Effect of Sr and La co-doping on structural and electrical properties of RF sputtered PZT thin films

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Abstract

Doping in lead-zirconate-titanate (PZT) thin films is on the rise for next generation micro-electro-mechanical systems (MEMS) and energy harvesting applications, owing to their improved ferro-electric and piezoelectric properties. Strontium, lanthanum and neodymium like elements are the most exploited for such applications. This paper reports realization of a PZT thin film with strontium and lanthanum co-doping in tandem, Pb₁₋ₓ−₁/₂Srₓ(La₀.₅₁,T₁₀.₄₄)O₃ x = 0.06, y = 0.03 (PSLZT), by RF sputtering process. Different process conditions like substrate temperature from 250 °C–350 °C and annealing temperature from 650 °C–750 °C are studied to achieve pyrochlore free PSLZT thin film. The structure, surface morphology, surface topography and ferroelectric characteristics are investigated using x-ray diffraction (XRD), Atomic Force Microscopy (AFM), Field Emission Scanning Electron Microscopy (FE-SEM) and P-E analyser, respectively. Nanoscale polarization switching processes and the local surface displacements are studied to ascertain that the PSLZT thin film exhibits the ferroelectric and piezoelectric properties. Experimental results reveal that the present PSLZT thin film has a polarization of 5.5 μC cm⁻², leakage current density of 10⁻⁵ A cm⁻² and piezoelectric charge coefficient, d₃₃, of 87 pm V⁻¹, which are suitable for realization of various new piezoelectric MEMS sensors.

1. Introduction

Lead-Zirconate-Titanate (PZT) thin films are the key materials for developing piezoelectric based micro-electro-mechanical systems (MEMS). They possess higher electromechanical coupling coefficients, piezoelectric coefficients and dielectric constants than the other widely used materials, ZnO and AlN [1–3]. The composition, near morphotropic phase boundary (MPB), is the best choice for various MEMS such as accelerometer [4], hydrophone [5], acoustic imaging [6], RF MEMS [7] etc. Improvements in piezoelectric and ferroelectric properties of PZT are reported to further enhance the performance of MEMS by adding dopants in PZT thin films [8–12], particularly for acoustical devices, where higher piezoelectric charge coefficient and moderate dielectric constant are essential for getting better receiving sensitivity.

The physical, dielectric and piezoelectric properties are influenced by the dopants that substitute A or B position of perovskite structure [13–15]. The composition, grain size, crystallographic orientation and mechanical boundary conditions alter the piezoelectric properties of the thin film. All these factors may vary significantly in thin films depending on the deposition technique and the substrate used. Therefore, for the optimization of the piezoelectric performance of the deposited films, each of these issues must be taken into consideration.

Doping of strontium, an isovalent dopant, with PZT improves dielectric permittivity and piezoelectric strain coefficient, with slight increase in the electromechanical coupling factor; thus makes PZT as hard [10, 16]. On
the existence of crystalline phases. Atomic Force Microscope (AFM, Make: Bruker Dimension Edge) was used to

the other hand, doping of lanthanum with PZT improves the dielectric loss factor and piezoelectric strain

coefficient [9, 17, 18]. Co-doping of strontium (Sr$^{2+}$) and lanthanum (La$^{3+}$) replaces Pb$^{2+}$ ion in A-site and very

few literature are reported in ceramics. Mehta et al studied structural properties of Pb$_{0.94}$Sr$_{0.06}$La$_{0.03}$Zr$_{0.52}$Ti$_{0.48}$O$_3$ and compared results with Pb$_{0.94}$Sr$_{0.06}$Zr$_{0.52}$Ti$_{0.48}$O$_3$ and

Pb$_{0.94}$La$_{0.04}$Zr$_{0.53}$Ti$_{0.47}$O$_3$ [19]. The tetragonality ratio (c/a)$^2$ decreases as the La/Sr ratio increases in the

composition. Volkan et al reported that MPB region extends from Zr/Ti ratio of 52/48 to 58/42 in the

composition Pb$_{0.94}$Sr$_{0.05}$La$_{0.01}$Zr$_{0.54}$Ti$_{0.46}$O$_3$ and obtained a piezoelectric coefficient, $d_{33}$, of 412 pC/N with
dielectric constant of 1800 [20]. Jiangguli Peng et al reported a piezoelectric coefficient, $d_{33}$, of 640 pC/N in their

composition Pb$_{0.94}$Sr$_{0.06}$La$_{0.02}$Zr$_{0.53}$Ti$_{0.47}$O$_3$ [21]. Premkumar et al reported a piezoelectric coefficient, $d_{33}$, of
325 pC/N in their composition Pb$_{0.94}$Sr$_{0.05}$La$_{0.01}$Zr$_{0.54}$Ti$_{0.46}$O$_3$ for tape casted thick film with dielectric
constant of 1300 [22].

