Welcome

Domain structure and electrical properties of highly textured $PbZr_{x}Ti_{1-x}O_{3}$ thin films grown on LaNiO₃-electrode-buffered Si by metalorganic chemical vapor deposition

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Thin films of highly (100) textured fine-grain (lateral grain size $\cong 0.1$ to 0.15 µm) PbZr_xTi_{1-x}O₃ (PZT) (x = 0 to 0.7) were grown on conductive perovskite LaNiO₃-buffered platinized Si substrates by metalorganic chemical vapor deposition. Domain configuration and crystalline orientation were studied using x-ray diffraction and transmission electron microscopy. The predominant domain boundaries of Ti-rich tetragonal-phase PZT and Zr-rich rhombohedral-phase PZT were found to be on the (110) planes and (100) planes, respectively. The equilibrium domain widths were observed and estimated numerically on the basis of transformation strain, grain size, and domain boundary energy. The peak value of the dielectric constant was 790 near the morphotropic boundary. Hysteresis behavior of these PZT thin films was demonstrated. A decrease in coercive field with the increment of Zr content was found; this variation was attributed to domain density and the multiplicity of polarization axes. Furthermore, the low leakage current ($J \le 5 \times 10^{-7}$ A/cm² at V = 4 V) was observed for all samples, and the involvement of several possible conduction mechanisms was suggested.

I. INTRODUCTION

In recent years, the fabrication of ferroelectric capacitors for high speed nonvolatile random-access memories (NVRAMs) and for integrated micro-electromechanical devices has attracted much attention.^{1,2} PbZr_xTi_{1-x}O₃ (PZT) has been shown to be one of the best candidates for applications to integrated ferroelectric devices.^{3,4} Metalorganic chemical vapor deposition (MOCVD), owing to its capabilities of processing large wafers with good uniformity and step coverage, has become one of the major techniques for fabricating ferroelectric thin films.⁵

Polarization fatigue is a major reliability problem which hinders the progress of integrated ferroelectric devices. Fatigue of hysteresis behavior resulting from domain wall pinning is commonly recognized to be caused

by trapped charge. The accumulation of oxygen vacancies near the electrode/ferroelectric interfaces would increase charge trapping rate and promote fatigue.^{6–8} To overcome the problems of degradation, metallic oxides like RuO₂, LaSrCoO₃ (LSCO), or SrRuO₃ (SRO) have been considered as promising electrodes for the metal/ insulator/metal structure because they act as a sink for oxygen vacancies.^{6,9-11} Among these oxide electrodes, perovskite electrodes are more attractive because they offer better resistance to fatigue. It was shown that there is no compositional dependence in fatigue characteristics for PZT thin films grown on perovskite SrRuO₃ with Zr concentration ranging from 30% to 70% while the resistance to fatigue shows evident degradation as the Zr concentration decreases from 50% to 30% for PZT deposited on the RuO₂ electrode.^{11,12} This phenomenon is suggested to result from the increase of equilibrium concentration of oxygen vacancies with Ti content and from the limited tolerance of RuO_2 to oxygen vacancies. The improvement of fatigue resistance by using perovskite

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oxide electrodes can be attributed to the better crystallographic compatibility of the ferroelectric/electrode interface and the higher tolerance to oxygen vacancies of the perovskite electrodes.

LaNiO₃ (LNO) is a rhombohedral perovskite ($a_0 = 0.383$ nm) metallic oxide with the surface resistivity as low as 225 $\mu\Omega$ cm for (100)-textured thin film.¹³ Successful deposition of epitaxial or textured PT or PZT thin films on LNO electrode layers by the sol-gel method, metalorganic decomposition (MOD) process, and pulse laser deposition (PLD) has been demonstrated by several groups.^{13–16} It was reported that the nonfatigue remanent polarization of PZT thin films deposited on LNO-coated Si persisted up to 2×10^9 cycles.¹⁵ Nevertheless, there is no report about the crystalline characteristics and electrical properties of PZT thin films grown on LNO electrode by MOCVD.

