Effect of manganese oxide insertion layer on the dielectric and ferroelectric properties of $\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ films grown by a sol-gel process*

Beihai Ma¹, Shanshan Liu^{1,2}, Zhongqiang Hu¹, Manoj Narayanan¹,
and Uthamalingam Balachandran¹

¹Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439

²Current Address: Mechanical Research & Development Group, Seagate Technology,
Bloomington, MN 55435

June 2014

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(1st revision on 19 January 2015)

(2nd revision on 18 February 2015)

For submittal to *Materials Research Bulletin*.

*This work was supported by the U.S. Department of Energy, Vehicle Technologies Program, under Contract DE-AC02-06CH11357.

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Beihai Ma^{§,1}, Shanshan Liu^{1,2}, Zhongqiang Hu¹, Manoj Narayanan¹,
and Uthamalingam Balachandran¹

¹Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439

²Current Address: Mechanical Research & Development Group, Seagate Technology, Bloomington, MN 55435

Abstract

We incorporated a ≈ 5 -nm-thick MnO_x insertion layer in the middle of a ≈ 1.38 - μm -thick $\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PLZT) film grown by a modified sol-gel process and measured the dielectric and ferroelectric properties of PLZT films with and without MnO_x insertion layer. By incorporation of the MnO_x layer, residual stress was reduced from ≈ 350 MPa to ≈ 125 MPa, dielectric permittivity decreased from ≈ 1300 to ≈ 950 , while dielectric loss increased from ≈ 0.04 to ≈ 0.07 as measured at 10 kHz. Also, remanent polarization increased from $\approx 9.1 \mu\text{C}/\text{cm}^2$ to $\approx 11.7 \mu\text{C}/\text{cm}^2$, coercive field increased from ≈ 28.7 kV/cm to ≈ 40.3 kV/cm, and internal bias field from ≈ 3 kV/cm to ≈ 14 kV/cm. We have observed decreased irreversible Rayleigh coefficient and dielectric nonlinearity on samples with MnO_x insertion layer. These changes in properties are attributable to Mn cation doping as acceptors near the MnO_x /PLZT interface, which forms oxygen vacancies and defect induced dipoles like $2\text{Mn}'_{\text{Ti}} - \text{V}_\text{O}^{\bullet\bullet}$ (or $\text{Mn}''_{\text{Ti}} - \text{V}_\text{O}^{\bullet\bullet}$), acting effectively as pinning centers to hinder domain wall movement.

Keywords: thin films; sol-gel chemistry; X-ray diffraction; dielectric property; Rayleigh law.

PACS: 77.22.Jp, 77.55.-g, 77.55.fg, 77.80.bn, 77.80.Jk

[§]Corresponding author. Phone: 1-630-252-9961; Fax: 1-630-252-3604; Email: bma@anl.gov.

INTRODUCTION

In recent years, ferroelectric $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) materials with large dielectric permittivity have attracted increased research interest because of their potential applications for decoupling capacitors, infrared sensors, micro-actuators, electro-optical components, and digital memories [1-4]. PZT ceramics can be modified by adding different dopants to maximize specific properties. These dopants can be categorized into two groups: “softeners” and “hardeners”. Typical softener ions are La^{3+} and Sb^{3+} in A-site or Nb^{5+} and Ta^{5+} in B-site substitutions in the PZT perovskite structure, which decrease the coercive field. Typical hardener ions are K^+ and Na^+ in A-site or Fe^{3+} , $\text{Mn}^{2+,3+}$, Ni^{2+} , and Sc^{3+} in B-site substitutions, which increase the coercive field. The mechanism by which the dopants affect the properties are rather complex, but can be explained by phenomenological theories of vacancy compensation in the lattice and space charge effects [5,6].

