substrate clamping [1–3]. There are several previous reports to investigate thickness dependence of ferroelectric materials. By studying piezoelectric nonlinear response, different non-180° domain wall activities in PZT thick films were reported [4]. Similarly, Xu et al. reported that extrinsic contribution to d_{33} was negligible for fine grain PZT (52/48) films with film thickness less than 2 μm [3]. In case of submicron thickness range, the increased piezoelectric response with increasing film thickness was also reported in the literature. Chu et al. observed the increases of piezoelectric coefficients in PZT (52/48) films with film thickness [5]. They explained that the drastic change of piezoelectric coefficients below submicron thickness range may be due to the strong clamping effect originating from the thermal mismatch between Pt bottom electrode and PZT films or changes in film microstructure. Hiboux et al. reported the effect of the thickness on d_{33} for (1 0 0)-textured PZT (45/55) films in the thickness range between 280 and 1300 nm. The increased d_{33} was explained in terms of enhanced domain wall contributions [6]. Park et al. observed the increased piezoelectric coefficients of {1 0 0}-fiber textured lead magnesium niobate–lead titanate (PMN-PT) (70/30) with film thickness between 0.25 and 2.1 μm [7]. Despite qualitative agreements among the previous reports, there is still lack of quantitative evaluation to explain

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the thickness dependence of piezoelectric coefficients especially where the extrinsic contribution is limited, *i.e.* submicron thickness range, non-MPB composition, etc.

It is well known that the piezoelectric response of ferroelectrics originates from both intrinsic and extrinsic sources [8,9]. The intrinsic contribution refers to the lattice contribution from the displacements of the 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_{ijl}) can be expressed as a function of polarization (P_k), relative permittivity (ε_{kl}), and electrostrictive coefficient (Q_{ijkl}) according to the following equation:

$$d_{ijl} = 2\varepsilon_0 \varepsilon_{kl} Q_{ijkl} P_k \quad (i, j, k = 1, 2, 3) \tag{1}$$

The analysis of the piezoelectric properties in PZT films can be performed by comparing the measured and calculated piezoelectric response from the constituent parameters such as polarization, dielectric constant, and electrostrictive coefficient.

In this article, we have systematically studied the effects of film thickness below submicron thickness range on the effective longitudinal piezoelectric coefficients of tetragonal PZT films. Quantitative approach to analyze intrinsic and extrinsic contributions to piezoelectric behavior has been attempted. In addition, possible factors such as effectiveness of poling, the influence of an interface, and residual stress are discussed.

2. Experimental procedure

The $Pb(Zr_{0.3}Ti_{0.7})O_3$ (PZT) films were prepared by a sol–gel process. The Pb, Zr, and Ti precursors are on lead acetate trihydrate $[Pb(O_2C_2H_3)_2 \cdot 3H_2O]$, titanium isopropoxide $[(Ti(OC_3H_7)_4]$, and zirconium *n*-propoxide $[Zr(OC_3H_7)_4]$. Methanol was used as a solvent for all precursors, and alkanolamine is used as a chelating agent [10]. 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 (1 1 1)-oriented Pt/Ti/SiO_2/Si. After spin coating, pyrolysis was performed 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 after coating of several layers to obtain the desired film thickness.

Film crystallinity and orientation were assessed by X-ray diffraction (Rigaku D/MAX B) using Cu Kα radiation. Scanning probe microscopy (Digital Instruments, Dimension 3000) was used to examine surface topography. 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} 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} 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 vacuum. The heating and cooling rate was approximately 18 K/min.

3. Results and discussion

3.1. Structural and texture analysis

The structural and texture analysis were performed using an X-ray diffraction. Fig. 1 shows the X-ray patterns for tetragonal PZT (30/70) films grown on Pt(1 1 1)/Ti/SiO_2/Si substrates as a function of film thickness ranging between 150 and 600 nm. Non-perovskite phases such as fluorite phase or pyrochlore phase were not observed within a detection limit. Since piezoelectric and ferroelectric properties of PZT films are very sensitive to the texture, a high degree of orientation is necessary to isolate physical properties by simplifying the systems' crystallography. In these tetragonal PZT films prepared by optimized sol–gel technique, only (1 1 1) peaks with high degree orientation were observed.

