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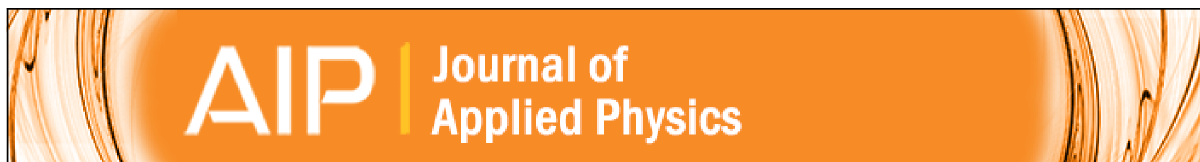

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Ferroelectric properties of $Pb(Zr,Ti)O_3$ films under ion-beam induced strain

Jung-Kun Lee[1,a)] and Michael Nastasi[2]
[1]*Department of Mechanical Engineering and Material Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, USA*
[2]*Nebraska Center for Energy Sciences Research, University of Nebraska, Lincoln, Nebraska 68583, USA*

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The influence of an ion-beam induced biaxial stress on the ferroelectric and dielectric properties of $Pb(Zr,Ti)O_3$ (PZT) films is investigated using the ion beam process as a novel approach to control external stress. Tensile stress is observed to decrease the polarization, permittivity, and ferroelectric fatigue resistance of the PZT films whose structure is monoclinic. However, a compressive stress increases all of them in monoclinic PZT films. The dependence of the permittivity on stress is found not to follow the phenomenological theory relating external forces to intrinsic properties of ferroelectric materials. Changes in the ferroelectric and dielectric properties indicate that the application of a biaxial stress modulates both extrinsic and intrinsic properties of PZT films. Different degrees of dielectric non-linearity suggests the density and mobility of non-180° domain walls, and the domain switching can be controlled by an applied biaxial stress and thereby influence the ferroelectric and dielectric properties. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4766413]

I. INTRODUCTION

The reversible polarization properties of lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) thin films makes this material very attractive for a number of potential applications including nonvolatile random access memories, micromechanical devices, and pyroelectric sensors. The reversible polarization and related ferroelectric properties of PZT can be altered through the application of mechanical stresses or an electric field.[1,2] Both theoretical and experimental studies have demonstrated that biaxial stress in thin films changes the polarization, permittivity, and Curie temperature of ferroelectrics.[3–5] Stress in ferroelectrics has also been found to change the extrinsic properties and related dielectric properties. It has been suggested that the different mechanical state of PZT films modifies the density and motion of non-180° domain walls and the polarization switching behavior to accommodate the strain, leading to a significant change in their piezoelectric and dielectric properties.[6–8] The contribution of the extrinsic parameters to an increase in the dielectric permittivity and tunability under biaxial tensile stress has been observed in other typical ferroelectric materials, $(Ba,Sr)TiO_3$ (BST).[9,10] Previous reports have also shown that mechanical stresses in ferroelectric films can affect the fatigue and imprint behavior, which have plagued the application of ferroelectric materials by changing the stability and the dynamics of domains under an external electric field.[11–13]

Intensive research has been performed to determine the complicated effects of extrinsic parameters in ferroelectric materials, thereby rekindling interest in the role of strain as an extrinsic driving force to overcome the barriers against the cooperative motion of ferroelectric dipoles. For example, $BaTiO_3$ and $SrTiO_3$ films epitaxially grown on $GdScO_3$ and $DyScO_3$ substrates show a several hundreds of degrees increase in Curie temperature (T_C) and produces room-temperature ferroelectricity, due to the strain generated by the lattice mismatch between the films and the substrates.[14,15] However, there is still a large technological barrier that inhibits the utilization and the study of strain in ferroelectric materials. The favored methods providing strain in films are to use epitaxial growth and the lattice mismatch between film and substrate and thermal stress differences between the grown thin films and the underlying substrates. In these approaches, the strain in films cannot be freely and systematically controlled due to several fundamental issues including the lack of appropriate substrates, the formation of dislocations, and the interfacial reactions that prevent effective transfer of uniform strain.[16] In addition, substrates that can apply sufficient strain to ferroic films are limited and sometimes include very rare and expensive components.[11,12]