It was generally considered that PZT in the Ti-rich tetragonal phase has lower crystallization temperature for solution-derived thin films on Pt or RuO₂ electrodes.¹⁷ However, rhombohedral phase PZT is more attractive in memory application and pyroelectric detection due to its lower coercive field, higher remanent polarization, and higher pyroelectric coefficient.¹¹ In this study, we found that the employment of the perovskite metallic LaNiO₃ layer in conjunction with MOCVD process is beneficial to fabricating highly (100)-textured PZT thin films in either Ti- or Zr-rich phases with good properties.

Zr-to-Ti stoichiometry has a predominant effect on the domain configuration and, thus, the electrical properties of PZT thin films. There are relatively few reports addressing these issues. The influence of Zr-to-Ti stoichiometry on the microstructure and 90° domain assemblage of chemical solution derived tetragonal PZT thin films was studied by Tuttle et al.,17 who showed no evident difference in domain width or domain population in the randomly oriented PZT thin films. To the contrary, our present study revealed significant differences in highly (100) textured thin films on the basis of both x-ray diffraction (XRD) and dark field cross-sectional transmission electron microscopy (XTEM) techniques. Moreover, the dependence of dielectric and hysteresis behavior of MOD-derived PZT on Zr-to-Ti stoichiometry was studied by Klee et al.¹⁸ Foster et al.¹¹ also reported the variation of optical and ferroelectric properties with respective to Zr-to-Ti stoichiometry of epitaxially grown PZT thin films by MOCVD on (001) SrTiO₃. However, the correlation between the domain structure and electrical properties was not emphasized in those studies. Most studies on compositional effects were carried out on randomly oriented PZT thin films deposited on RuO₂ and Pt electrodes or epitaxially grown thin films on single-crystal oxide substrates. It is important to understand that the discrepancies in measured electrical properties are the direct result of different microstructures originating from different processing techniques and different bottom electrodes. In this paper, we have systematically varied the Zr-to-Ti stoichiometry to obtain highly (100)-oriented tetragonal and rhombohedral PZT thin films on LNO electrode-coated Si substrates. The evolution of microstructure including grain morphology and domain configuration has been investigated to reflect their effects on the ferroelectric properties.

The direct current (dc) conducting behavior of a metalferroelectric-metal (MFM) capacitor structure is another important factor for the realization of ferroelectric devices and has been intensively studied by many groups. Conduction mechanism of perovskite ferroelectrics like (BaSr)TiO₃ (BST) or PZT thin films under different electric field strength has been described by Dietz et al. and by Sudhama et al.^{19,20} It is suggested that the electrical conduction mechanism of PZT thin films can be of Schottky effect, Poole-Frenkel effect, or space charge limited current effect (SCLC). In all mechanisms, the bottom electrode plays an important role because it affects not only the Schottky barrier formed at the electrode/ferroelectric interface but also the crystalline quality of the PZT overlayer. Al-Shareef et al.²¹ demonstrated that PZT thin films deposited on RuO₂ electrode showed larger leakage current than on Pt electrode due to the existence of the pyrochlore phase. The use of a hybrid electrode RuO₂/Pt was shown to effectively reduce the leakage current. Up to now, there are still few reports regarding the electrical conduction behavior of PZT thin films using perovskite oxide electrodes. In this paper, the low leakage current of PZT thin films will be demonstrated and the involvement of several current conducting mechanisms under different electrical field strengths will be discussed.

