Deposition of PZT thin films with {001}, {110}, and {111} crystallographic orientations and their transverse piezoelectric characteristics

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ABSTRACT

$Pb(Zr_xTi_{1-x})O_3$ [PZT] thin films of morphotropic phase boundary (MPB) composition having {001}, {110}, and {111}-orientations were fabricated on silicon substrates $(111)Pt/Ti/SiO_2/Si$ using a metal organic decomposition spin-coating technique. The influence of crystallographic orientation on the transverse piezoelectric coefficient e_{31}^* of the films have been determined. The largest e_{31}^* was found in {110}-oriented film. The differences observed in e_{31}^* have been explained on the basis of domain wall contributions which are dependent on film texture. The influence of thin film texture on polarization switching characteristics have also been studied. Copyright © 2012 VBRI Press.

Keywords: PZT; preferentially oriented thin films; transverse piezoelectric coefficient; fatigue; domain switching.

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Introduction

Lead zirconium titanate (PZT) thin films with the morphotropic phase boundary (MPB) composition is extensively used for Micro Electro Mechanical System (MEMS) applications due to high piezo characteristics offered by them. For MEMS applications, the in-plane transverse piezo coefficient, e_{31}^* is the most important parameter to be considered [1, 2]. The factors which influence e_{31}^* are film thickness, film texture and compositional gradient across the film thickness [3, 4]. In microactuators, PZT films are typically 0.5-2.0 μm in thickness. Thicker films are prone to have higher porosities and therefore lower dielectric breakdown strength. In thin films the piezoelectric characteristics are significantly influenced by the contribution from domain wall movement [5, 6]. However, there is considerable scatter in data in the literature with respect to this extrinsic contribution to piezoelectric strain. It has been recently shown that PZT thin films with MPB composition having {110}-preferred orientation exhibited high values of e_{31}^* [7]. It is therefore of interest to compare the extent of extrinsic contributions to e_{31}^* in textured thin films of PZT having MPB compositions. For MEMS applications like microbending actuators, high frequency filters, micropumps and pressure sensors, development of dense, crack-free piezoelectric films integrated on silicon substrates is essential [8, 9]. Of the various methods employed to deposit PZT thin films, chemical-solution deposition (CSD) offers several advantages such as precise stoichiometry, lower processing temperatures and economy. Therefore, in the present study, we report fabrication of PZT thin films by CSD method and study the influence of preferred crystallographic orientation on e_{31}^*

Experimental

Highly stable precursor solution of PZT was synthesized by a hybrid Metallo-Organic Decomposition (MOD) and sol-gel process adapting the procedure as discussed in our earlier work [10, 11]. The reactants, lead acetate (Merck, India) and zirconium acetyl acetone (Merck, India) were refluxed in 2-ethyl hexanoic acid (Sigma Aldrich, India). The substituted acetic acid and the excess 2- ethylhexanoic acid were removed through distillation and the brownish residue was dissolved in isopropyl alcohol containing titanium isopropoxide (Sigma Aldrich, India) in the presence of chelating agent diethanolamine (Sigma Aldrich, India) to yield a stable precursor solution. The solution was spin coated on to platinised silicon substrate [(111)Pt/Ti/SiO$_2$/Si; Inostek, Korea], dried at 110^0C for 10min and then annealed at 650^0C for 20 min after subjecting to an intermediate soaking for 10 min at 400^0C. The coating and thermal treatment cycles were repeated to get {111}-oriented films of thickness 2.0 μm. Before the deposition of PZT thin film, SrTiO$_3$ (ST) layer having 50nm thickness was used as the seeding layer. Different buffer layers like TiO$_2$, and PbTiO$_3$ were employed to get {001}, and {110}-preferred orientations respectively [12, 13]. When TiO$_2$ layer was used, SrTiO$_3$ layer as described above was coated over it. The crystallographic orientation and phase of these deposited films were determined using x- ray diffractometer (XRD; Model: D55005, Bruker,