To circumvent these issues, we exploited ion implantation induced strain in substrates to engineer a state of biaxial stress in PZT ferroelectric films on top of ion-implanted substrates. The structural disorder that is produced from the physical collision between implanted ions and host lattice during the ion implantation process expands the implanted region, which creates a state of biaxial compressive stress in the implanted region.[17] Hence, a film residing on a substrate that has been implanted will be placed in a state of biaxial stress, and the sign of the stress in the film will depend on which substrate side has been implanted. When the film-deposited face of the substrate is implanted, the film will be under tensile stress. In contrast, ion implantation into the opposite side of the substrate (non-film deposited face) induces a compressive biaxial stress in the film. This relationship between the stress state and the implanted substrate side is schematically shown in Fig. 1. The present work is devoted to exploring the effect of stress on the polarization switching, ferroelectric fatigue, dielectric properties, and domain

a)Author to whom correspondence should be addressed. Electronic mail: jul37@pitt.edu.

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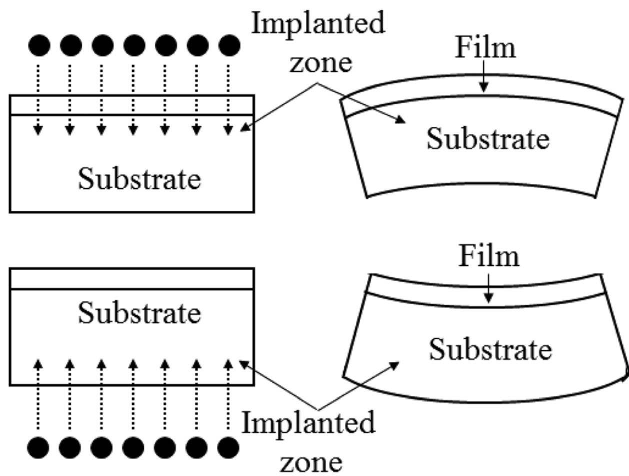

FIG. 1. Schematics showing a biaxial stress state of films on substrates which are exposed to ion implantation.

stability of PZT films whose biaxial stress state are engineered by using ion implantation. The experiments and phenomenological calculations show that the external stress triggers ferroelastic switching and changes domain configuration, leading to a variation in the ferroelectric and dielectric properties of stressed PZT films.

II. EXPERIMENTAL

PZT (Zr:Ti = 6:4) precursors were prepared from a metallorganic solution of lead acetate trihydrate, zirconium n-butoxide, and titanium isopropoxide in 2-methoxy ethanol solvent. To compensate for lead loss during the annealing, 10 mol. % excess lead was added to the precursor solution. The solutions were spin coated at 3000 rpm for 30 s and heat-treated on a hot plate at 350 °C for drying and organic pyrolysis. To control the preferred orientation of PZT films, 1500 Å Pt(200)/100 Å TiO_2/3000 Å SiO_2/Si substrates were used. Then, the intermediate heat-treatment was carried out to control the crystallization of PZT thin films at 600 °C for 5 min. This spin coating, drying, and intermediate heat-treatment were repeated until the final film thickness was about 2000 Å. The films were annealed at 700° for 60 min in ambient condition. The composition of thin films was confirmed from the quantitative analysis by the energy dispersive spectroscopy (EDS).

After the preferred orientation was confirmed by x-ray diffraction (XRD) analysis, the substrates containing PZT films with ⟨001⟩ preferred orientations were ion-implanted at room temperature with 300 keV He ions at a fluence of $1 \times 10^{16}/cm^2$. To change the sign of the implantation-induced stress, either the film deposited face or the opposite face of the substrate was implanted. The projected range was roughly 1.2 μm according to calculations using the SRIM 2003 code.[18] The change in the curvature of substrates during ion-implantation was measured by using a laser system and the Stoney equation.[19] Curvature measurement showed that an in-plane stress of about 300 MPa (or an in-plane strain of about 0.2%) is applied the PZT films following substrate implantation. The value was positive (tensile stress) when the He ions were implanted into PZT film surface of substrate and was negative (compressive stress) when implanted into the opposite side of substrate. After the top platinum electrode with the diameter of 200 μm was deposited, the ferroelectric properties of PZT films were characterized by RT66A ferroelectric tester (Radiant Technologies, USA). For P-E loop measurement, electric field with the peak amplitude of 250 kV/cm and the frequency of 1 MHz was applied to the films at room temperature. In addition, the dielectric properties of PZT films were characterized by impedance analyzer (HP4194).