The film surface microstructure was investigated using an atomic force microscopy as shown in Fig. 2. Dense and uniform microstructures were observed for all these PZT films. The

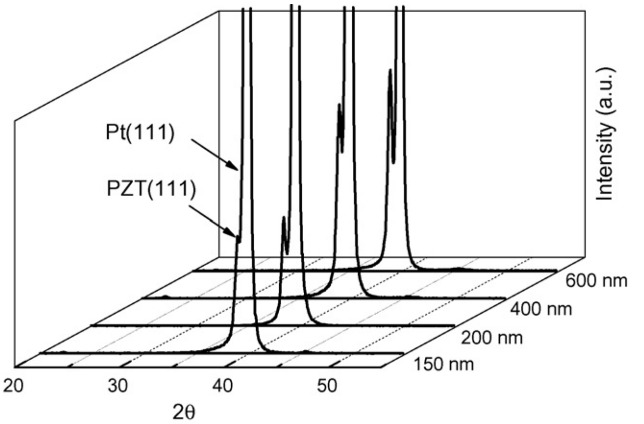

Fig. 1. X-ray patterns of tetragonal PZT (30/70) with film thickness. All PZT films were grown on (1 1 1)-textured Pt/Ti/SiO_2/Si.

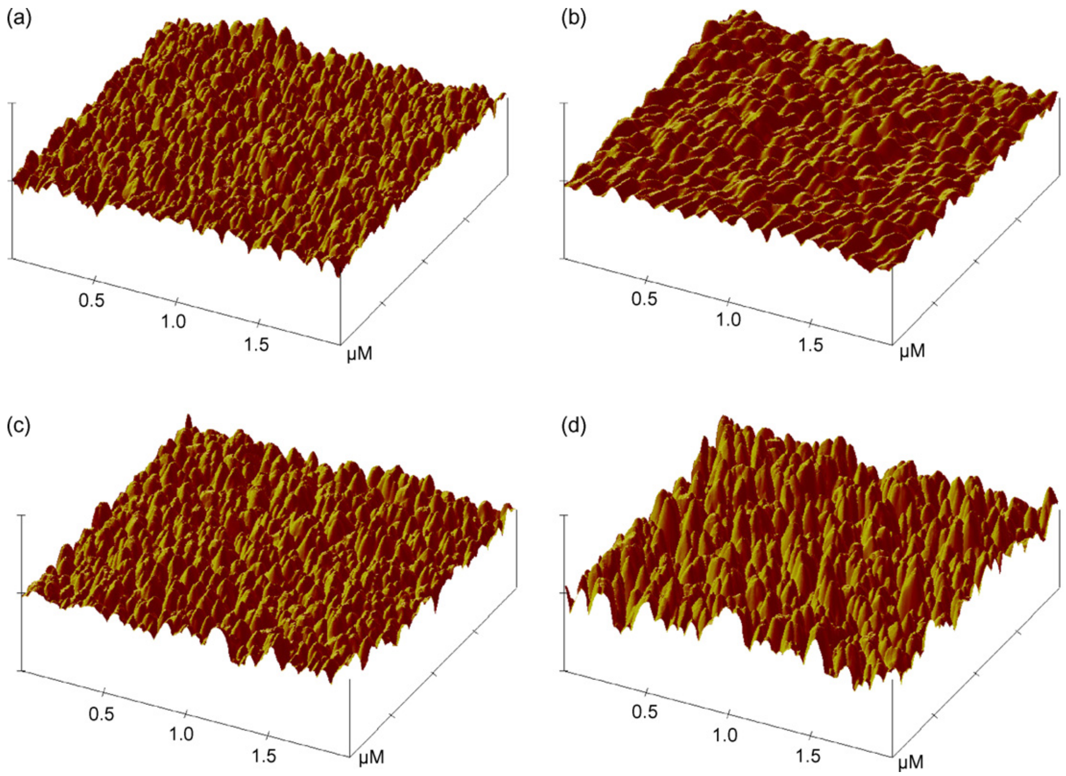

Fig. 2. AFM topography of PZT (30/70) for different film thickness: (a) 150 nm, (b) 200 nm, (c) 400 nm, and (d) 600 nm.

average grain size increases slightly from 70 to 110 nm with film thickness. The surface roughness (rms value) also slightly increases from 2.5 to 4.1 nm. Although subtle change occurs with film thickness, the microstructure and the degree of texture are reasonably consistent.