Germany). Gold top electrodes (dia. ~0.35mm) were deposited by vacuum evaporation using a vacuum coater (Model: 12A4D, Hind High Vacuum, India). Dielectric and ferroelectric characteristics were determined using an Impedance analyzer (Model: 4294A, Agilent Technologies, USA) and Piezoelectric evaluation system (Model: TF Analyser 2000, aixACCT, Germany) respectively. Fatigue was studied using the piezoelectric evaluation system. For the measurement of the piezoelectric properties, rectangular specimens of dimensions (5.5 x 1.5) mm^2 were diced out from the substrates. The transverse piezoelectric properties of the PZT thin films were evaluated using unimorph cantilevers of PZT/Pt/Ti/SiO$_2$/Si. The details of the measurements have been described in the previous reports [14, 15]. Application of sine wave voltage between upper and bottom electrodes generates the deflection by the transverse inverse piezoelectric effect, and the tip displacement was measured using a laser Doppler vibrometer (Model: AT-3500, Graphtec, Japan) and a laser interferometer (Model: AT-1100, Graphtec, Japan). Microstructural analysis of the film was recorded using a High Resolution Scanning Electron Microscope (HRSEM, Model FEI Quanta FEG 200, USA). Compositional analysis of thin films was carried out by energy dispersive analysis of x-rays (EDX) equipped with scanning electron microscope (Model: Genesis Apex 2, Ametek, Japan).

Results and discussion

The x-ray diffraction (XRD) patterns of the PZT thin films are shown in **Fig. 1**. The films formed when SrTiO$_3$ is used as the buffer layer has a pure perovskite phase with a strong {111}-preferred orientation (**Fig. 1a**). To fabricate films with {001}-orientation, TiO$_2$ buffer layer of thickness ~30nm was used as reported earlier [12] (**Fig. 1b**). In order to achieve {110}-orientation (**Fig. 1c**), the heat treatment conditions were modified. Before annealing at 600^0C, the films were subjected to an intermediate pyrolysis at 300^0C for 10min. The compositional analysis carried out on the thin films (**Table 1**) revealed the efficiency of the precursor system used to achieve the desired MPB composition.
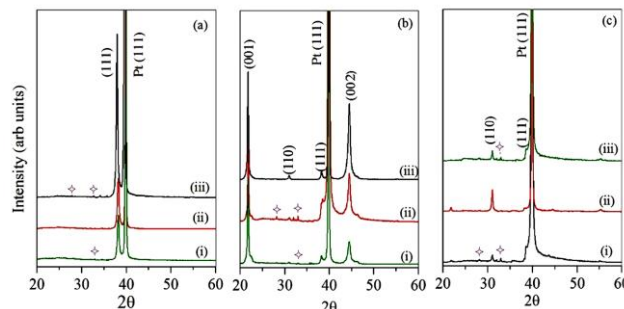

Fig. 1. XRD patterns of textured PZT thin films of thickness (i) 0.5 μm; (ii) 1.0 μm, and (iii) 2.0 μm on Pt/Ti/SiO$_2$/Si substrate (a) {111}, (b) {001}, and (c) {110} orientation :shows the pyrochlore phase.

The morphology and cross section of the films are shown in **Fig. 2**. Small grains (~15 nm diameter) found in the surface of the films are those of Pyrochlore phase. Since these grains are not seen across the film thickness, their presence is attributed to PbO loss from the film

surface [16, 17]. It is also seen that in all the cases, the films have a dense, columnar microstructure.

Table 1. Compositional analysis of PZT thin films.

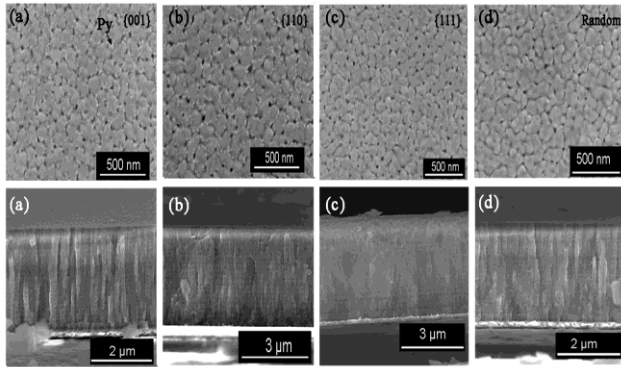| Film orientation	Pb/ (Zr+Ti)	Zr/ (Zr+Ti)
{001}	1.0166	52.448
{110}	1.0017	52.641
{111}	1.0279	52.808
Random	1.0225	52.624

Fig. 2. HRSEM of the PZT thin film (Surface and cross sectional view). (a){001}, (b) {110}, (c) {111} and (d) random orientation. Smaller grains marked Py represent Pyrochlore phase.