$(\text{Pb}_{1-y}\text{La}_y)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PLZT) systems are known as relaxor ferroelectrics. The degree of their relaxor nature depends on the lanthanum content. The ferroelectric long-range order is broken at high levels of La^{3+} doping, which cause an excess of A-site vacancies. This condition results in the formation of polar nano-regions (PNR), which are related to the origin of the relaxor properties. Perez-Delfin et al. [7] reported that Mn-acceptor doping in bulk PLZT (9/65/35) resulted in increased coercive field, reduced dielectric permittivity, decreased remanent polarization, and lessened temperature dependence. Choi et al. [8] reported improved densification at the boundary of Mn-doped and undoped regions, and suggested that low-level (<2 mol.%) doping can enhance dielectric properties. Our recent study [9] showed that thin insertion layers of ZrO_2 can effectively reduce leakage current density and improve the dielectric performance under a bias field. The possible reason for the enhanced performance is that the ultrathin ZrO_2 layers inserted in the PLZT matrix can effectively trap those free charge carriers and therefore, reduce the leakage current density. The formation of mixed-valence transition metal cation oxygen vacancy nanostructures within a dielectric ceramic thin film can potentially impede domain wall movement of PNRs. To this purpose, we incorporated ultrathin (≈ 5 -nm thick) layer of MnO_x in the middle of PLZT thin films grown on platinumized silicon (PtSi) substrates by sol-gel process. Residual stress was determined by X-ray diffraction. Domain wall movement

was investigated by subcoercive field modulation. In this study, we report the effect of ultrathin layer of MnO_x insertion on the residual stress, dielectric and ferroelectric properties, and domain wall movement behavior of $\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PLZT 8/52/48) thin films grown on PtSi substrates by sol-gel synthesis.

Experiment

PLZT (8/52/48) films were deposited on PtSi substrates by a modified sol-gel process [10]. Precursor solutions of 0.5 M PLZT were prepared by a modified 2-methoxyethanol (2MOE) synthesis route [11] using an appropriate amount of titanium isopropoxide, zirconium n-propoxide, lead acetate trihydrate, and lanthanum nitrate hexahydrate (all from Sigma-Aldrich). The resulting stock solution contained 20% excess lead to compensate for lead loss during the heat treatments described below. Premium-grade platinized silicon (PtSi) wafers were acquired from Nova Electronic Materials (Flower Mound, Texas). They consisted of $\approx 375\text{-}\mu\text{m}$ -thick $\langle 100 \rangle$ oriented silicon with 500-nm-thick thermally oxidized silicon dioxide coated with 20-nm-thick titanium and 200-nm-thick platinum. The sputter-coated platinum (Pt) film has $\langle 111 \rangle$ preferred orientation. Prior to being coated, the substrates were ultrasonically cleaned in distilled water, then wipe-cleaned with acetone and methanol in sequence. Before being used for coating, the PLZT precursor solution was filtered through Restek polytetrafluoroethylene (PTFE) syringe filters (Restek Corp., Bellefonte, PA) with 0.22- μm open pore size. The filtered PLZT precursor solution was spin coated with a Laurell WS400 spin processor (Laurell Technologies, North Wales, PA) at 3000 rpm for 30 s on the PtSi substrates, pyrolyzed at 450°C for 10 min, and annealed at 650°C for 5 min for each coating. After every three layers of coating, additional annealing was performed at 650°C for 15 min. Those steps were repeated to build the PLZT film with desired thickness. All pyrolysis and annealing were performed in air in Lindburg tube furnaces. Each coating resulted in a PLZT film of $\approx 0.115\text{-}\mu\text{m}$ thickness after pyrolysis and crystallization. Film thickness was determined from cross-sectional images with scanning electron microscopy (SEM).

