



Nanograins dependent dielectric constant, tunability, phase transition, impedance spectroscopy and leakage current of $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ thin films

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ABSTRACT

Nanostructured $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ (PST) ($x=0.1, 0.2$ and 0.3) thin films have been prepared by chemical solution deposition process using spin coating technique. The solution as such was deposited on Pt/Ti/SiO₂/Si substrates and annealed at 650 °C/3h. Nanograins dependent dielectric properties of PST films show dielectric constant up to the higher frequency region, low losses, large tunability and phase transition at small temperature. The impedance data has been fitted by Cole–Cole model to study the effect of grain boundaries on the dielectric properties. The current–voltage characteristics have been measured to study leakage current in PST films and described by Poole–Frenkel emission model. It is suggested that the key carrier transport process in PST films is emission of electrons from a trap state near the metal–film interface into a continuum of states associated with each conductive dislocation. The activation energy value for carrier transport in PST films is obtained from temperature-dependent current–voltage characteristics.

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1. Introduction

PbTiO₃ thin films with compositional modification towards Pb and Ti sites recently demonstrated excellent dielectric properties especially in higher frequency region >1 MHz. These thin films are considered as potential materials for high frequency tunable device components [1–3] and ultra-large scale integration for dynamic random access memory capacitors [4,5]. For such applications, the two most important requirements are, first, capacitance of relaxor characteristics up to the higher frequency region and second, large tunability. Since the tunability of thin films is usually related with several factors, such as film stress, microstructures, oxygen defects, and interfaces. Besides these, the phase transition temperature (T_c) plays an important role in determining the tunable properties. As the tunability is directly associated with the dielectric constant at zero electric field and the tunable properties decrease remarkably as the temperature increases. Also, it is well known that T_c is the temperature where we achieve maximum value of capacitance. So, if T_c of PbTiO₃ thin film is reduced, then higher tunability and large capacitance could be obtained at low operating temperature. The doping of Sr for Pb in $(\text{Pb,Sr})\text{TiO}_3$ (PST) thin film plays a vital role in reducing grain size and T_c , than Sr for Ba in $(\text{Ba,Sr})\text{TiO}_3$ (BST) thin films. High growth temperature, small tunability and large leakage current densities are some of the major disadvantages of BST films on

comparing with PST [6–8]. Moreover, addition of cations to the A-site of the perovskite structure (ABO₃) not only reduces its phase transition temperature but also broadens the transition peak which results in diffuse phase transition.

In our recent work [9,10] we have observed the effect of Sr substitution for Pb in PST film in reducing the grain size, lattice distortion, and phase transition temperature. The observed results are more significant over that reported for BST thin films [11,12]. Since small nanograins exhibit large insulating boundaries between them and create a barrier for current conduction, it therefore raises the value of dc resistivity with low leakage current. The dispersionless dielectric properties thus appear up to the higher frequency region. The decrease in grain size of PST films with Sr substitution may due to lower grain-growth rates by the slower diffusion of Sr²⁺ with Pb²⁺ ions [13]. Chung et al. [14] studied PST thin films and reported low leakage current with large tunability value. The other reported results [15–17] for PST films confirmed remarkable electrical, ferroelectric and piezoelectric properties. However conduction mechanism and impedance spectroscopy have not been widely investigated. Complex impedance spectroscopy is a flexible tool for simultaneous electrical and dielectric characterizations of materials [18,19]. Contribution of various microscopic elements such as grains, grain boundary and interfaces to total dielectric response in polycrystalline films can be identified by a reference to an equivalent circuit, which contains a series of array of parallel RC elements. The experimental data contains three variables, real and imaginary components of the electrical response and frequencies together with four inter related electrical response formalisms: impedance (Z^*), admittance (Y^*), relative

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permittivity (ϵ^*), and electric modulus (M^*). Here, the purpose of impedance spectroscopy is to study the effect of PST nanograins and large insulating boundaries between the grains on dielectric properties at lower and higher frequency regions by Cole–Cole model.

Our previous work on PST thin film [10] also describes the room temperature conduction mechanism, which involves transport of electrons due to Poole–Frenkel (PF) emission. The PF emission is the bulk limited process caused by field-enhanced thermal excitation of trapped electrons into the conduction band. The trap centers due to nanograins are generated by the defect states, which are highly disordered [20]. The emission of electrons due to these trap centers stabilizes the dielectric relaxation up to the higher frequency region [21]. The temperature-dependent conduction mechanism study is an important tool for evaluating the activation energy of electrons movement between defect states within PST nanograins.

In the present paper, we report the effect of size of nanograins on dielectric properties, tunability, impedance spectroscopy and electron transport mechanisms of $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ (PST) thin films [$x = 0.1$ (PST10), 0.2 (PST20), and 0.3 (PST30)]. PST thin films were prepared by chemical solution deposition known as sol–gel combined metallo-organic decomposition method. The temperature-dependent dielectric constant, $\tan\delta$, tunability, complex impedance and conduction mechanism have been extensively investigated.