The transverse piezoelectric properties of the PZT thin films were evaluated from the deflection of PZT/Pt/Ti/SiO$_2$/Si cantilevers by applying unipolar sine wave voltage. Prior to the deflection measurements, we observed the resonant frequency of the test sample because the deflection characteristics were analyzed on the basis of the static deflection of an ideal unimorph cantilever model [18]. In this experiment, we measured the tip displacement at a frequency of 1000 Hz. From the tip displacements, the transverse piezoelectric coefficient e_{31}^{*} was evaluated, as per equation (1), which is used when the substrate thickness is much higher than that of the piezoelectric film [7, 14].

$$e_{31}^{*} = \frac{d_{31}}{s_{11,p}^{E}} \cong -\frac{h_s^2}{3 s_{11,s} L^2} \frac{\delta}{V}$$

(1)

where δ, V, L, h, and s$_{11}$ are the tip displacement, applied voltage between top and bottom electrodes, length of the cantilever, thickness, and the elastic compliance, respectively [18]. The subscripts of "s" and "p" denote the substrate and the piezoelectric film, respectively. The elastic compliance, s$_{11,s}$ of the substrate is given by the reciprocal of its Young's modulus. The Young's modulus of the silicon substrate is 168 GPa. From the above equation we evaluated the piezoelectric properties of PZT thin films and the electric field dependence of e_{31}^{*}, is shown in **Fig. 3**.

Being a MPB composition, tetragonal and rhombohedral phases co-exist in PZT thin films. The domains in tetragonal compositions with different

orientations are shown in **Fig. 4(a)**. For {001}- oriented PZT two types of domains are, 90^0 domains $\left(\vec{a}\right)$ and 180^0 domain $\left(\vec{b}\right)$ with respect to film normal (**N**) [**Fig. 4a**(i)]. The domains associated with {110} - oriented film are at an angle of 45^0 $\left(\vec{c}\right)$ and 90^0 $\left(\vec{d}\right)$ whereas for {111}-orientation, all the three domains $\left(\vec{e}\right)$ are at an angle of 54^{0}44′ with **N**.
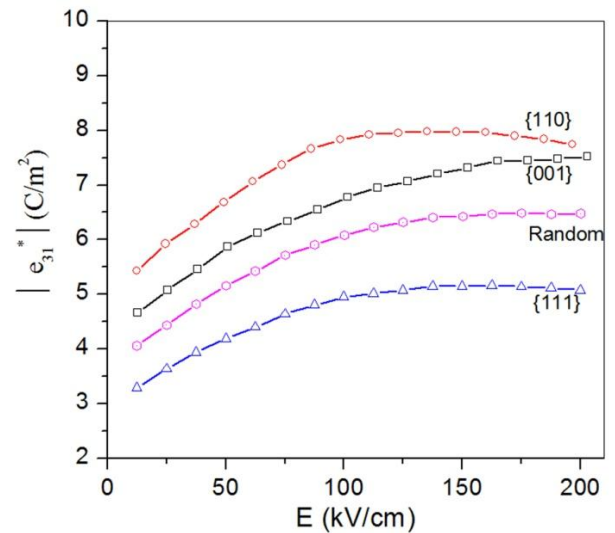

Fig. 3. Transverse piezoelectric coefficient, |e$_{31}$*| of PZT thin films as a function of orientation.
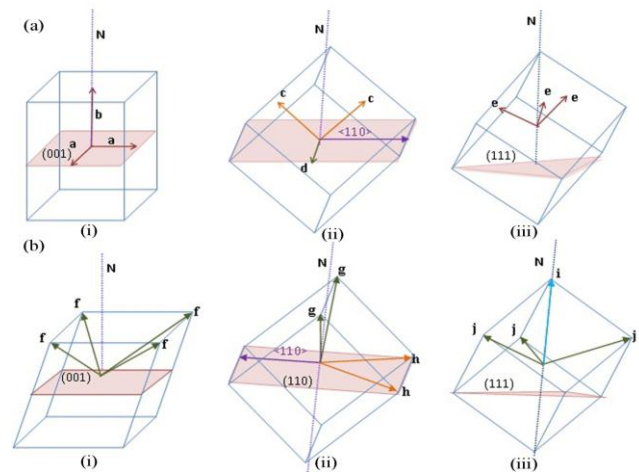

Fig. 4. Domains along various directions in (a) Tetragonal and (b) Rhombohedral PZT (i) {001}, (ii) {110} and (iii) {111}.

The domains associated with rhombohedral compositions associated with different film orientations are as shown in **Fig. 4(b)** where there are four 54^{0}44′ domains $\left(\vec{f}\right)$ with respect to film normal (**N**) for {001}-oriented PZT. The domains associated with {110}- oriented films are at an angle of 35^{0}16′ $\left(\vec{g}\right)$ and 90^0$\left(\vec{h}\right)$ w.r.t. to

film **N** where as for {111}-orientation, there are three 71^0 domain $\left(\vec{j}\right)$ and one 180^0 domain $\left(\vec{\iota}\right)$ w.r.t. film normal **N.**

Table 2. Electrical characteristics of PZT thin films.