Ion beam treatment to produce the tensile stress may leave radiation-induced defects in PZT films. If the radiation dose is larger than a critical number, the ion radiation starts to influence the piezoelectric coefficients of PZT films as well as the substrate clamping state. Therefore, we evaluated the effect of the implantation damage on the properties of PZT film under the tensile stress. A companion set of implantations were performed using 25 keV He ions with a fluence of $7 \times 10^{14}/cm^2$. These implantation parameters result in the same amount of radiation damage (displacements per atom) in the film as produced by 300 keV He ions at a fluence of $1 \times 10^{16}/cm^2$ but without imparting any stress into the substrate. No significant change in the ferroelectric and dielectric properties of the PZT films was observed, indicating that the property changes that are observed in the stressed films arise from the applied stress rather than from irradiation damage.

III. RESULTS

Fig. 2 shows the polarization hysteresis for the as-grown and stressed PZT films. Electric field during the measurement was normal to the film plane (Fig. 2). Changes in remnant polarization (P_r), saturated polarization (P_s), and coercive field (E_c) are observed for the films in a state of biaxial stress. The PZT films under compressive stress show an increase in P_r and P_s and a small increase in E_c. In contrast, a tensile stress decreases P_r and P_s and increases E_c. It is noted that the films with a tensile stress show a substantial level of imprint and big increase in coercive field. This is partially due to ion-implantation induced defects. Since the ions passed through PZT films to produce the tensile stress, a small amount of lattice disorder with charged defects can be generated during the ion implantation process for PZT films with a tensile stress. Given that the charged defects are mobile under the external electric field, they may preferentially occupy the domain walls and cause the imprint behavior with the increase in the coercive field.

Fig. 3 shows the polarization-fatigue behavior of the PZT films. The normalized difference between the switched and nonswitched polarization is plotted as a function of switching cycles. The data show that the fatigue characteristics of PZT films depend upon the sign of the applied stress. The polarization of as-grown films starts to degrade after 10^6 cycles and is reduced to 70% of the initial polarization after 10^{11} cycles. The presence of a tensile stress accelerates the ferroelectric fatigue, significantly degrading the polarization properties down to 50% of the initial polarization after 10^{11} cycles. However, the films under compressive stress show

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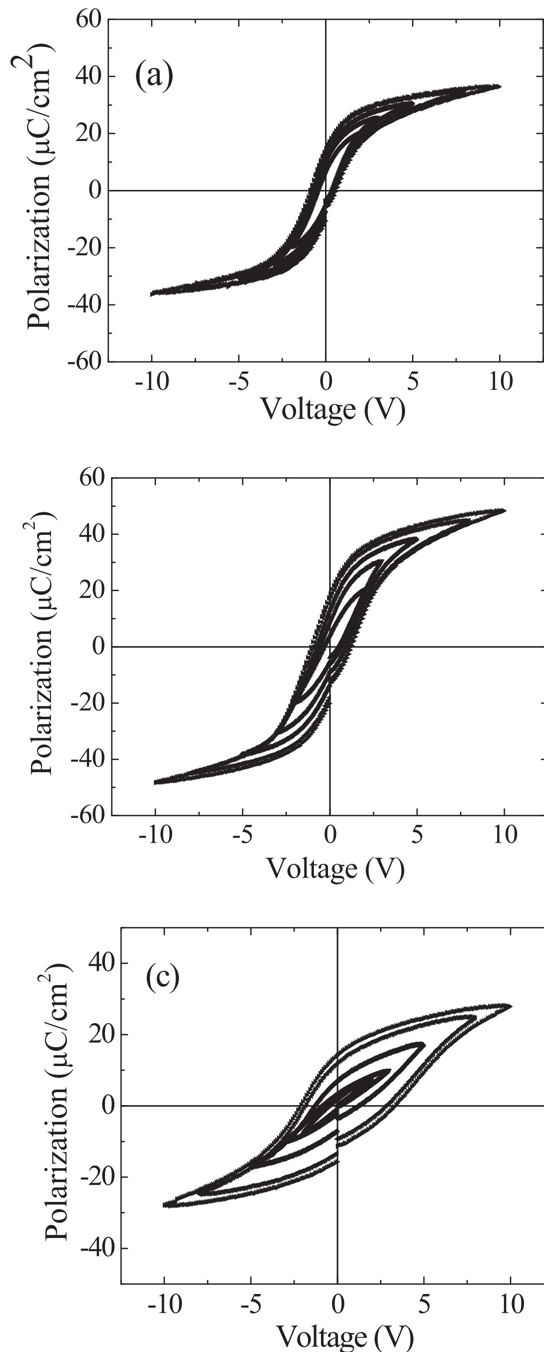