3.2. *Evaluation of piezoelectric response*

3.2.1. *Ferroelectric polarization*

The polarization hysteresis loops for different thickness were measured at maximum driving field of 250 kV/cm as shown in Fig. 3. All films show quite square hysteresis loops and abrupt switching near coercive field. As film thickness increases, the remanent and saturation polarization values at the same field slightly increase with increasing film thickness, and the slope at E_c becomes steeper. Subtle E_c decrease with increasing thickness was also observed. The values of P_r are 23, 24.2, 25, and 25.4 $\mu C/cm^2$ for 150, 200, 400, and 600 nm, respectively. It is speculated that this polarization behavior be from reduced interfacial effect with increasing film thickness. It has been suggested that the effect of dead layer which is an insulating and non-ferroelectric layer formed at the ferroelectric/electrode interface on the ferroelectric polarization behavior. Tagantsev et al. suggested that the dead layer is responsible for a shearing of the hysteresis loop [11]. The existing dead layer is proposed to explain the increase of E_c with decreasing thickness [12]. The electric field within the intrinsic dead layer is much larger than the average field throughout the film due to its low dielectric nature of dead layer. The charge injection from the electrode above a threshold field will occur, thereby leading to screening charges for the polarization in the core of the film. Therefore, enhanced interfacial effect with decreasing film thickness results in slanted hysteresis loop and higher coercive field consistent with the result.

3.2.2. *Dielectric properties*

The temperature dependence of dielectric constant was performed to quantitatively evaluate intrinsic and extrinsic contribution to the dielectric response as shown in Fig. 4. Since domain wall motions are thermally activated process, it is

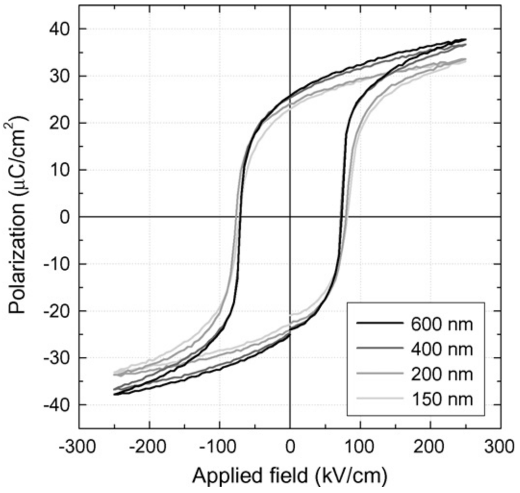

Fig. 3. Ferroelectric hysteresis loops measured at maximum driving field of 250 kV/cm for each thickness.

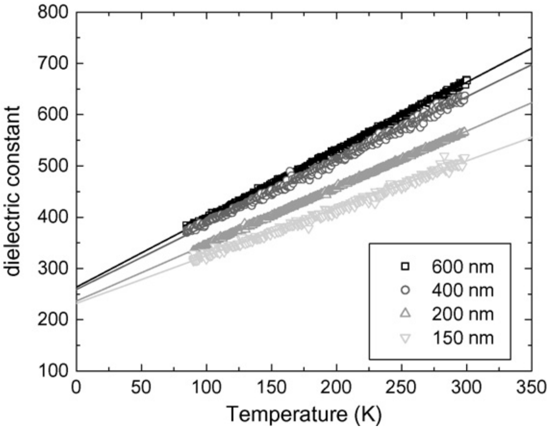

Fig. 4. Temperature dependence of dielectric constant for different film thickness.

possible to extract the intrinsic response by freezing out the extrinsic component of the polarization and dielectric response at lower temperature approaching 0 K [13,14]. Therefore the dielectric properties measured near 0 K could be completely from the intrinsic contribution. Since the behavior of the dielectric constant with temperature shows 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. 4 increase with thickness from ~225 to ~265.

To verify the domain wall contribution to dielectric response as a function of PZT composition, ac amplitude dependence was investigated. It is known that the domain wall contribution to dielectric and piezoelectric properties of ferroelectric materials can be characterized by observing nonlinear behavior at subcoercive field because the domain walls response to weak dynamic fields [15,16]. 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:

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

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 is the Rayleigh constant. The Rayleigh constant can be determined by measuring the amplitude dependence of the small signal permittivity. From a linear fit to above equation, the Rayleigh constant and the initial permittivity can be determined from the slope and intercept, respectively. Fig. 5(a) shows the result of amplitude dependence of dielectric constant as a function of thickness. The Rayleigh constants for different thickness are determined from the slope of Fig. 5(a) and these values are shown in Fig. 5(b). The increase of Rayleigh constant was observed as the film thickness increases. This indicates that the enhanced domain wall activity is responsible for increased dielectric constant at room temperature as the film thickness increases. As will be shown in Section 3.2.3, non-180° domain (90° domain in tetragonal PZT) wall motion for these films is negligible. It is believed that the extrinsic contribution to dielectric constant is mostly from 180° domain wall motion. Therefore, it is speculated that the existence of interface layers and the constraint imposed by the substrate have an influence on both the intrinsic and domain wall contribution to the dielectric response of PZT films.