After application of seven PLZT layers on the PtSi substrate, a 5-nm-thick MnO_x film was deposited by reactive electron-beam evaporation using a Mn metal target. The base pressure of the electron-beam evaporation system was maintained at $\approx 1 \times 10^{-7}$ torr. During the deposition,

the PLZT-coated PtSi substrate was heated to 250°C and ultrahigh-purity oxygen was flowed through the system at ≈ 1 sccm rate to maintain a deposition pressure of $\approx 1.5 \times 10^{-6}$ torr. Upon finishing deposition of the 5-nm-thick MnO_x film, the sample was retrieved from the electron-beam evaporation system and put in a Lindburg furnace for 10 min annealing at 450°C in air to stabilize the MnO_x film before continued coating PLZT by solution deposition process. Following the formation of MnO_x on PLZT, additional five coatings of PLZT were deposited. In the end, samples used for this study have 12 layers of PLZT ($\approx 1.38 \mu\text{m}$ thick) coated on PtSi substrates, with and without a ≈ 5 -nm-thick MnO_x layer inserted in the middle of the PLZT film. The sample without MnO_x insertion layer was used as control sample for comparison.

Platinum top electrodes with thickness of ≈ 100 nm were deposited on the samples by electron-beam evaporation through a shadow mask to define ≈ 250 - μm -diameter top electrodes. Samples with Pt top electrodes were annealed at 450°C in air for 5 min. for electrode conditioning. Phase development and residual stress in the processed films were studied using a Bruker AXS D8 Discover with GADDS diffraction system. A Signatone QuieTemp® probe system (Lucas Signatone Corp., Gilroy, CA) was used for electrical characterization. An Agilent E4980A precision LCR Meter was used to determine the capacitance and dissipation factor under an applied bias field and at different frequencies. A Radiant Technologies Precision Premier II tester measured the polarization-electric field hysteresis loops.

Results and Discussion

FIGURE 1 SHOWS X-ray diffraction patterns of PLZT films grown on PtSi substrates by chemical solution deposition with and without the MnO_x insertion layer respectively. The diffraction peaks of PLZT films can be indexed according to a pseudo-cubic perovskite structure (JCPDS 56-0900). The two small peaks (at $2\theta \approx 34.5^\circ$ and $\approx 36^\circ$) marked by asterisks are associated with $\text{Cu-K}\beta$ diffractions of PLZT (111) and Pt (111) as shown in Fig. 1a and Fig. 1b. It is not surprise to see that X-ray diffraction patterns for samples with and without MnO_x insertion layer are nearly identical, except for those tiny peaks at $2\theta = 28 - 29^\circ$ which are associated with β - and γ -phase MnO_2 [12]. Due to the extreme thin thickness of MnO_x (≈ 5 nm), it is hardly invisible to laboratory scale X-ray diffraction. A 250-nm-thick MnO_x sample was prepared on a glass substrate using the same deposition and annealing conditions. XRD study on

this sample revealed that MnO_x film consists of both Mn_2O_3 and MnO_2 phases. After annealing at 450°C in air for 30 min, the MnO_x film on glass is semiconducting with a sheet resistance $R_s \approx 3 \text{ k}\Omega/\square$.

Fig. 1. X-ray diffraction patterns of PLZT films grown on PtSi substrates (a) with and (b) without MnO_x insertion layer.

Fig. 2. Fracture cross-sectional SEM micrograph of a $\approx 1.38\text{-}\mu\text{m}$ -thick PLZT film deposited on PtSi substrates with a MnO_x insertion layer.

Figure 2 shows a cross-sectional SEM image of the fracture surface of a PLZT film deposited on PtSi substrates with a MnO_x insertion layer. This sample had seven coatings of PLZT prior to the deposition of ≈ 5 -nm-thick MnO_x layer, followed with additional five layers of coating. The total thickness of PLZT is $\approx 1.38 \mu\text{m}$ as determined from the cross-section SEM shown in Fig. 2. It is evident that the PLZT film is dense and uniform. The thin MnO_x layer is distinctively visible with higher electrical conductivity when compared to the adjacent PLZT matrix.