FIG. 2. Out-of-plane polarization vs. E-field relation in (001) oriented PZT films under different strain states; (a) as-grown, (b) under the compressive stress, (c) under the tensile stress.

negligible changes in both the switching and nonswitching polarization up to 10^{11} cycles. These data show that the direction of stress is critical to the appearance of ferroelectric fatigue in PZT films.

Fig. 4 shows the permittivity as a function of AC electric driving field amplitude before and after stress is applied to the PZT films. In as-grown and compressively stressed PZT films, the dependence of the permittivity on the amplitude of the AC electric field is more pronounced. The permittivity at 5 MV/m is about two times larger than that at 2.5 MV/m, showing the large dielectric nonlinearity for as grown and compressed PZT films. However, the films under tensile

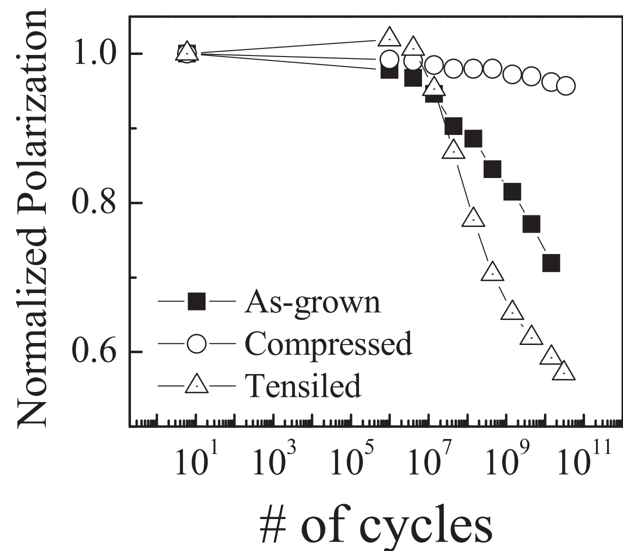

FIG. 3. Normalized polarization (P_{sw}-P_{ns}) as a function of switching cycles for as-grown and stressed PZT films.

stress exhibit much less variation in permittivity with increasing amplitude of the AC electric field. At a field of 5 MV/m, the permittivity increases by roughly 30%. In addition, the permittivity of PZT films under compressive stress is much larger than the permittivity of PZT films under tensile stress (Fig. 4).

IV. DISCUSSIONS

The Landau-Devonshire phenomenological theory, which relates the Gibbs free energy of ferroelectrics with the polarization and stress, was used to quantify the intrinsic effect of the external stress on the polarization and permittivity of ferroelectric materials.[20,21] When the ferroelectric material is under 2-dimensional clamping, the mixed mechanical boundary condition of thin films should be considered, and the

