Electrical and optical properties of sol-gel derived La modified PbTiO3 thin films

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Abstract

Lanthanum modified lead titanate (Pb\textsubscript{x}La\textsubscript{y}Ti\textsubscript{1-x}O\textsubscript{3}) PLTx (x = 0.08 i.e. PLT8) sol-gel derived thin films have been prepared on indium tin oxide (ITO) coated glass and quartz substrates using lead acetate trihydrate, lanthanum acetate hydrate and titanium isopropoxide as precursors along with 2-methoxyethanol as solvent and acetic acid as catalyst by spin coating method. The microstructure and surface morphology of the films annealed at 650 °C have been studied by X-ray diffraction technique and atomic force microscope (AFM). XRD has shown a single phase with tetragonal structure and AFM images have confirmed a smooth and crack-free surface with low surface roughness. The dependence of leakage current on applied voltage show ohmic behavior at low field region with a space charge conduction mechanism at high fields. The wavelength dispersion curve of thin films obtained from the transmission spectrum of thin films show that the films have high optical transparency in the visible region.

Keywords: Sol-gel coatings; Thin films; PLT; Electrical properties

1. Introduction

Ferroelectric materials exhibit high dielectric permittivities and strong piezoelectric and pyroelectric effects. While there are limitations to the applications of ferroelectric materials in bulk form owing to the high operating voltages required, advances in thin-films fabrication technology along with parallel developments in integrated-circuitry and electro-optic technologies have led to an explosion of interest in the ferroelectric thin films. The unique properties of ferroelectric materials, combined with the design flexibility and miniaturization offered by thin film geometries have fuelled this explosion. Thin films of ferroelectric devices are being considered for applications in numerous electronic and electro-optic devices ranging from non-volatile semiconductor memories, large-scale electro-optic applications such as optical waveguide devices, multilayer capacitors for integrated circuitry, SAW devices, pyroelectric devices and ultrasonic transducers [1,2]. Sol-gel technique for the synthesis of thin films is being increasingly used because it offers an excellent control over the stoichiometry, lower processing temperature, easier
introduction of dopants for tailoring the properties and the process can also be integrated with the existing silicon technology [3,4].

Lead titanate (PT) is one of the most highly investigated ferroelectric material both in thin film and bulk forms, owing to its superior ferroelectric properties [5]. However this material has poor mechanical properties due to its large tetragonal strain which makes poling of PT materials difficult. Hence much attention has been focussed on the modification of PT by doping with the purpose of obtaining improved mechanical and electrical properties. The incorporation of off-valent (La$^{3+}$, Sm$^{3+}$, Nd$^{3+}$, Gd$^{3+}$) and isovalent ions (Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$) into PT ceramics is reported to enhance the mechanical stability along with good dielectric, ferroelectric, piezoelectric and pyroelectric properties [6]. The substitution of these ions results in the reduction of lattice anisotropy leading to hard and dense ceramics with high mechanical strength [7-9]. In our previous work, we reported the ferroelectric and pyroelectric properties of sol-gel derived (Pb,Ca)TiO$_3$ thin films [10,11].

Recently, lanthanum modified lead titanate (PLT) thin films have been studied for their possible use in optical waveguides, dynamic random access memories, non-volatile memories and pyroelectric detectors [12-14]. In view of the increasing interest in PLT thin films, we have made a comprehensive study of the structural, electrical and optical properties of these films. The results of these studies are presented in this paper.