II. EXPERIMENTAL PROCEDURE

(100)-textured LNO (0.2 μ m) thin films were deposited on Pt(0.15 µm)/Ti(0.05 µm)/SiO₂(0.15 µm)/Si substrates by radio frequency (rf) magnetron sputtering at 300 °C. The processing procedure and electrical properties of the LaNiO₃/Pt/Ti multilayer electrode have been described elsewhere.¹⁵ The subsequent PT and PZT $(\cong 0.15 \text{ to } 0.2 \text{ }\mu\text{m})$ thin film growth was carried out in a low-pressure, horizontal, cold-wall quartz MOCVD reactor with a resistive substrate heater. The mixture of the metalorganic precursor vapor was introduced into the reactor through an inlet flange on one end of the reactor system. The metalorganic sources used were lead tetramethyl heptanedionate, Pb(TMHD)₂, zirconium tertbutoxide, Zr(OC₄H₉)₄, and titanium isoproproxide, $Ti(OC_3H_7)_4$. The vapor delivery used high-purity nitrogen as the carrier gas. PT thin films were grown at substrate temperatures ranging from 450 to 600 °C. PZT thin films with Zr concentration ranging from 15 to 70% were grown at 600 °C. A systematic variation of Zr-to-Ti stoichiometry was achieved by varying the Zr source flow rate during growth with minor adjustment of the flow rates of Ti and Pb. Shown in Table I are typical deposition conditions of PZT thin films on LNO thin layers.

X-ray diffraction (XRD) scans were carried out using a 4-circle diffractometer with Cu K_{α} radiation. Crosssectional transmission electron microscopy (XTEM) micrographs were taken using a Philips CM-12 microscope operated at 120 kV. The chemical composition of the PZT thin films were determined using the nanoprobe x-ray energy dispersive spectroscopy (EDS) installed on a TEM with electron beam converging to 30 nm. Furthermore, the relative compositions of these PZT thin films were confirmed by x-ray diffraction through the Bragg angle variation of PZT (200)/(002) peaks and using Pt(111) peak as a internal reference. To measure the electrical properties, Au (2000 Å) square patterns $(200 \times 200 \ \mu\text{m})$ were evaporated onto PZT thin films as the top metal electrode of the metal-insulator-metal structure. The whole structure was then annealed at 500 °C in O₂ atmosphere to improve the adhesion of Au electrode and reduce possible trapped charges. Dielectric constants were measured using a HP 4275 LCR (inductance-capacitance-impedance) meter by performing frequency scans in the range of 10 kHz to 1 MHz with a oscillation voltage of 0.05 V. Dc leakage current was tested using a HP 4140B pA meter; the voltage was applied to the top electrode and swept from 0 to 10 V using steps of 0.01 V with 1 s waiting time for each step. A Sawyer-Tower circuit was employed for measuring the hysteresis behavior (P-E loop) using a 1 kHz sinusoidal wave.

III. RESULTS AND DISCUSSION

A. Structure of multilayer bottom electrode

The bottom electrode layers used in our study consist of a LaNiO₃/Pt/Ti multilayer structure deposited on thermally oxidized Si wafer. Figure 1 shows the XTEM of the whole capacitor structure used in our study. The LNO layer shows columnar grains with average grain size

TABLE I. Typical deposition conditions of PZT thin films.

Deposition temperature	600 °C
Deposition pressure	10 torr
Growth rate	3–5 nm/min
N ₂ flow	900 sccm
O_2 flow	400 sccm
Pb(TMHD) ₂ (118 °C) flow	20-40 sccm
$Zr(OC_4H_9)_4$ (35 °C) flow	10-40 sccm
$Ti(OC_3H_7)_4$ (35 °C) flow	10-25 sccm



FIG. 1. XTEM micrograph of PZT/LNO/Pt/Ti/SiO₂/Si layered capacitor structure.

around 50-80 nm, and the Pt/Ti layer exhibits granular microstructure with typical grain size around 100 nm. The fine grain structures of the multilayer electrode and the subsequently deposited PZT layer provide a good microstructural uniformity for further device integration and miniaturization. The use of such a multilayer electrode system offers several benefits. Tseng et al.¹⁴ described that pulse laser deposition of PLZT thin film on LNO/Pt/Ti multilayer electrode-coated Si showed superior properties over the LNO single-layer electrode in remanent polarization, dielectric constant, and leakage current. The surface resistivity of the LNO/Pt/Ti multilayer electrode used in this study is about 56.2 $\mu\Omega$ cm, measured using a four-point probe method. The surface resistivity is appreciably lower than an LNO single-layer electrode ($\rho \cong 225 \ \mu\Omega$ cm), and the lower surface resistivity is owing to the parallel conductance of the Pt underlayer. The low surface resistivity of the LNO/Pt/Ti multilayer electrode reduces the distortion of measured PZT properties in dielectric constant and remanent polarization. Moreover, the Pt/Ti metallic bilayer improves the endurance of the device because the metallic layer serves as the sink for releasing thermal stress. The properties of the subsequently MOCVD grown PZT thin films are described in a later section.