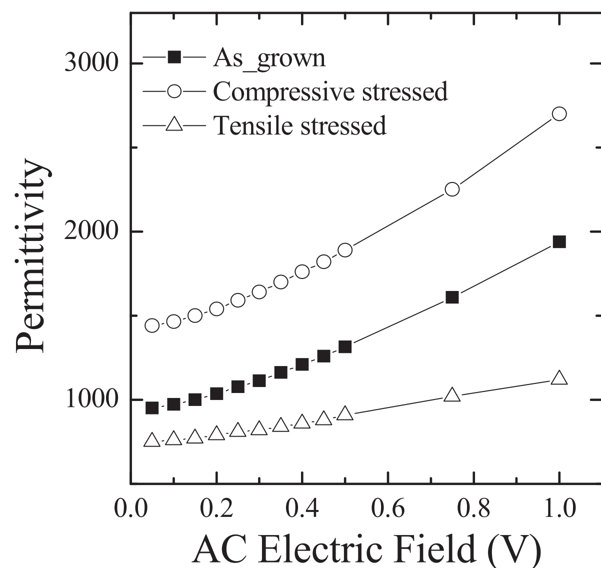

FIG. 4. Permittivity of as-grown and stressed PZT films as a function of AC electric voltage at 10 kHz (AC voltage in the x-axis is a root-mean-square value).

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thermodynamic potential of the clamped ferroelectric films are modified as following:[22,23]

$$\begin{aligned}\tilde{G} &= a_1^*(P_1^2+P_2^2)+a_3^*P_3^2+a_{11}^*(P_1^4+P_2^4)+a_{33}^*P_3^4\\&\quad+a_{13}^*(P_1^2P_3^2+P_2^2P_3^2)+a_{12}^{*}{}^2P_1^2P_2^2\\&\quad+a_{111}(P_6^1+P_2^6+P_3^6)+a_{112}[P_1^4(P_2^2+P_3^2)\\&\quad+P_3^4(P_1^2+P_2^2)+P_2^4(P_1^2+P_3^2)]\\&\quad+a_{123}P_1^2P_2^2P_3^2-E_1P_1-E_2P_2-E_3P_3.\end{aligned} \quad (1)$$

The coefficients of the free energy expansion are given by

$$a_1^* = a_1 - u_m\frac{Q_{11}+Q_{12}}{S_{11}+S_{12}}, \quad a_3^* = a_1 - u_m\frac{2Q_{12}}{S_{11}+S_{12}}, \quad (2)$$

$$a_{11}^* = a_{11} + \frac{Q_{11}+Q_{12}}{2(S_{11}^2-S_{12}^2)}[(Q_{11}^2+Q_{12}^2)S_{11}-2Q_{11}Q_{12}S_{12}], \quad (3)$$

$$a_{33}^* = a_{11} + \frac{Q_{12}^2}{2(S_{11}^2+S_{12}^2)}, \quad (4)$$

$$a_{12}^* = a_{12} - \frac{1}{S_{11}^2-S_{12}^2}[(Q_{11}^2+Q_{12}^2)S_{11}-2Q_{11}Q_{12}S_{11}] + \frac{Q_{44}^2}{2S_{44}}, \quad (5)$$

$$a_{13}^* = a_{12} + \frac{Q_{12}(Q_{11}+Q_{12})}{S_{11}+S_{12}}, \quad (6)$$

where a_1, a_{ij}, and a_{ijk} are the dielectric stiffness and higher-order stiffness coefficients at constant stress, E_i $(i=1,2,3)$ are the components of an electric field $\mathbf{E}$ in film, and Q_{ij} are the electrostrictive constants. In Eqs. (1)–(6), the Cartesian coordinate system is used and 3-axis in Eq. (1) is normal to the film plane.

Using the Eqs. (1)–(6), we calculated the polarization and the permittivity of PZT films as a function of external strain. Thermodynamic constants of Haun's work for bulk PZT ceramics with Zr:Ti = 6:4 have been used in this calculations.[18] Fig. 5 shows the results of the calculations regarding the influence of the external stress on the polarization and permittivity along ⟨001⟩ direction of PZT films (Fig. 5). The calculations predict that the compressive stress and tensile stress will have opposite effects on the ferroelectric and dielectric properties; tensile stress decreases the polarization and increases the permittivity while compressive stress increases the polarization and decreases the permittivity. This calculation predicts well the observed changes in the polarization under the strain. However, the phenomenological calculations do not explain the experimentally observed variation in permittivity that decreases under tensile stress and increases under compressive stress. Since Eq. (1) shows the change in intrinsic factors based on phenomenological theory, this discrepancy between their predicted and the experimental observed permittivity values shows that the external stress modifies the extrinsic properties of PZT films as well as intrinsic ones.[4,24,25]