2. Experimental procedure

Films of the required composition PLTx ($x = 0.08$ i.e. PLT8) are prepared using lead acetate trihydrate, lanthanum acetate hydrate and titanium isopropoxide (all from Aldrich, USA) as precursors, along with 2-methoxy ethanol as solvent and acetic acid as catalyst. The sol is prepared by dissolving lead acetate trihydrate in acetic acid. Excess 10 mol% lead acetate is added in order to compensate the lead loss during subsequent thermal treatment. The solution is refluxed with 2-methoxy ethanol. Finally, Titanium-isopropoxide in stoichiometric ratio is added to the solution with constant stirring to prepare PLT8 sol. Filtered sol is dispensed using a 0.2 mm syringe filter and spin coated at a speed of 3000 rpm for 30 s on ITO coated 7059 corning glass substrate and quartz substrates to deposit multiple coatings. The number of coatings in the fabrication of PLT8 thin film is 9 and its thickness after the annealing at 650 8C for 2 h, as measured by Talystep Surface Profiler is 0.7 mm. After each coating, the films were heated at 150 8C in a furnace for 2 min. After every two coatings, the films were kept in a furnace already maintained at 450 8C for 20 min to remove residual volatile organics. The films were finally rapidly annealed at 650 8C for 2 h in the furnace for crystallization. The film structures are characterized by X-ray diffractometer (Regaku mixflex, Japan, Cu Ka radiation $\lambda =1.5405\ A$). The microstructure of the films is characterized by atomic force microscope (MD-TNT, Russia). Al top electrodes of 1 mm in diameter are deposited by using microprocessor controlled Electron Beam Vacuum Coating Unit (Balzers, Leichtenstein) through a mask to form ferroelectric capacitors for electrical measurements. The $P—E$ hysteresis loop measurements have been conducted using a Sawyer Tower circuit RT 66A (Radiant Technologies Inc.). I-V characteristics of the films have been studied using a dc power supply and a Keithley electrometer. The dependence of the capacitance of the sample on the dc voltage (C-V) has been studied by using an HP 4263B LCR meter. The optical transmission spectrum of the PCT film has been recorded in the wavelength range 300-900 nm by Cary-17 spectrophotometer and the refractive index and extinction coefficient have been calculated by using method proposed by Manifacier et al. [15].

3. Results and discussion

The X-ray diffraction (XRD) pattern of the PLT8 film on quartz substrate annealed at 650 8C for 2 h, shown in Fig. 1, show well resolved peaks. The $hkl$ values of diffracting planes responsible for the peaks are identified using the ASTM data. The lattice constants ($c$ and $a$) of the unit cell calculated using $hkl$ values for PLT8 film are 3.98 and 3.83, respectively, and the $c/a$ ratio of PLT8 is 1.04. Thus, the films
exhibit perovskite phase with tetragonal structure. The \( a/a \) ratio of PT is \( \approx 1.06 \) [16] and tetragonality is found to decrease with the introduction of La content which is in agreement with the results reported by others [17,18].

The AFM (3D and 2D) surface images of the as deposited and annealed PLT8 films on quartz substrates at 650 °C for 2 h are shown in Figs. 2 and 3, respectively. AFM images are characterized by slight surface roughness with a uniform crack free densely packed microstructure. The surface roughness of the films is calculated using the equipment’s software routine. The value of surface roughness for the as deposited film is 1.89 nm whereas, for annealed film it is 5.06 nm. For the as deposited PLT8 film, there is no formation of grains in 2D image. After the film is annealed at 650 °C for 2 h, grains are well formed with the average grain size \( \approx 200 \) nm. The value of surface roughness of the annealed PLT8 film is of the same order as that reported by Koo et al. for PLT films on MgO substrates [19]. As is clear, the surface roughness increases as film is annealed. This is because grain growth occurs with temperature thereby, increasing the grain size. This is due to an increase in surface mobility with annealing, thus allowing the film to lower its total energy by growth of grains and decreasing the grain boundary area. Thus, thin films become more granular, thereby increasing the surface roughness.