B. Effects of growth temperature on the microstructure and electrical properties of PbTiO₃ thin films

Shown in Figs. 2(a)–2(d) are the XRD θ –2 θ scan profiles of PbTiO₃ (PT) thin films grown on LNO/Pt/Si at 450, 500, 550, and 600 °C, respectively. The LNO peak was not so evident due to the close match between (100) peaks of PT and LNO and the weaker diffracted intensity of LNO layer. All films exhibit (100)_t preferential orien-



FIG. 2. XRD θ -2 θ scans of PT thin films grown at different temperatures: (a) 450 °C, (b) 500 °C, (c) 550 °C, (d) 600 °C.

tation. However, the $(002)_t$ peak appeared as the growth temperature (T_s) exceeded 550 °C. The *c*-oriented domain population was evaluated using the integrated intensity ratio of I(002)/[I(200) + I(002)]. The resultant values are 0.17 and 0.25 for 550 and 600 °C grown films, respectively. The lateral grain sizes are about 0.08, 0.15, 0.2, and 0.25 μ m for growth temperatures of 450, 500, 550, and 600 °C, respectively, as observed by XTEM. For thin films grown below 550 °C, with no $(001)_t$ peak observed in the XRD spectra, the predominant domain structure are 180° domains with the *c* axis lying on the substrate surface. The thin domain plate size is around 2-5 nm, as shown in a plan-view TEM micrograph in Fig. 3. The domain size observed is smaller than the value predicted using the model developed by Arlt *et al.*,²² which will be discussed in Sec. III. C.

Shown in Fig. 4 are the dielectric constant and loss tangent measurements of PT thin films grown at different temperatures in the frequency range from 10 kHz to



FIG. 3. Plan-view TEM micrograph showing the domain structure of PT thin film grown at 550 $^{\circ}\mathrm{C}.$

1 MHz. The dielectric constants ($k = \epsilon_r/\epsilon_0$) of PT thin films decrease from 293 to 155 with the reduction of growth temperature from 600 to 450 °C. For all measurements, the dielectric losses are less than 0.08 in the measured frequency range. The hysteresis behavior of PT thin films grown on LNO at 600 and 550 °C are shown in Figs. 5(a) and 5(b), respectively. For 600 °C grown PT thin films, the coercive field (E_c) is about 90 kV/cm and the remanent polarization (P_r) is 12.5 μ C/cm² under 400 kV/cm. For PT thin films grown at 550 °C, $E_{\rm c}$ is around 100 kV/cm and P_r is 2.5 μ C/cm² under 400 kV/cm. For perovskite ferroelectric thin films, the dielectric properties and hysteresis behavior are mainly influenced by grain size, interfacial layer, and domain structures. Especially, Frey et al.²³ reported a drastic effect of interfacial layer on the dielectric properties of fine-grained BaTiO₃; an interfacial layer as thin as 8 Å can alter the measured apparent dielectric and hysteresis properties of ultrafine-grain material. Therefore, the reduction of dielectric constant and a relative increase of the dielectric loss for PT thin film grown at low temperature ($T_{\rm s} \leq 500$ °C) can be attributed to the effect of possible interfacial defects between grains or PT/ electrode interface. Moreover, the slim P-E loop of low-



FIG. 4. Dielectric constant and loss measurements of PT thin films grown at different temperatures.

temperature-grown films ($T_{\rm s} \le 550$ °C) is due to the lack of switchable 90° domain assemblage, as described in the previous paragraph.