It is apparent that doping with both Sr and La in PZT is found to provide better piezoelectric charge and

electric field coefficients in cases of ceramic and thick film form. However, these compositions are to be realized in

thin film form on Si substrate to develop advanced MEMS based piezoelectric sensors with enhanced sensitivity.

Therefore, in this paper an attempt has been made to deposit Pb$_{0.895}$Sr$_{0.06}$La$_{0.03}$Zr$_{0.52}$Ti$_{0.48}$O$_3$ (PSLZT) thin film by RF

to platinized silicon substrates and to investigate the effect of process conditions on its structural,
morphology, ferroelectric and piezoelectric properties.

2. Experimental details

Pb$_{0.895}$Sr$_{0.06}$La$_{0.03}$Zr$_{0.52}$Ti$_{0.48}$O$_3$ is processed using powders of PbO, ZrO$_2$, TiO$_2$, SrCO$_3$, La$_2$O$_3$ (>99% purity)

by solid oxide route with 2% and 10% excess of PbO. These excess percentages of PbO are used to compensate

the probable loss that occurs during sintering and thin film deposition processes. The powders are ball milled for

24 h with stabilized zirconia balls in deionized water medium, followed by drying. Powders are granulated and

compacted in the form of disc and sintered at 1280 °C for 2 h in PbO environment to obtain PSLZT target disc of

50 mm diameter with higher density [22]. RF planar magnetron sputtering along with controlled substrate

heating was used to deposit the PSLZT thin films. The schematic structure of the PSLZT thin film with top and

bottom electrodes is shown in Figure 1. Silicon substrate is chosen because of the compatibility of it in integration

with Si MEMS process technologies.

The substrates were ultrasonically cleaned in acetone, iso-propanol and deionized water and dried using

nitrogen gas. Both substrate and PSLZT target with 2% or 10% excess of PbO were loaded in a SS chamber and

subsequently the chamber was evacuated up to 2 × 10$^{-5}$ mbar. Proper sputtering conditions were established

by igniting the plasma on the target using Ar gas and RF power. In order to initiate the deposition of PSLZT thin

film on platinized Si substrate, oxygen gas was introduced in the chamber and proper partial pressure level

(Ar/O$_2$) was maintained throughout the deposition with substrates heating. Later the deposition rate was

increased by increasing the RF power substantially to certain level and adjusting the target to substrate distance.

The details of experimental parameters are given in table 1. Optimization of PSLZT thin film deposition

conditions was done by varying the experimental parameters like, substrate temperature, partial pressure of

Oxygen, distance between target and substrate etc. Thereafter, the thin films were subjected to post deposition

annealing at various temperature from 650 °C to 750 °C in the oxygen atmosphere for 90 min.

The fabricated thin films are characterised using x-ray diffractometer (XRD, Make: Rigaku) for investigating

the existence of crystalline phases. Atomic Force Microscope (AFM, Make: Bruker Dimension Edge) was used to
study the surface morphology and piezoelectric measurements. Surface topographies were examined by Field Emission-Scanning Electron Microscope (FE-SEM, Make: Carl-Zeiss). For electrical measurements, chromium/gold (Cr (10 nm)/Au (100 nm)) top electrodes, with dimension of 1 mm dia. were patterned through a shadow mask using e-beam evaporation technique on the deposited PSLZT thin films. The ferroelectric measurements were performed at room temperature using the TF analyzer (Make: Aixacct GmbH) for an applied field range from $-500 \text{ kV cm}^{-1}$ to $500 \text{ kV cm}^{-1}$ for a frequency range of 100 Hz to 1 kHz.

3. Results and discussion

The XRD obtained for the as-deposited thin films shows the amorphous phase formation and no discrete crystalline phases are observed. Therefore, it is necessary to perform post annealing process on the deposited film to get perovskite phase.