As reported earlier [13], PLZT films deposited on PtSi substrates by chemical solution deposition bear tensile stress due to thermal expansion mismatch. The silicon substrate and PLZT film exhibit coefficient of thermal expansion (CTE) of $\approx 3.6 \times 10^{-6}$ and $\approx 5.4 \times 10^{-6} \text{ K}^{-1}$, respectively. Upon cooling, the substrate shrinks less than the PLZT film coated on it; this causes tensile stress in the PLZT films coated on PtSi substrate. To investigate the effect of MnO_x insertion layer on residual stress in the PLZT films, we have measured XRD at various tilt angles for both samples with and without MnO_x layer. Figure 3 shows lattice d-spacing as a function of $\sin^2\psi$ measured by XRD on the PLZT films with and without the MnO_x insertion layer. Lattice d-spacing determined from the PLZT (211) diffraction peak is shown in Fig. 3a, and that determined from the PLZT (310) diffraction peak is shown in Fig. 3b. The residual stress σ_ϕ of PLZT films can be estimated with the following formula [14],

$$\sigma_\phi = \left(\frac{E}{1 + \nu} \right)_{(hkl)} \cdot \frac{1}{d_{\phi 0}} \cdot \frac{\partial d_{\phi\psi}}{\partial \sin^2 \psi} \quad (1)$$

where E and ν are Young's modulus and Poisson ratio of the thin film, and $d_{\phi 0}$ and $d_{\phi\psi}$ are the lattice d-spacing in a stressed sample that was measured at tilt angles of zero and ψ , respectively. Experimentally, stress in the thin film sample can be calculated by performing a linear fit of the d-spacing measured at various tilt angles as a function of $\sin^2\psi$, then plugging the measured slope into Eq. 1. As shown in Figs. 3a and 3b, the slope measured for the sample with the MnO_x embedded layer is substantially lower than that measured for the sample without the MnO_x layer. Using the Young's modulus of $\approx 72 \text{ GPa}$ and Poisson ratio of ≈ 0.3 [13], we calculated a residual stress of $\approx 125 \text{ MPa}$ and $\approx 350 \text{ MPa}$ for the $1.38\text{-}\mu\text{m}$ -thick PLZT films grown on PtSi substrates with and without the MnO_x . Our results suggested that a ≈ 5 -nm-thick MnO_x insertion layer can

effectively reduce residual stress in the PLZT film grown on top of the MnO_x layer. This reduction in residual stress is likely related to the fact that Mn cations in the MnO_x layer can have multiple valance and thus to accommodate different number of surrounding oxygen atoms. The thermal stress in PLZT film can be partially released by causing slight local distortion in the MnO_x sublattice. Detailed microscopy investigation is ongoing.

Fig. 3. Lattice d-spacing as a function of $\sin^2\psi$ measured for (a) PLZT (211) and (b) PLZT (310) diffraction peaks for 1.38- μm -thick PLZT grown on PtSi substrates with and without MnO_x insertion layer.

Figure 4a shows the permittivity and dielectric loss as a function of applied bias field measured at room temperature for the PLZT films grown on PtSi substrates with and without MnO_x . Dielectric characterizations were conducted with an Agilent E4980A precision LCR meter at 10 kHz using oscillation signal amplitude of 100 mV. The data conformed to butterfly-shaped curves, which are typical for ferroelectric materials measured under the Curie temperature. For the PLZT grown on a PtSi substrate without MnO_x , we measured a dielectric constant of ≈ 1300 and dielectric loss of ≈ 0.04 at zero bias field, while for the sample with MnO_x layer, we measured a dielectric constant of ≈ 950 and dielectric loss of ≈ 0.07 at zero bias field. The MnO_x layer in the middle of PLZT film thus reduced dielectric permittivity and increased dielectric loss. Our results are in agreement with the earlier reports that low level doping of manganese in bulk PZT materials leads to reduced permittivity, decreased resistivity, and increased dielectric loss because the manganese cations (Mn^{2+} and Mn^{3+}) act as acceptor dopants causing increased oxygen vacancies and hole concentrations [15,16]. Increased charge carrier

concentration leads to decreased resistivity and increased dielectric loss. In addition, we observed a distinct peak shift in the butterfly curve shown in Fig. 4a for samples without MnO_x insertion layer. This peak shift is related to the local polarization field induced by residual stress. The MnO_x insertion layer can effectively relieve residual stress in the PLZT film, therefore sample with ultrathin MnO_x insertion layer showed less a peak shift because of the reduction in residual stress and the depletion of induced local polarization field.