C. Domain structures of PZT thin films with respect to Zr-to-Ti stoichiometry

The Zr-to-Ti ratio influences the microstructure of PZT thin films in several ways including the preferential orientation, the domain population, and the domain widths. Shown in Fig. 6 are the XRD θ -2 θ spectra of highly textured PZT thin films with various Zr-to-Ti ratios. In the tetragonal phase, the preferred crystalline orientation changes gradually from highly (100) to (001) with increasing Zr content. The transition of the preferential orientation can be due to the lattice constant variation. The PZT with 45% Zr content showed a comparatively broader Bragg peak located at around 45° and was deconvoluted into (200)_t and (002)_t peaks. The *c*-oriented domain population could then be obtained for PZT with different Zr content. The relative integrated intensities I(002)/[I(200) + I(002)] are 0.25, 0.35, and 0.5



FIG. 5. Hysteresis behaviors of PT thin films grown at (a) 600 $^{\circ}\text{C}$ and (b) 550 $^{\circ}\text{C}.$

for PZT thin films with Zr content 15%, 30%, and 45%, respectively, showing a continuing increase of *c*-oriented domain population with increasing Zr concentration.

The grain size and domain configuration variance of both tetragonal and rhombohedral PZT thin films were studied using XTEM and shown in Figs. 7(a)-7(c). Darkfield TEM micrographs were taken close to (100) pole. For tetragonal phase PZT (i.e., Zr/Ti = 30/70 and 45/55), the polarization is along one of the six $\langle 001 \rangle_c$ direction and a/c 90 degree domain walls are lying on the (011)_c plane. Thus, the 45° inclined domain boundaries are clearly observed, in Figs. 7(a) and 7(b). On the other hand, rhombohedral phase PZT (Zr/Ti = 70/30) has its polarization axis along the $(111)_c$ orientation, and the energetically favorable domain boundaries can be on either the $(110)_c$ or $(100)_c$ planes for epitaxial $(100)_c$ oriented rhombohedral PZT thin film, as described by Streiffer et al.²⁴ In the current study, it was found that the domain boundaries of the rhombohedral phase PZT thin films lie mostly along the $(100)_c$ plane and are perpendicular to the film surface, as seen in Fig. 7(c). The cause to the dominance of $(100)_c$ type domain wall will be illustrated in a later section.



FIG. 6. XRD θ -2 θ scans of PZT thin films with different Zr-to-Ti stoichiometries: (a) Zr/Ti = 15/85, (b) Zr/Ti = 30/70, (c) Zr/Ti = 45/55, (d) Zr/Ti = 60/40, (e) Zr/Ti = 70/30.

Arlt *et al.*²² have developed a model to describe the relationship among 90° domain width, grain size, and tetragonality (c/a ratio) of a ferroelectric crystal. The expression is shown as below:

$$w = \sqrt{\frac{32\pi\sigma G}{E\epsilon^2}} \quad , \tag{1}$$

where w is the equilibrium domain width, $\sigma = 3 \times 10^{-3} \text{ J/m}^2$ for PbTiO₃ is the surface energy per unit area of domain boundary,²⁵ G is the grain size, $E(C_{11} = 1.2 \times 10^{11} \text{ N/m}^2$ for PbTiO₃) is Young's modulus, and ϵ is the magnitude of transformation strain from cubic to tetragonal phase due to constraint imposed by grain boundaries. The strain term ϵ is defined as [(c/a) - 1]/2 for tetragonal phase ferroelectrics. According to Eq. (1), it can be found that the larger the c/a ratio is, the smaller is the domain width. The c/a ratio of PZT decreases from 1.06 to ~1.025 with increasing Zr content from 0% to 45%. The domain sizes of tetragonal PZT (30/70) and PZT (45/55) were calculated to be around 10 and 18 nm, respectively, using Eq. (1). These values are consistent with the domain size observed by XTEM [i.e., ~10 nm for PZT (30/70) in Fig. 7(a) and \sim 20 nm for PZT (45/55) in Fig. 7(b)]. It is noted that Arlt's model predicts the equilibrium domain width under the grain boundary constraint. From the XTEM observation, domains with enlarged width were found near the film surface [e.g., Figs. 7(a) and 7(b)] where strain relief could easily occur during the paraelectric-to-ferroelectric phase transition.