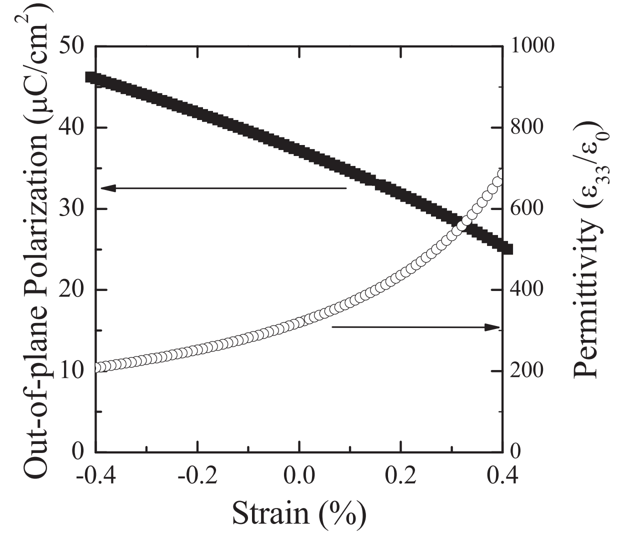

FIG. 5. Results of theoretical calculations on changes in the polarization and permittivity of PZT film (Zr:Ti = 6:4) when biaxial stress is applied.

Modified thermodynamics in Eq. (1) have shown that 2-dimensional clamping determines the in-plane strain and influences the stable polarization, internal stresses, and out-of-plane strains. Therefore, the crystal structure of strained PZT films does not coincide with that of the PZT bulk with the same Zr/Ti ratio. When Zr/Ti ≥ 0.4, the stable structure of strained PZT films is monoclinic ($P_1 = P_2 \neq 0$, $P_3 \neq 0$) at room temperature.[19] This indicates that the ion implantation induced strain turns the structure of PZT film (Zr:Ti = 6:4) to be monoclinic. In the monoclinic phase, the biaxial strain and stress on (001) plane can change the thermodynamically favorable domain configuration.

The dielectric nonlinearity, i.e., the increase in permittivity with increasing AC field, has been used as an indicator to assess the role of the extrinsic source associated with domain wall motion.[4,5,26,27] The dependence of the dielectric non-linearity on the stress, shown in Fig. 5, suggests that the applied biaxial stress of PZT films controls domain wall motion, leading to the deviation between the experimental results and the predictions. External stress in ferroelectrics is known to rotate the polarization directions, which is known as ferroelastic switching. There are two kinds of domain walls in PZT films: 180° domain walls and non-180° domain walls. Since only non-180° domain walls have ferroelastic behavior between them, the increase in the dielectric non-linearity and the permittivity under compressive stress indicates that the compressive stress increases the extrinsic contribution by activating the non-180° domain walls of as-grown PZT films. Recent theoretical studies on the domain structure explain well this stress effect on domain configuration of PZT films in both rhombohedral and tetragonal structure-regimes using a phase-field model.[28,29] They have described the evolution of the polarization field base on Ginzburg-Landau equations and simulated domain shape, domain wall orientation, and surface morphology of PZT films. Their domain stability map shows that 180° domain walls and domains with out-of-plane polarization become dominant by applying a compressive strain into PZT films.

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However, under a biaxial strain, the area of domains with in-plane polarization increases with the tensile strain.

Experimental observation and theoretical explanation in this study are well supported by prior studies demonstrating the effect of stress on the ferroelectric domain morphologies. It has been observed that biaxial compressive stress in films tends to align the ferroelectric dipoles to be normal to the surface and that tensile stress causes them to be parallel to the surface.[1,25] In addition, Nagarajan *et al.* have found that the fraction and period of domains with in-plane polarization increases with decreasing compressive strain in tetragonal PZT films and that relaxation of compressive strain decreases the out-of-plane polarization component.[30,31] Therefore, we believe that ion-implantation induced compressive stress in this study forms 180° domain walls through the consumption of non-180° domain walls and makes the non-180° domain walls metastable, which results in an increase in the density of 180° domain walls and in the mobility of non-180° domain walls. In as-grown PZT films thinner than $2\,\mu$m, the mobility of non-180° domain walls is smaller than that of 180° domain walls and the contribution of 180° domain walls to the dielectric response is dominant over that of non-180° domain walls.[4] Therefore, a decrease in the density of non-180° domain walls and an increase in the mobility of non-180° domain walls under compressive stress are expected to increase the extrinsic contributions to the dielectric response, consistent with the experimental observation of this study.