Figures 2(a) – (c) shows XRD patterns of the thin film deposited using 2% excess PbO target, for different substrate temperatures (250 °C–350 °C) and annealing temperatures (650 °C–750 °C), respectively. XRD pattern shown in figures 2(a), (b) reveals that for substrate temperatures above 300 °C, the diffraction pattern was dominated by the non-ferroelectric pyrochlore phase $[\text{Pb}_2(\text{Zr}_{x}\text{Ti}_{1-x})_2\text{O}_7]_{-\varepsilon}$ and no perovskite phase formed. This is due to intrinsic volatile nature of lead (Pb) compound happened during deposition processes at the elevated substrate temperature [23].

The XRD corresponding to the substrate temperature at 250 °C shown in figure 2(c) indicates that the pyrochlore phase starts vanishing after post annealing process. However, a dominant (002) plane is observed but without any indication of (001) plane. This highlights that the thin film makes a transformation from pyrochlore phase to pseudo cubic phase. Non-homogeneous distribution of $\text{Pb}^{2+}$ and dopants ($\text{Sr}^{2+}$ and $\text{La}^{3+}$) on the A-site in co-doped PZT would lead to pseudo cubic pattern observed in XRD.

In order to avoid this unwanted phase formation, the thin film fabrication process was repeated with an excess PbO of 10% in PSLZT target with substrate temperature of 250 °C followed by annealing at 750 °C. The XRD obtained for the PSLZT thin film is shown in figure 3. It exhibits a polycrystalline perovskite phase formation with the presence of (100), (110) and (111) planes. It is further noted that pyrochlore phase is not present in the thin film which indicates the coexistence of perovskite phases [22]. In order to understand the existence of perovskite phase in the film, the XRD data was analysed by deconvoluting the (2 0 0) peak and observed the presence of tetragonal (T) and rhombohedral (R) phases. Splitting of diffraction peaks into (002)T, (200)T and (200)R at $2\theta$ between 43.7°–44.3° (inset of figure 3) indicates existence of both tetragonal and rhombohedral perovskite phases in the annealed PSLZT thin film.

The observations shown in figures 2 and 3 indicate that the post deposition annealing processes is important for enhancing the pervoskite nature and to obtain PSLZT polycrystalline thin film on platinized Si substrate.

Figure 4 shows the AFM of the PSLZT thin film deposited at substrate temperature of 250 °C and annealed at 750 °C. The experiment was carried out in the tapping mode to evade any deterioration to the surface of the film. The topography of the film shows smooth and void free surface, i.e. the grains are uniformly distributed. The root means square (RMS) roughness of the film is around 14 nm on a scanning area of 10 $\mu$m $\times$ 10 $\mu$m. The average particle size is around 35–40 nm.

Figure 5 (a) shows that microstructure of PSLZT thin film deposited at 250 °C substrate temperature and annealed at 750 °C for 30 min. The films were crack free with reasonably uniform microstructure and also no structural accumulation was observed due to co-doping of La and Sr Cross sectional SEM image confirms the dense PLSZT thin film structure with ~ 700 nm thickness as shown in figure 5(b).

The presence of pyrochlore phase during the initial development of PSLZT thin films deposited with 2% excess of PbO target confirms the linear ferroelectric behaviour and no domain switching current with respect to applied electric field as shown in figure 6. The reduction of activation energy required to form pervoskite phase

### Table 1. Experimental parameters used for deposition of PSLZT thin film.

| Experimental parameters | Value |
|-------------------------|-------|
| Base pressure (mbar)    | $2 \times 10^{-5}$ |
| Working pressure (mbar) | $20 \times 10^{-3}$ |
| RF Power (W)            | 50    |
| Substrate temperature (°C) | 250–350 |
| Distance between target and substrate (cm) | 8–10 |
| Sputtering gas ratio (Ar:O$_2$) | 6:4 |
| Substrate rotation (rpm) | 5     |
may be due to the presence of intermetallic phase between platinized Si substrate and piezo thin film which alter the amount of oxygen vacancies \[24\]. It enhances the defect formation with slowing down of formation of pervoskite phase of PSLZT thin film. This has been supported by XRD observation shown in figure 2(c).
Figures 7(a)–(c) shows results of polarization (P-E) and switching current versus the applied electric field and capacitance versus voltage measurements of pyrochlore free pervoskite phase of PSLZT thin film deposited using 10% excess of PbO target. P-E and I-E shows hysteresis performance and ferroelectric domain switching behaviour of PSLZT thin film. This hysteresis loop displayed clear saturation with remnant polarization ($P_r$) of 5.5 $\mu$Ccm$^{-2}$ and coercive field ($E_c$) of 97.5 kVcm$^{-1}$. It also indicates that co-doped process shift the composition towards a thinner hysteresis loop.