In Sec. III. B, the domain structure of lower temperature ($T \leq 550$ °C) grown PbTiO₃ thin films was described. The domain structure was observed to be composed of primarily 180° domains with domain size ranging from 2 to 5 nm, which is smaller than the predicted value (\cong 10 nm) using Arlt's analytical method. Since Arlt's equation was derived on the basis of the consideration of strain energy and surface energy of domain boundaries, while the major factor for controlling the size of 180° domains is the electrostatic energy, the deviation of the calculated and actual domain sizes was observed.

For the rhombohedral phase PZT (70/30), despite the difference of polarization axis and domain boundary plane as compared with the tetragonal counterparts, the domain width is around 30 nm, similar to that found in the tetragonal phase PZT. The dominance of (100) type domain boundaries in the rhombohedral phase PZT can be understood by following Arlt's approach. From Eq. (1), the determining factors of equilibrium domain width are mainly the surface energy of domain boundaries due to the paraelectric to ferroelectric phase transition. The dominance of (100) type domain boundaries can be attributed to the less strain imposed from grain boundaries.

The surface morphology of PZT thin films is also influenced by the domain structure, as shown in the XTEM micrographs. For PZT (30/70) thin film, Fig. 7(a), the surface of a specific grain is 45° inclined from the surface normal. PZT (45/55) shows a moderate roughness, Fig. 7(b). On the other hand, the surface of the rhombohedral phase PZT (70/30) is relatively flat except near the grain boundary area, Fig. 7(c). The difference in surface morphologies of PZT thin films with respect to their Zr to Ti stoichiometry is attributed to the strain relief as described in the previous paragraph along with the pres-



FIG. 7. Dark-field XTEM micrographs of PZT thin films: (a) Zr/Ti = 30/70, (b) Zr/Ti = 45/55, (c) Zr/Ti = 70/30. (The domain boundaries are indicated by arrows.)

ence of different type of domain boundaries. Similar effects have also been theoretically analyzed by Streiffer *et al.* for PZT thin films grown on $SrTiO_3$.²⁴

D. Ferroelectric properties of PZT thin films

Shown in Fig. 8 are the dielectric constants ($k = \epsilon_r/\epsilon_0$) of PZT thin films, which increase from 293 for PbTiO₃ to 790 for PZT (45/55). The dielectric losses are less than 0.1 in the measuring frequency range. Dielectric constants close to the morphotropic boundary are lower than those values reported by Klee et al.¹⁸ but are close to the values reported by Foster et al.¹¹ The major factor affecting the dielectric constants is the film orientation. The solution-derived PZT thin films in the study of Klee et al.¹⁸ were of (111)/(100) mixed orientations, while the MOCVD-derived PZT films in the study of Foster et al.¹¹ and the present study were predominantly (001) or (100) oriented. PZT at morphotropic boundary consists of both tetragonal and rhombohedral phases with their polarization axes along $\langle 100 \rangle_c$ and $\langle 111 \rangle_c$. The flexibility of polarization vectors responding to electric field for the (111)/(100) mixed oriented films could give higher dielectric constant values than (100)- or (001)oriented films.

The hysteresis behavior of PZT thin films grown on LNO is shown in Figs. 9(a)-9(d). All hysteresis loops show saturation at 200 kV/cm applied field. It is worth noting that saturated hysteresis loops can only be observed for thin films annealed at 500 °C for 30 min after top electrode deposition. Unannealed PZT thin films generally show unsaturated, slanted hysteresis loops with evident shift along electric field axis. It was suggested by



FIG. 8. Dielectric constant of PZT thin films with various Zr-to-Ti stoichiometries.

Klee *et al.*¹⁸ and later by Lee *et al.*²⁶ that the deformation of hysteresis loop is associated with the internal field due to trapped charges such as lattice vacancies or impurity atom located at grain boundaries or domain walls. Under suitable annealing condition, those trapped charges can be removed and domain motion can be more easily activated.



FIG. 9. Hysteresis behaviors of PZT thin films with various Zr-to-Ti stoichiometries: (a) Zr/Ti = 30/70, (b) Zr/Ti = 45/55, (c) Zr/Ti = 60/40, (d) Zr/Ti = 70/30.