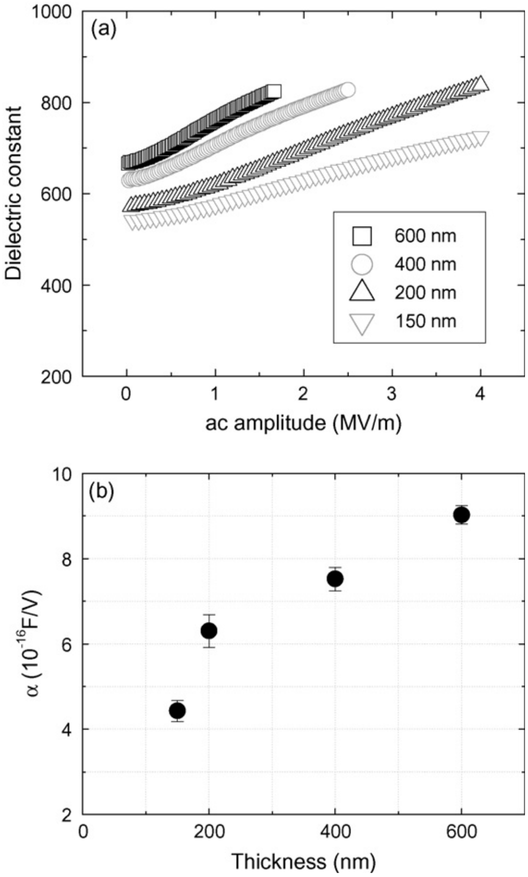

Fig. 5. (a) Field dependence of dielectric constant at different film thickness and (b) calculated Rayleigh constant for each thickness.

3.2.3. Piezoelectric properties

Fig. 6 shows the dc field dependence of effective d_{33} on thickness for these PZT (30/70) films. It was found that the effective piezoelectric coefficients (d_{33}) increased with increasing film thickness from 34 to 48 pm/V between 150 and 600 nm. All piezoelectric hysteresis loops showed square shape and better squareness was achieved with increasing thickness consistent with P–E hysteresis loop.

There have been several reports that effective d_{33} increases with film thickness [3,5,6]. However, it is difficult to find detailed explanations why d_{33} increase with submicron thick PZT films. Reduced extrinsic contribution with decreasing film thickness is used as a general statement. Therefore, a detail analysis was performed to find dominant factors on piezoelectric response for PZT thin films especially below submicron thickness range. Due to difficulty in separation of intrinsic and extrinsic contribution to d_{33} in thin films, Rayleigh law has been suggested to evaluate domain wall (extrinsic) contribution to d_{33} in thin film. When non-180° domain walls move, the consequence of irreversible component of this movement induces a nonlinear and hysteretic piezoelectric response, even

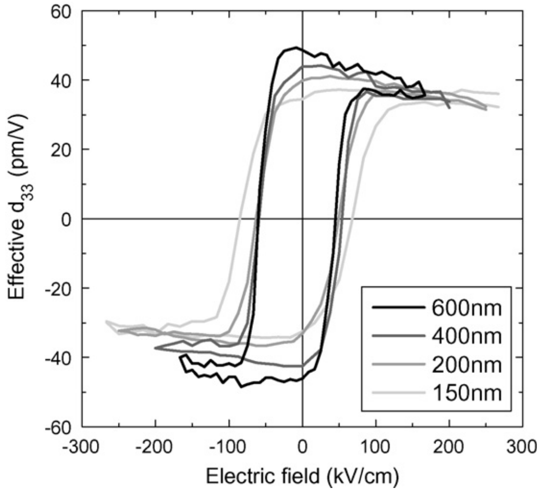

Fig. 6. The piezoelectric hysteresis loops of effective d_{33} for PZT films with different film thickness measured by a double beam laser interferometry.

at relatively low external electric fields and pressure [19,21]. Therefore, nonlinear behavior is observed when non-180° domain wall motion contributes to the piezoelectric response.