It is noted that the change in the dielectric nonlinearity of PZT films by external stresses is different from the previous study on $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ films.[32] According to Gharb *et al.*, $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ films show very small dependence ($<4\%$) of the dielectric nonlinearity on the mechanical stress, which is different from our results. This indicates that a different ferroelectric system may show a different correlation between the domain wall mobility and the mechanical stress. There are a few previous works on the influence of the external stress on the dielectric nonlinearity of Pb-based ferroelectrics. Hydrostatic compressive stress was found to produce a significant change in the dielectric nonlinearity for both hard and soft PZT ceramics through an irreversible domain wall movement and a deageing phenomenon.[33] Zhou *et al.* has found that dynamic biaxial stress changed the nonlinearity of soft PZT ceramics, leading to different levels of field induced polarization and strain.[34] The dielectric nonlinearity also depends on doping which can modify the dynamics of domain walls.[35,36] A small amount of Mn doping into $Pb(Zn_{1/3}Nb_{2/3})O_3$ makes its piezoelectric properties harder and moves its dielectric nonlinearity behavior from a regime of Rayleigh law to a regime of quadratic behavior.[35] However, if the domain wall mobility is similar, the dielectric nonlinearity of soft PZT ceramics shows a universal behavior, regardless of the specific composition of materials.[37] These previous studies indicate that the dynamics of domain walls of ferroelectric materials can be significantly modified by several factors including the external stress, leading to a different dielectric nonlinearity. Further work is on-going to explore the effect of the ion-implantation induced stress on the domain configuration of PZT films using transmission electron microscopy.

The change in the domain wall configuration under applied stress also explains the opposite effect of the tensile and compressive stress on the appearance of ferroelectric fatigue. It has been shown that the switching of stabilized non-180° domain walls in $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ single crystals needs the increase in both elastic energy and electrical energy, which significantly contribute to the ferroelectric fatigue.[38] It is noted that the residual stress affects the appearance of the ferroelectric fatigue by changing the level of the elastic energy increase. The tensile stress of PZT films increases the change in the elastic energy during a polarization switching along out-of-plane, resulting in the increase in the thermodynamic instability. This instability associated to the polarization switching of tensile stress PZT films accelerates the local diffusion and trapping of defects such as oxygen vacancy at domain boundaries and prevents the free motion of domain boundaries, leading to the early appearance of the ferroelectric fatigue.[39,40] In contrast, since the compressive stress increases the density of non-180° domain walls and domains with out-of-plane polarization, the elastic energy is less required for the polarization switching along out-of-plane. Therefore, the fatigue behavior due to defect trapping and mechanical cracking is suppressed in PZT films under a compressive stress.

V. CONCLUSIONS

The effect of an externally applied biaxial stress on ferroelectric and dielectric properties was investigated. We have shown the novel approach to control the strain of thin films by using ion-implantation induced strain and the effect of finely tuned strain on the physical properties of PZT films. Compressive stress showed increases the out-of-plane polarization, permittivity, and fatigue resistance. The different degrees of dielectric nonlinearity observed in the permittivity as a function of AC excitation voltage indicates that the extrinsic effect, i.e., domain wall motion, contributes to the dependence of ferroelectric and dielectric properties on the applied stress. It is suggested that the compressive stress activates the non-180° domain walls of as-grown PZT films and suppresses the ferroelastic participation during the polarization switching, leading to higher extrinsic contributions and fatigue resistance. In contrast, PZT films which were exposed to produce the tensile stress, showed decreases in out-of-plane polarization, permittivity, and fatigue resistance. The opposite observations in the PZT films with the tensile stress are explained by the stress effect as well as the ion-implantation induced defects.

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