The remanent polarizations (P_r) of the PZT thin films are around 13 and 12.5 μ C/cm² for tetragonal phase PZT with 30 and 45 at.% Zr content, respectively. Rhombohedral phase PZT shows lower P_r values, which are 10 and 8 μ C/cm² for 60% and 70% Zr content PZT, respectively. Factors affecting the remanent polarization value include grain size, preferential orientation, and film stress. Fine-grain PZT thin films generally show smaller $P_{\rm r}$ values because of the higher density of grain boundaries, which would trap space charges and hinder the domain motion. However, the effect of grain size might not be the dominating factor that affects the P_r value in the present study. It was reported by Klee et al.¹⁸ that solution-derived (001)/(111) mixed oriented PZT thin films with lateral grain sizes around 0.1-0.2 µm display $P_{\rm r}$ values exceeding 20 μ C/cm². The most important factor can be the preferential orientation. For tetragonal PZT thin films, they were highly $(100)_t$ oriented and exhibit lower P_r values when compared with the reported P_r values of highly (001)_t-oriented epitaxial films. For rhombohedral PZT, the lower P_r values can be attributed to its $\langle 111 \rangle_c$ polarization axes. The measured remanent polarization value is the projection of the actual $\langle 111 \rangle_c$ - oriented remanent polarization value on $\langle 001 \rangle_c$ axes. The third factor concerns the differential thermal expansion stress. It was illustrated by Tuttle *et al.*²⁷ that the P_r values of (111)-oriented PZT thin films deposited on Pt/Si are different from those deposited on Pt/sapphire. Detailed studies of film stress versus temperature revealed that PZT thin films deposited on platinized Si sustained larger tensile thermal stress than other platinized oxide single-crystal substrates like MgO or sapphire and generally showed slanted hysteresis loop.

For PZT thin films, the coercive field (E_c) decreases as the Zr concentration increases. The E_c values decrease from 80 to 40 kV/cm. Similar studies have been reported by Klee *et al.*¹⁸ for PZT thin films deposited on Pt electrode which are also consistent with the results reported by Foster *et al.*¹¹ for PZT thin films epitaxially grown on SrRuO₃/SrTiO₃ substrates. It is speculated that the variation of E_c values is probably due to the domain boundary density variation with respect to the Zr-to-Ti ratio for PZT thin films in their tetragonal phase. PZT thin films with higher Ti content contain more domain boundaries due to the smaller equilibrium domain width and tetragonality (higher transformation stress), thus resulting in higher coercive field. The lower E_c value found in the rhombohedral PZT as compared with the tetragonal phase can be attributed to the multiplicity of eight $\langle 111 \rangle_c$ polarization axes of the rhombohedral phase as compared with the six $\langle 100 \rangle_t$ axes of tetragonal phase. Moreover, the component of the normal electric field for aligning of $\langle 111 \rangle_c$ -oriented dipole can be smaller than the electric field required for altering $\langle 100 \rangle_t$ dipole to $\langle 001 \rangle_t$ orientation for these highly $(100)_t$ textured thin films.

E. Dc current-voltage characteristics

Shown in Fig. 10 is the leakage current measurement (log J versus $V^{1/2}$ plot) of the PZT thin films. For all the measurements, a voltage was applied to the top electrodes and swept from zero to positive voltage (0 to 10 V). The sweep step was 0.01 V with a waiting time of 1 s/step. Two distinct and nearly linear regions with a transition occurring near 4 V (voltage^{1/2} = 2 V^{1/2}) were observed for all curves. The leakage current of perovskite ferroelectric thin films has been intensively studied. 19,20,21 The low-field (voltage $^{1/2} < 2 V^{1/2}$) conduction with low current density ($J \le 5 \times 10^{-7} \text{ A/cm}^2$) is generally recognized as a contribution from mobile charge in the ferroelectric film. For the high-field region (volt $age^{1/2} > 2 V^{1/2}$), the conducting mechanism may be due to the Schottky effect, Poole-Frenkel effect, or space charge limited current. Dietz et al.¹⁹ characterized the leakage current of (Ba,Sr)TiO₃ (BST) thin films and il-