In order to investigate the effect of non-180° domain wall contribution, piezoelectric coefficient d_{33} is measured as a function of the amplitude of ac field for PZT thin films with different thickness as shown in Fig. 7. There was no increase of the d_{33} with an increase of ac amplitude. This result suggests that non-180° domain wall motion in response to the applied field is negligible in this thickness range for these tetragonal PZT films. Similar behavior was observed in the PZT thin films at the MPB composition prepared by sol–gel methods [3]. In addition, it has been reported that the nonlinearity of tetragonal composition is more strongly suppressed as compared to morphotropic phase boundary and rhombohedral composition [4]. When considering crystallographic orientation, 90° domain wall motions for ideally (1 1 1) oriented tetragonal films does not produce any mechanical strain because all the allowed polarization vectors have equal projections onto the substrate normal [21]. Therefore, it is quite reasonable that these tetragonal PZT thin films have quite limited domain wall contribution. The increasing piezoelectric response is mainly the result of enhanced intrinsic contribution.

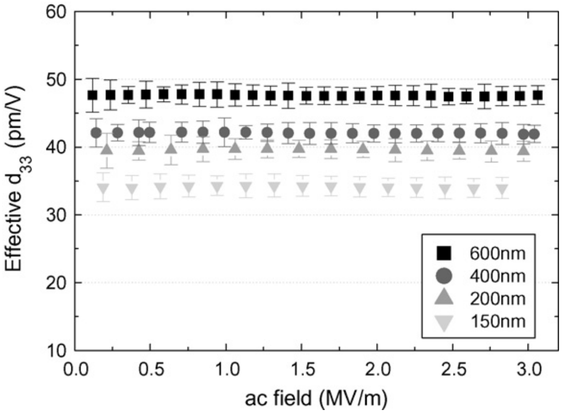

Fig. 7. The dependence of ac driving field on the piezoelectric response of PZT films with different film thickness.

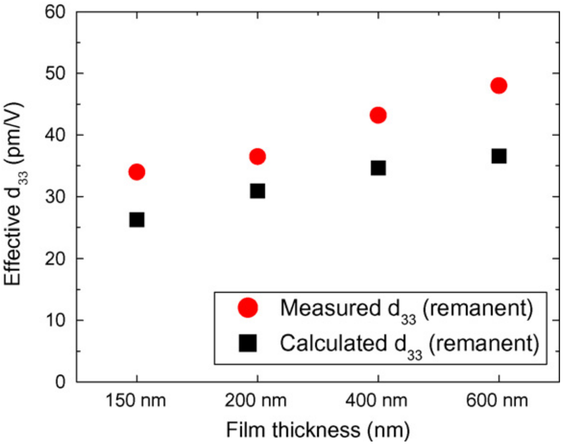

Fig. 8. The comparison of calculated and measured effective d_{33}.

Since no extrinsic contribution exist in these films, the longitudinal piezoelectric coefficient d_{33} can be described as $d_{33} = 2\varepsilon_0\varepsilon_{\text{init}}\tilde{Q}_{33}^{(1\,1\,1)}P(E)$ from the semiempirical phenomenological theory [9]. From the polarization measurement, the remanent polarization was increased from 23 to 25.4 μC/cm^2. The temperature dependence of dielectric constant shows the increase of intrinsic dielectric constant from around 205 to 265. The effective electrostrictive coefficient for PZT (30/70) is calculated as 0.0307 m^4/C^2 [9]. Fig. 8 shows the comparison between measured d_{33} determined from piezoelectric hysteresis loop and calculated d_{33} based on a modified phenomenological equation. Although there is a gap between two values, the increase of d_{33} can be explained in terms of intrinsic contribution to piezoelectric coefficient. The difference between two effective d_{33} values may result from errors in estimating intrinsic dielectric constants due to constraints of reaching 0 K, and/or underestimation of calculated electrostrictive coefficients due to absence of elastic constants in the single crystal PZT for the observed composition.