Electrical characterization of the thin films of PLT8 on ITO coated corning glass 7059 substrate have been carried out by recording the variation of capacitance \( C \) with voltage \( V \) and the variation of current density \( J \) with applied electric field \( E \). Measurements of \( C—V \) are made by applying simultaneously on a sample an ac voltage and a dc field.
which changes as a step-like function. The ac voltage is used to measure the capacitance, which is then plotted as a function of the dc bias field. Capacitance exhibits large variation with the applied voltage as shown in Fig. 4. A butterfly loop is observed when the bias voltage is swept between the positive and negative magnitudes. The bias voltage dependent capacitance and presence of loop reflect the ferroelectric behavior of the PLT thin film at room temperature. The dependence of capacitance on voltage is non-linear in nature. Initial rise in the capacitance with dc field is probably due to increased movement of the domain walls which become free from defects [20] and due to partial switching of some domains by the dc ± ac field combination. The capacitance shows two peaks on either side of the zero value of the abscissa, which is an indication of ferroelectric domain switching in the films. The center of the butterfly loop is however, not located at zero bias field, but shifted towards the positive bias field (~0.5 V). This might be due to lag of polarization with the applied field. This lag occurs because domains do not orient back to the original positions while retracing the path. The capacitance peak heights differ slightly for positive and negative polarity and this can be attributed to the existence of space charge in thin films. At high dc field, the capacitance decreases which reflects two processes: (a) decrease in the number of domains as they become aligned with the field and (b) inhibition of the movement of residual domain walls by the dc field [20].
The $P-E$ hysteresis loop for PLT8 films on ITO coated corning glass 7059 substrate has been shown in Fig. 5. It has been observed that our PLT8 films have lower remnant polarization $P_r$ viz. 12.5 mC/cm$^2$; as compared to 30 mC/cm$^2$ for PT films [21] and lower coercive field $E_c$ viz. 144 kV/cm, as compared to 250 kV/cm for PT films [21]. The ferroelectric properties are largely dependent on the small grain size and large biaxial stress (~100 MPa) present in the sol gel derived films which is due to the thermal expansion coefficient mismatch between the film and the substrate [22].

The variation of current density $J$ with applied electric field $E$ on ITO coated corning glass 7059 substrate is shown in Fig. 6. The voltage is applied in 0.5 V steps and the current is measured after a steady state is achieved (which is in a few seconds) for each voltage. For a given applied voltage, the current is found to decay with time. The measurements were taken after the current was stabilized. Two different regions can be seen i.e. one in the low field region below 140 kV/cm and another in the high field region above 140 kV/cm. In the low field region, the current density is almost proportional to the applied field suggesting the ohmic conduction. At higher fields, the current density increases non-linearly, which is attributed to space charge conduction, which is significant in the films heat treated in air [23,24]. Since the thickness of the present film is well above 0.05 μm, the tunneling process can be neglected [27].

The optical transmission curve measured in the range 300-900 nm of PLT8 film on quartz substrate annealed at 650 °C is shown in Fig. 7. The transmittance has a sharp absorption edge (≈355 nm). The transmittance exhibits oscillations due to the insulators in which the trap sites are filled with charges and these, consequently, result in a strong increase in the number of free charges at high electric field [25]. At higher voltages, it follows a square-law dependence. It bears a striking resemblance to carrier space charge limited (SCL) injection current [26]. Since the thickness of the present film is well above 0.05 μm, the tunneling process can be neglected [27].
interference effect of light between two interfaces, the air-film and film-substrate. Figs. 8 and 9 show the dependence of refractive index \(n\) and extinction coefficient \(k\) of the film on wavelength. Refractive index may be attributed to the factors which are related to the crystallinity, density, electronic structure and the defects. The wavelength dependence of refractive index shows the typical shape of a dispersion curve. The value of \(n\) and \(k\) are 2.36 and 0.008, respectively, at 633 nm. The high value of refractive index (2.36) is an indication of high density of the film and low value of extinction coefficient (0.008) illustrates nature of high quality transparent films.

4. Conclusions

Sol-gel derived transparent, dense and crack-free PLT polycrystalline films have been grown on quartz substrates for XRD, AFM and optical measurements and on ITO coated corning glass 7059 substrates for electrical measurements. The AFM image of PLT8 film shows the excellent microstructural quality and chemical homogeneity of the films. The \(C-V\) characteristics of the film show a typical butterfly loop, confirming the ferroelectric properties of the film, which are related to ferroelectric domain switching. \(J-E\) measurements display an ohmic behavior at low field region with a possible space charge conduction mechanism at high fields (>140kV/cm). The optical properties show that these films have high optical transparency in the visible region and low extinction coefficient which are desirable properties for a material to be used in optical devices.

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References