The reduction in ferroelectric hysteresis confirms that the donor ions (La and Sr) are incorporated into the PZT lattice and not acting as secondary phase in PSLZT [25, 26] and figure 5(a), surface morphology of PSLZT thin films also endorses the above observation. The asymmetry observed in both switching current and polarization loops are caused by the presence of internal bias field into the thin film capacitor structure (Au/Cr/PSLZT/Pt) due to charge trap near the electrode area [27].

The pinning of domain wall movement lowers the remnant polarisation and increases the coercve field due to A-site vacancies and porosities of the thin film. Capacitance and loss factor ($\tan \delta$) of the co-doped PZT thin films with respect to voltage are shown in figure 7(c). Inverse butterfly loop of C-V curve confirms the ferroelectric nature and two maxima reflecting the domain reversal property of ferroelectric thin film. Similarly, the pattern of loss factor confirms the above said property. A small shift (asymmetry) in the C-V curve indicates that accumulation of space charges at the metal ferroelectric interface layer.
Leakage current density versus electric field (J-E) of deposited PSLZT thin films was measured against the applied electric field and is shown in figure 8(a). The J-E curve shows the leakage current density is from $10^{-5}$ to $10^{-9}$ A cm$^{-2}$ for the applied voltage of ±4 V. The deposited film can be used for sensing applications as the film...
possesses low leakage current. The effect of co-doping on the breakdown voltage of metal-ferroelectric-metal (MFM) structure is shown figure 8(b) and compared with undoped PZT thin films.

Decrease in leakage current by about two order compared to undoped PZT thin films.

The functional characterises of the PSLZT thin films were investigated using piezoresponse force microscopy (PFM) by acquiring phase images arbitrarily at different spots, to visualize domain structure evolution under external electric field. Figures 9(a) and (b) shows combination of PFM amplitude and PFM phase signals of PSLZT thin film. These images confirm the existence of polarized regions (i.e. upward and
downward domains) in the thin films. The hysteresis loops are generated using a conductive AFM tip by applying an AC field over a sample surface and biased with respect to the tip. The tip’s deflection is sensitive to the local charge density from the local polarization and the results are shown in figure 9(c). These loops confirm the ferroelectric response of the film. The in-plane and out-of-plane polarization states were examined and the local piezoelectric charge coefficient, d33, around the sampling tip, was found to be \( \sim 87 \text{ pm V}^{-1} \) which is higher than reported d33 value of undoped PZT \([29]\). The asymmetry in the butterfly loop could be due to different work functions between two electrodes.

**Figure 8.** Measurement of (a) leakage current density versus electric field and (b) leakage current density versus breakdown electric field of PZT and PSLZT thin films.

4. Conclusion

In summary, La and Sr doped PZT thin film was deposited on platinised Si substrate by RF sputtering technique. The as grown PSLZT thin films shows amorphous phase due to high density of oxygen and lead vacancies. The crystalline pervoskite phase was optimized by using excess lead oxide target material, appropriate substrate temperature and post deposition annealing conditions. Structural and electrical characteristics were studied and confirmed the pyrochlore free piezo thin films. The co-doped PZT thin films indicate minimum leakage current density and better piezoelectric coefficient (\( \sim 87 \text{ pm V}^{-1} \)). The above enhancement of piezoelectric properties is due to doping of Sr and La which replaces partially oxygen vacancies and enhances the domain wall movement. The asymmetric behaviour of the charge distribution that exists because of presence of remaining oxygen vacancies, which gives rise to internal fields could be responsible for the reduced ferroelectric properties. These results indicate that PSLZT is one of the potential candidate material for future underwater sensor applications particularly MEMS based hydrophones and micro-power harvesting systems. Further studies about
the effect of Zr/Ti ratio, sputtering power and annealing treatment on the structural and electrical properties of co-doped PZT thin films are currently in progress in order to have a complete understanding of Sr, La co-doped piezoelectric thin films, which will fill an important technological gap between thin film and bulk ceramic.

Figure 9. AFM and PFM analysis PSLZT thin films deposited at substrate temperature of 250 °C and annealed at 750 °C (a) PRM amplitude (b) PRM phase and (c) Phase/amplitude versus bias voltage hysteresis loops.
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