2. Experimental details

PST coating solutions were prepared by using lead 2-ethylhexanoate $(\text{C}_7\text{H}_{15}\text{COO})_2\text{Pb}$ with 20 mol% Pb in excess, strontium 2-ethylhexanoate $(\text{C}_7\text{H}_{15}\text{COO})_2\text{Sr}$ and tetra-*n*-butyl orthotitanate as the starting precursors. These precursor solutions were mixed in the molar concentration of Pb:Sr:Ti with 10, 20 and 30 mol% Sr in xylene. The coating solution was deposited on Pt/Ti/SiO₂/Si substrate by spin-coating technique with 4300 rpm for 60 s. The spin-coated films were dried at 350 °C for 5 min to remove the solvent and organic residuals. The spin-on coating and drying steps were sequentially repeated three times. As deposited PST films were annealed at 650 °C for 3 h in O₂ atmosphere. The thickness of the films was measured by using the Talystep stylus instrument (Ambios Technology). The final thickness of PST film after three coating was approximately 600 nm. The electrical measurements were made on metal-insulated-metal (MIM) capacitor configuration, with Pt as both the top and bottom electrodes. Pt dots with diameter of 0.5 mm were deposited as top electrodes on the film surface through a shadow mask by rf sputtering. The dielectric constant (ϵ), dissipation factor ($\tan\delta$) and tunability were measured by using Agilent 4284A Precision LCR meter and impedance spectra using Precision Impedance analyzer (Wayne Kerr 6500B). The current–voltage measurements were carried out using source meter (Keithley 2611 system).

3. Results and discussion

The X-ray diffraction results from earlier study [10] showed that the PST films in our case were polycrystalline with pure perovskite structure, and the values of tetragonal distortion (c/a) and average grain size reduced with increasing Sr concentration. The values of average grains' size using Scherer's relation were 77 ± 1 nm, 49 ± 0.5 nm and 37 ± 1 nm, respectively, for PST10, PST20 and PST30 films. With Sr concentration, the reduction in grain size of PST films occurred due to slow diffusion of cations and anions. This could be attributed to the fact that doping of SrO with PbO creates oxygen vacancies separately and causes slow diffusion mass transfer as described as



Because the ionic radii of cations, i.e., Sr^{2+} (1.32 Å) and Pb^{2+} (1.33 Å), are similar, it therefore coordinates the cations intrinsically

without via oxygen vacancies ($\text{V}_\text{o}^{\bullet\bullet}$). It results into slow diffusion process during heat treatment causing small growth of grains. A similar phenomenon for crystal growth was considered by A.V. Belyakov [22]. The microstructural analysis [10] showed that the PST films exhibited dense microstructure where the average grain size reduced with increasing Sr content. The values of grains' size from microstructure were 80 nm, 46 nm, 39 nm and RMS (root-mean-square) roughness were 1.11 nm, 2.63 nm and 2.8 nm, respectively, for PST10, PST20 and PST30 films.

Fig. 1(a) and (b) gives the frequency dependence of simulated dielectric constant and simulated dielectric loss of PST thin films with varying Sr concentration measured at different temperatures. The simulated dielectric constant is the value of dielectric constant which is extracted from their parasitic behavior. The simulated capacitor has 0.5 mm diameter electrode with 600 nm thick dielectric (thickness of film) and produces 3 μH value of inductance in a series of the dielectric-dispersion characteristics as in Fig. 1(a). The extraction of dielectric constant from their parasitics involves a calibration method called SOL (short-open-load) [23]. Generally, the parasitics can significantly influence the dielectric constant–frequency characteristics especially in thin films. So, the SOL calibration of these frequency dependent dielectric characteristics shows dielectric constant and resonant frequency of PST thin films which are highly dependent on the size of PST nanograins. The resonant frequency is shifted towards higher frequency region on decreasing the size of PST nanograins. The dispersionless dielectric constant is observed up to 3 MHz for PST10, 8 MHz for PST20 and 10 MHz for PST30 films. The dispersion appears due to the dipoles resulting from changes in volume states of cations and space charge polarization. The room temperature and temperature-dependent values of dielectric constant of PST films are greatly decreased with increasing Sr concentration. This decrease in dielectric constant may arise due to a decrease in grain size with increasing Sr concentration. Sivakumar et al. [24] observed that small grains have low dielectric constant up to the higher frequency region. The stability in dielectric constant is also observed at higher Sr content of PST films that may arise due to small value of c/a ratio. Lichtensteiger et al. [25] studied ferroelectric and tetragonal behavior of PbTiO_3 and reported that the reduction in c/a ratio of PbTiO_3 has highly suppressed electrical polarization resulting into stable polarizable signal because the electric dipoles are formed with uniform alignments and show barrier during electrical polarization. At 1 MHz, the values of dielectric constant are 714, 736 and 750 for PST10, 263, 269 and 287 for PST20, and 49, 52 and 57 for PST30 films, respectively, at 298, 323, and 373 K. The variation of dielectric constant with temperature in all PST films is as expected, which is typical in most of the ferroelectrics.

Similar inferences can also be drawn from frequency dependent simulated dielectric loss curves [Fig. 1(b)]. The low losses in the films are due to small leakage current that results from nanograins. The loss factor is reduced with increasing Sr concentration. The reduction in dielectric constant and loss factor with varying Sr concentration of PST films may be explained on the basis of domain wall mobility. As discussed by Eq. (1), the intrinsic coordination of Sr^{2+} with Pb^{2+} ions creates extrinsic oxygen vacancies, which increases defect in the PST system. These defects will increase the domain wall's energy, pin the domain walls and block the domain switching again hence the domain wall's mobility is reduced. Therefore, the present PST films contain nanograins having large insulating gaps between them. So, the domain wall mobility is reduced with small nanograins causing low dielectric constant and loss factor. A similar domain wall mobility effect was reported by Li et al. [16] for PST films. In comparison of the above data for PST with thin films of pure PbTiO_3 [26,27], the Sr-substituted PbTiO_3 grows in nanograins resulting into small value of tetragonal distortion, stable dielectric constant up to the higher frequency region and low loss factor. The observed simulated values

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