Beyond this comparison, it is necessary to consider other factors attributable to piezoelectric response because the stability of poly-domain configuration is very important for polycrystalline PZT materials. In another word, parameters affecting better domain alignments along the electric field should be considered. It is well known that ferroelectric materials need to be poled for piezoelectric applications since the individual domains of unpoled ferroelectrics are canceled by averaging over all possible domain configurations. The mechanism of poling is not yet clearly understood in thin films, but the poling is known to improve the piezoelectric coefficients, thereby reduce the aging of piezoelectric response [17,18]. Since the poling is accompanied by the voltage shift in the polarization hysteresis loop, the voltage shift after poling test indicates the degree of domain stabilization of one direction over the other one, the poling test for different thickness was performed to observe the efficiency of poling. Fig. 9 shows voltage shift of PZT with film thickness at same voltage. Even at same voltage, the voltage shift was increased

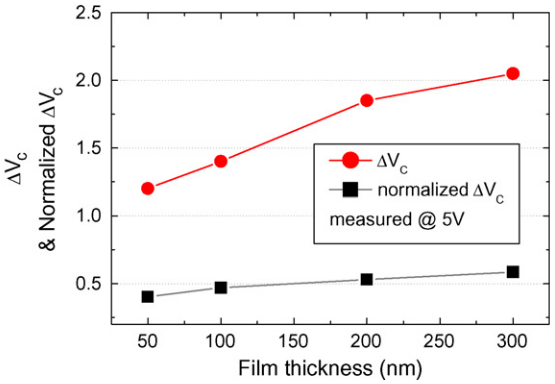

Fig. 9. The voltage shift with film thickness of PZT thin films after poling test. The poling test was performed by keeping the PZT films in a $+P_r$ or $-P_r$ state and then heating it a predetermined time for 4400 s at 150 °C.

with film thickness. When the voltage shift is normalized on the basis of initial coercive voltage, this trend does not change. This result suggests that aligning of the ferroelectric domains along the field direction is more effective with film thickness. Although the poling (known as ''imprint'') mechanisms in thin film PZT is not clearly understood, but the effectiveness of poling with thickness may be explained by the change of residual stress. The total residual stress developed in the thin film can be categorized as either intrinsic or extrinsic stress [19]. The intrinsic stress (also growth stress) arise from the volume changes accompanying phase transformation at the transition temperature, the formation of grain boundaries during crystal growth, microvoids or gas entrapment in the films, and the shrinkage due to evaporation and pyrolysis of organic species during heat treatment. The extrinsic stress is induced by the lattice mismatch between thermal expansion coefficients of the film and substrate. The residual stress resulting from thermal expansion mismatch between the PZT film, Pt electrodes, and underlying Si substrate was found to be the order of ~1 GPa [20]. This may be sufficiently large such that spontaneous polarization is expected to be confined to the plane of the film, thereby no distinguishable components of remanent polarization in the film normal direction can occur, for any field less than the breakdown field, applied normal to the film [21].

In chemical solution derived ferroelectric films, Sengupta et al. has demonstrated the stress development as a function of film thickness using lead titanate films. As the number of coating layers increase, i.e., the increase of thickness, they observed that residual stress of lead titanate films changes from tensile stress to compressive stress [22]. It is believed that the tensile stress stabilizes domains oriented parallel to the plane of the layers; whereas compressive stress favors polarization alignment perpendicular to the substrate [23]. Kumazawa et al. have also demonstrated that both the remanent and spontaneous polarizations decreased when the PZT film was loaded with tensile stress [24]. Therefore, it can be speculated that the stress development towards less tensile and/or compressive state with film thickness may facilitate domain reversal with an external field and promote better efficiency of poling in the film normal direction.

4. Conclusions

The effects of film thickness below submicron thickness range on the effective longitudinal piezoelectric coefficients of polycrystalline, (1 1 1)-textured, tetragonal PZT (30/70) films have been investigated. A quantitative evaluation of ferroelectric and dielectric properties was performed to investigate intrinsic and extrinsic contribution. The general statement (''reduced non-180° domain wall motions with decreasing thickness'') for the explanation of decreased piezoelectric response with film thickness is found to be not appropriate for at least these PZT films below submicron thickness range. The reasons for the increase of longitudinal piezoelectric coefficients with increasing film thickness are primarily due to the increase of intrinsic contribution and improved efficiency of poling (this is also considered as the intrinsic contribution in polycrystalline film). Primary parameter responsible for increasing d_{33} is found to be increasing intrinsic dielectric constant based on a semiempirical phenomenological equation. We believed that the interfacial layers and residual stress are most important parameters to have an influence on intrinsic contribution to the piezoelectric response with film thickness for these PZT films.

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