Orientation	ε_r	$\tan\delta$	Dielectric tunability at E= 200kV/cm	$2P_r$ $(\mu c/cm^2)$	$2E_c$ (kV/cm)	$|e_{31}^*|(C/m^2)$ at 100kV/cm
{110}	1081	0.05	62%	40	100	7.8
{001}	961	0.07	48%	40	150	6.8
{111}	915	0.06	39%	22	125	5.0
Random	798	0.05	50%	33	160	6.1
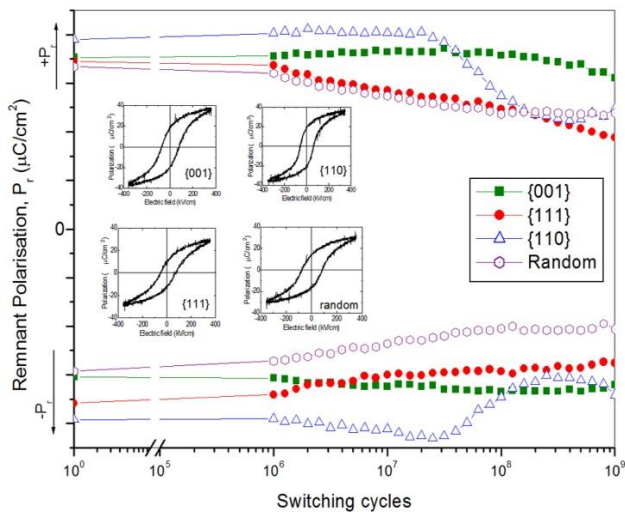
Fig. 5. Fatigue characteristics of oriented PZT thin films. Inset shows the P-E loops (before fatigue) for various orientations.

The switching of the non-180^0 domains, dictated by the crystal symmetry, lead to nonlinearity in e_{31}^*. In {110}-PZT films, the <110> vector facilitates polarization rotation [**7**]. This accounts for the observed high magnitude and nonlinearity in piezo response. Polarisation rotation in such {110}-oriented films also accounts for the high values of ε_r (1081), dielectric tunability (62% at 200kV/cm) and remnant polarization, P_r ($2P_r = 40\mu C/cm^2$). In {001} - PZT, the domains $\left(\vec{a}\right)$ switch by 90^0 whereas in {111}-PZT the domains $\left(\vec{j}\right)$ switch by only 71^0 leading to lower values of e_{31}^* when compared to that in {001}-PZT. This is also confirmed by the differences in their dielectric characteristics (ε_r, $\tan\delta$ and tunability) (**Table 2**). In randomly orientated films, the e_{31}^* lies between that of {111} and {001}-oriented film as more domains are involved in the switching process.

As preferentially oriented films have different domain configurations, it is of interest to study their effect on polarization fatigue characteristics. For this purpose, thin film capacitors were subjected to a fatigue pulse having an amplitude of 10V at a frequency of 1MHz. **Fig. 5** shows the variation of P_r as a function of switching cycles. It is observed that in {111}-PZT, after 10^6 cycles, there is degradation of switchable polarization whereas in {110}-PZT, onset of polarization fatigue is seen only after 10^7 cycles. In thin films presence of internal electric field also

strongly influences the fatigue characteristics. Higher fatigue endurance in {110} –PZT suggest that internal electric field developed along <110> is lower when compared to that developed along <111>. The PZT film with {001}-orientation exhibit excellent fatigue endurance characteristics showing negligible fatigue even after 10^9 cycles. This is because the polar axis is aligned along [001] due to the high degree,

$$\left[I_{(001)}/I_{(00l)} + I_{(110)} + I_{(111)} = 92\% \right]$$ of {001}-orientation. It can also be inferred that no net internal field develop along <001>.

Conclusion

Dense, crack- free PZT thin films of MPB composition with {001}, {110}, and {111}-orientations were deposited on to Pt/Ti/SiO$_2$/Si substrate employing a hybrid MOD and sol- gel method using spin coating technique. All the films exhibited columnar microstructure. The extent of extrinsic contribution to the transverse piezoelectric coefficient e_{31}^* have been explained on the basis of the differences in the domain wall contributions dictated by different crystallographic orientations of the thin films. Because of the high average value of e_{31}^* (-6.6 C/m^2) and improved fatigue endurance characteristics, {001}-oriented PZT films have potential advantages in MEMS applications.

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