FIG. 10. log(J) versus $V^{1/2}$ plot of PZT thin films. The two distinct nearly linear regions are indicated by dashed lines.

lustrated Schottky barrier limited current. Yoo *et al.*²⁸ suggested the dominance of the Schottky effect in the high-field region. Sudhama *et al.*²⁰ demonstrated the conducting behavior in different electric field strength and suggested the ohmiclike behavior in low field while the high-field current conducting might involve Schottky effect, Poole–Frenkel effect, and space charge limited current. For all specimens used in this study, the microstructure has been confirmed by XTEM to be composed of highly oriented textured grain; thus, the contribution of grain boundaries lying parallel to the plane of electrode is negligible.

The relationship between current density (*J*) and electric field (*E*) due to the Schottky effect can be expressed as the following:^{19,20}

$$J_{\rm s} = AT^2 \, \exp\left(\frac{-q\Phi_0 + \beta_{\rm s} E^{1/2}}{K_{\rm B}T}\right) \quad ,$$
 (2)

where A is the Richardson–Dushman constant, T is the absolute temperature, q is the electronic charge, Φ_0 is the Schottky barrier height, K_B is the Boltzman constant, and β_S is a constant. From Eq. (2), $\log(J)$ has a linear relation with $V^{1/2}$ if the conducting mechanism is Schottky effect dominated and is generally in agreement with our observation.

Although the actual mechanism controlling the I-Vbehavior of PZT thin films can be even more complicated, we might be able to describe the I-V behavior of these PZT thin films with the following approach. In the low-field region (voltage < 4 V; region I in Fig. 10), the I-V curve of the PZT thin films capacitor exhibits ohmiclike behavior contributed by mobile charges and leakage current density is typically lower than 5×10^{-7} A/cm². In higher field (4 V < voltage < 6.5 V; region II in Fig. 10), the $\log(J)$ versus $V^{1/2}$ plot shows a linear region and indicates the dominance of Schottky effect. For highfield strength (voltage > 6.5 V), the deviation from lin-earity in $\log(J)$ versus $V^{1/2}$ plot indicates a complex mechanism involving Schottky effect, Poole-Frenkel effect, and space charge limited current; furthermore, the effect of series resistance from contact or probe tip may also contribute to the nonlinearity.

IV. CONCLUSIONS

Highly textured PT thin films have been grown on an LNO electrode over a large temperature range (450–600 °C) using MOCVD techniques. The optimal growth temperature for requisite electrical properties was found to be 600 °C. TEM observation showed that the 90° domain started to form only for growth temperature higher than 550 °C. The predominant domain structure is of the 180° type with their polar axis lying on the substrate surface for PT thin films grown at lower temperatures.

Domain configuration of PZT thin films (grown at 600 °C) in both tetragonal and rhombohedral phases was studied. The significant variation in domain widths and domain densities of PZT thin films with respective to Zr-to-Ti ratio was measured and compared with the estimation based on Arlt's model. Furthermore, it was found that the predominant domain boundaries of tetragonal phase PZT are (110) planes whereas, for rhombohedral phase PZT thin films, they are mostly lying on the (100) plane.

The dielectric and ferroelectric properties were measured. Postdeposition heat treatment was found to be essential for improved electrical properties of the multilayer capacitor structure. Annealing of PZT thin films after top electrode deposition was found to be effective for improved dielectric and ferroelectric properties. The lower remanent polarization value in the rhombohedral phase PZT as compared with the tetragonal phase can be attributed to the difference in polarization orientation for these (100)-textured thin films. It was also found that coercive fields decrease with increasing Zr content. This behavior is believed to be due to the domain boundary density variation with respect to the Zr-to-Ti ratio in their tetragonal phase. Moreover, the lower coercive field for the rhombohedral PZT in comparison with tetragonal phase can be attributed to the multiplicity of $\langle 111 \rangle$ and $\langle 100 \rangle$ polarization axes. Dc conducting measurements were also made; the low leakage current of 5×10^{-7} A/cm² in the device operating voltage range was found. The dominating conduction mechanism in a different field strength range was illustrated.

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