Fig. 4. Dielectric properties measured as a function of (a) applied field and (b) frequency on 1.38- μm -thick PLZT films grown on PtSi substrates with and without MnO_x insertion layer.

Figure 4b shows the permittivity and dielectric loss as a function of frequency measured at room temperature for the PLZT films grown on PtSi substrates with and without MnO_x . For frequency < 100 kHz, the dielectric permittivity of the sample without MnO_x layer exhibits good linear dependence on the logarithm of frequency. With further increase in frequency (> 100 kHz), dielectric loss starts increasing and dielectric permittivity increases slightly, followed by a steep drop at higher frequency, which is not shown in Fig. 4b. This typical dielectric dispersion in parallel-plate capacitor testing is a result of space charge relaxation, namely, the Maxwell-Wagner relaxation caused by space charge polarization in the film/electrode interfaces [17]. By contrast, dielectric permittivity of the sample with MnO_x layer exhibits a steep drop at low frequency (< 1 kHz), accompanied by a decrease in dielectric loss with frequency. We observed a minimum in dielectric loss at ≈ 10 kHz. In the frequency region between 1 kHz and 100 kHz, dielectric permittivity of the sample with MnO_x insertion layer decreases linearly, then slightly

increases at frequency >1000 kHz. This frequency dispersion revealed the existence of a second polarization, which is likely related to the collective motion of ionic charge carriers (oxygen vacancies due to B-site substitution by Mn^{2+} and Mn^{3+} cations) near the PLZT/ MnO_x interface [18]. A second relaxor peak is observed at ≈ 300 kHz.

Fig. 5. (a) P-E hysteresis loops and (b) internal bias field of 1.38- μm -thick PLZT films grown on PtSi substrates with and without MnO_x insertion layers.

Figure 5a shows the polarization-electric field (P-E) hysteresis loops measured with standard triangle waveform at room temperature on the PLZT films grown on PtSi substrates with and without MnO_x . The data were obtained at a field sweeping period of 10 ms (corresponding to a frequency of 100 Hz). From the P-E loop with a maximum applied electric field of ≈ 220 kV/cm, we found remanent polarization (P_r) of $\approx 11.7 \mu\text{C}/\text{cm}^2$ and $\approx 9.1 \mu\text{C}/\text{cm}^2$ and coercive field (E_c) of ≈ 40.3 kV/cm and ≈ 28.7 kV/cm for the samples with and without the MnO_x insertion layer, respectively. The increased remanent polarization and coercive field in the sample with MnO_x layer are attributed to acceptor doping on the B-site near the PLZT/ MnO_x interface. The manganese acceptor doping can also lead to decrease in resistivity locally near the PLZT/ MnO_x interface.

In addition to ferroelectric hardening effect, having MnO_x insertion layer incorporated in PLZT films also led to shifting in hysteresis loops. As shown in Fig. 5a, hysteresis loop

measured for sample with MnO_x insertion layer noticeably shifted to left. This imprint effect can be attributed to Mn doping in PLZT at the PLZT/ MnO_x interface and resulting in an internal bias field [19]. Figure 5b showed the internal bias field E_i as a function of maximum applied field measured on samples with and without MnO_x insertion layers. Internal bias field E_i increases monotonically with increasing maximum applied field E_{max} . For PLZT films without MnO_x insertion layers, E_i increases gradually from ≈ 0.5 kV/cm to ≈ 3.1 kV/cm with increasing applied field E_{max} from ≈ 100 kV/cm to 550 kV/cm. E_i measured on PLZT films with MnO_x insertion layers is significantly higher than that measured on those without MnO_x insertion layers. It increases rapidly from ≈ 4.5 kV/cm to ≈ 13 kV/cm with applied field E_{max} from ≈ 100 kV/cm to ≈ 300 kV/cm, and then flattened out at $E_i \approx 14$ kV/cm with further increasing E_{max} to ≈ 550 kV/cm. The strengthened internal bias field measured on samples with MnO_x insertion layers is in good agreement with the internal bias field values reported for PZT with <1 mol.% Mn doping [19].

Fig. 6. Frequency dependence of relative permittivity measured with various levels of ac oscillation signal for 1.38- μm -thick PLZT films grown on PtSi substrates (a) without and (b) with MnO_x insertion layer.

Sub-coercive field amplitude sweeps were applied perpendicular to the MnO_x insertion layers to investigate domain wall movement in PLZT films. Figure 6 shows relative permittivity (ϵ') as a function of frequency for the samples with and without MnO_x insertion layers. These measurements were conducted utilizing small oscillation signals ($E = E_0 \sin \omega t$) of various amplitude E_0 . Relative permittivity ϵ' was found to increase with increasing oscillation signal

amplitude E_0 but decrease with increasing ac signal frequency. For samples without MnO_x , ε' showed good linear dependence on the logarithm of frequency, as shown in Fig. 6a. For samples with MnO_x , ε' exhibited nonlinear dependence. It decreases rapidly with frequency at low frequency (<2 kHz), followed by a gradual decrease in the intermediate frequency region, and then another rapid decrease at >100 kHz, as shown in Fig. 6b. Two kinks occurred at ≈ 2 kHz and ≈ 100 kHz. The rapid drop in permittivity at low frequency is likely related to the additional oxygen vacancies and electron holes introduced as a result of B-site substitution by the divalent and trivalent manganese cations near the PLZT/ MnO_x interfaces [15].

Fig. 7. Relative permittivity as a function of ac oscillation field amplitude measured on 1.38- μm -thick PLZT films grown on PtSi substrates (a) without and (b) with MnO_x insertion layer.

Table I. Rayleigh parameter measured for 1.38- μm -thick PLZT films grown on PtSi substrates with and without MnO_x insertion layer.

PLZT films on PtSi	Frequency (kHz)	α' (cm/kV)	ε'_{init}	$\alpha' / \varepsilon'_{init}$ (cm/kV)
without MnO_x insertion layer	1	14.09 ± 0.37	1273.4 ± 3.9	0.0111
	10	12.24 ± 0.32	1190.5 ± 3.5	0.0103
	100	10.31 ± 0.28	1117.4 ± 3.0	0.0092
with MnO_x insertion layer	1	11.02 ± 0.46	1057.6 ± 4.9	0.0104
	10	8.22 ± 0.39	907.2 ± 4.2	0.0091
	100	5.53 ± 0.30	772.2 ± 3.2	0.0072

To quantitatively assess the contribution of the extrinsic effect on permittivity, we plotted ε' as a function of ac field amplitude (E_0). As can be deduced in Fig. 7, data measured at various frequencies (from 1 kHz to 100 kHz) fit well to the Rayleigh law [20],

$$\varepsilon' = \varepsilon'_{init} + \alpha' \cdot E_0 \quad (2)$$

where ε' , ε'_{init} , α' , and E_0 are the relative permittivity, initial (zero-field) permittivity, irreversible Rayleigh coefficient, and the applied ac field amplitude, respectively. Note that ε'_{init} consists of intrinsic lattice polarizability and reversible domain wall motion contributions to permittivity. Reversible domain wall motions account for the part of the domain wall that would, if the field were suddenly removed, return to the original position, i.e., the state prior to application of the ac field. Also $\alpha' \cdot E_0$ represents the irreversible displacement of the walls.

The Rayleigh parameters derived from least square fitting of the experimental data to Eq. (2) are summarized in Table I. The ratio of irreversible-to-reversible contributions to dielectric nonlinearity ($\alpha' / \varepsilon'_{init}$) decreases with increasing frequency for the samples whether fabricated with or without the MnO_x insertion layer. The $\alpha' / \varepsilon'_{init}$ ratio that we calculated for the sample without MnO_x is comparable to that reported for PZT and PLZT films grown on PtSi substrates [21,22]. As evident in Table I, for the PLZT grown on PtSi substrate with MnO_x insertion layer, we obtained lower permittivity, decreased irreversible Rayleigh coefficient, and reduced dielectric nonlinearity. These differences are attributed to the B-site substitution by manganese cations in the PLZT films resulting in acceptor doping, which can lead to additional oxygen vacancies and defect dipoles like $2\text{Mn}'_{\text{Ti}} - \text{V}_\text{O}^{\bullet\bullet}$ (or $\text{Mn}''_{\text{Ti}} - \text{V}_\text{O}^{\bullet\bullet}$) near the PLZT/ MnO_x interface. Oxygen vacancies are likely associated with the acceptors producing local electric field and strain field. When a continuous MnO_x is inserted in the PLZT matrix, those fields associated with acceptor doping at the MnO_x /PLZT interface can effectively modify the strain state of the entire film, causing relaxation and release of the stresses. Thus, the sample with MnO_x showed substantially reduced residual stress when compared to the sample without MnO_x , as indicated by Fig. 3. Manganese doping in PLZT can also affect the coercive field and make the acceptor-

doped material hard [23]. Those defect dipoles can act as pinning centers to retard domain wall movement and lead to reduced irreversible domain wall motion. Our results are in good agreement with those reported for low level (<2 mol.%) Mn doping in PLZT films grown on PtSi substrates [7].

Conclusions

We have grown 1.38- μm -thick ferroelectric PLZT films on platinized silicon substrates with and without a $\approx 5\text{-nm}$ -thick MnO_x insertion layer. With insertion layer, the residual stress in PLZT films is greatly reduced, from $\approx 350\text{ MPa}$ to $\approx 125\text{ MPa}$. In addition, dielectric permittivity measured at zero field decreased from ≈ 1300 to ≈ 950 while dielectric loss increased from ≈ 0.04 to ≈ 0.07 . From the P-E loop with a maximum applied electric field of $\approx 220\text{ kV/cm}$, we found P_r of $\approx 11.7\text{ }\mu\text{C/cm}^2$ and $\approx 9.1\text{ }\mu\text{C/cm}^2$ and E_c of $\approx 40.3\text{ kV/cm}$ and $\approx 28.7\text{ kV/cm}$ for the samples with and without MnO_x insertion layer, respectively. We also observed increased internal bias field, decreased irreversible Rayleigh coefficient, and reduced dielectric nonlinearity in the sample with MnO_x . The change was attributed to B-site acceptor doping of Mn near the MnO_x/PLZT interface. Oxygen vacancies and defect dipoles like $2\text{Mn}'_{\text{Ti}} - \text{V}_\text{O}^{\bullet\bullet}$ (or $\text{Mn}''_{\text{Ti}} - \text{V}_\text{O}^{\bullet\bullet}$) can effectively act as a pinning center to hinder domain wall movement.

Acknowledgment

This work was funded by the U.S. Department of Energy, Vehicle Technologies Program, under Contract DE-AC02-06CH11357. Authors are grateful to Prof. M. Lanagan at the Pennsylvania State University for his fruitful discussion. Authors thank Dr. R. E. Koritala at Argonne National Laboratory for her help with SEM studies. This work benefited from the use of the Electron Microscopy Center for Materials Research at Argonne National Laboratory.

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