Effect of annealing temperature on microstructure of chemically deposited calcium modified lead titanate thin films

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Abstract

Thin ferroelectric films of calcium modified lead titanate Pb\textsubscript{1-x}Ca\textsubscript{x}TiO\textsubscript{3}(PCT) have been prepared by chemical deposition process. The as deposited amorphous films were thermally treated for crystallization and formation of perovskite structure. Characterization of these films by X-ray diffraction (XRD) have been carried out for various amounts of calcium (Ca)-doping (0.20, 0.24, and 0.28) on indium tin oxide (ITO) coated corning glass substrates. For a better understanding of the crystallization mechanism, the investigations were carried out at various annealing temperatures (450, 550, and 650 °C). Characterization of these films by XRD shows that the films exhibit tetragonal phase with perovskite structure. Atomic force microscope images (AFM) are characterized by slight surface roughness with a uniform crack-free, densely-packed structure. Also, Fourier transform infrared spectra (FT-IR) of the as deposited film and annealed thin films (x = 0.24) at 650 °C on silicon (Si) substrates were taken to get more information about the film formation. Dielectric studies of the films were carried out and reported.

Keywords: PCT films; Sol-gel; Microstructure; AFM; FT-IR

1. Introduction

Modified lead titanate compositions have recently been tested in the form of thin films [1,2] aiming at applications such as non-volatile memories, surface acoustic wave, delay lines, pyroelectric sensors, optical shutters, and modulators [3-5]. Their piezoelectric, electrooptic, and pyroelectric properties have been proved to be interesting for such applications, if they can be prepared in perovskite structure [2]. Much interest has recently been shown in lead titanate (PbTiO\textsubscript{3}) thin films with compositional modifications at lead (Pb) and titanium (Ti) sites by calcium/lanthanum (Ca/La) and Zirconium (Zr), respectively, due to their potential applications [6-8]. Out of these modified material films, Pb\textsubscript{1-x}Ca\textsubscript{x}TiO\textsubscript{3}(PCT) thin films have large pyroelectric coefficients and unusually high anisotropic piezoelectric coupling factors [9-13]. It has been shown that these thin films are expected for the wide applications in the rapidly progressing field of integrated microelectronics, optical, acoustic, and optoelectronic devices, such as microsensors, micro-actuators, and pyroelectric devices.
There are various techniques used for the deposition of thin films [14]. Among these techniques, sol-gel deposition is a promising method which starts with the synthesis of a stable and uniformly mixed precursor solution, which is applied to a substrate by spin, dip or spray coating to form a gel and is followed by a sequence of drying, pyrolysis, and annealing stages to form an inorganic, crack, and flow-free ceramic crystallized in a required phase. This method invariably involves a post-deposition heating at \( \sim 650 \) °C to induce crystallization of the ferroelectric layer. However, this treatment can lead to formation of undesirable phases, and has a significant effect on the final ferroelectric properties of the films [14,15]. This is due to undesired reactions produced during heating and with the crystallization of non-ferroelectric phases (pyrochlore structure) along with ferroelectric perovskite phase.

The properties of the films deposited by sol-gel technique depend on the chemistry of solutions [16], the coating conditions [17], the crystal orientation of the substrate [18], the nature of the bottom electrode [19], and the thermal treatment used to promote crystallization. These factors determine the development of undesirable phases, the structure, and the microstructure of the films [20]. In view of the interest shown by various workers in the studies of the chemistry, composition of the solutions [13-16], the coating conditions [17], and the importance of these factors on the final ferroelectric properties of the films [14,15], we have studied the effect of variation of annealing temperature and Ca-doping on the structure and microstructure of these films by taking X-ray diffraction (XRD) patterns and atomic force microscope (AFM) micrographs. Also, the effect of annealing temperature on the Fourier transform infrared (FT-IR) spectrum of lead calcium titanate (PCT) films on silicon (Si) substrates has been studied. The effect of variation of dielectric constant with temperature of PCT films has also been studied. The results of these studies and their discussion are presented in this paper.

2. Experimental

In view of the compatibility of the solution deposition technique with many semiconductor fabrication technologies and better stoichiometric control of complex metal oxides [21], most of the studies on PCT thin films have used sol-gel technique. In our study, we have prepared \( \text{Pb}_{1-x}\text{Ca}_x\text{TiO}_3 \) films (\( x = 0.20, 0.24, \) and 0.28, i.e., PCT 80/20, PCT 76/24, and PCT 72/28, respectively) using lead acetate trihydrate, calcium acetate hydrate, and titanium isopropoxide (all from Aldrich, USA) as precursors along with 2-methoxyethanol as a solvent and acetic acid as a catalyst. The sol is prepared by dissolving lead acetate trihydrate in acetic acid. The solution is refluxed at 110 °C for 3 h in a three-neck flask assembly to remove water of crystallization. Excess 10 mole% lead acetate is added in order to compensate the lead loss during subsequent thermal treatment. Similarly, calcium acetate hydrate is also dissolved in acetic acid and refluxed. Both the solutions are mixed together and refluxed with 2-methoxy ethanol. Finally, Ti isopropoxide in stoichiometric ratio is added to the solution with continuous stirring to prepare PCT sol. The reactions were carried out in the ambient atmosphere. The shelf-life of the precursor or the sol was found to be \( \sim 20 \) days. Filtered sol is dispensed from a syringe and spin-coated at a speed of 3000 rpm for 30 s on indium tin oxide (ITO) coated 7059 corning glass and Si substrates. The purpose of ITO coated substrates was its use as a bottom electrode. After each coating, the films are heated at 150 °C in a furnace for 2 min and after every two coatings, the films are kept in a furnace already maintained at 450 °C for 20 min to remove residual volatile organics. The films are finally rapidly annealed at 650 °C for 2 h in the furnance for crystallization. The thickness of the films is determined using a Talystep method and is \( \sim 0.6 \) mm. The film structure is characterized by XRD (Rigaku mixiflex, Japan Cu Ka radiation, \( \lambda = 1.5405 \) Å). The microstructure of the films is characterized by AFM (MD-TNT, Russia). The XRD patterns and AFM photographs of the samples for various amounts of Ca-doping and annealing temperatures have been taken and analyzed. Also, FT-IR spectra of PCT films on Si substrates, both as deposited and annealed at 650 °C for 2 h, have been taken to study the film formation by using Vector 22 spectrometer (Bruker Analytik, GmbH, Germany). Aluminum top electrodes of 1 mm in diameter are deposited in vacuum through a mask to form the ferroelectric capacitors for electrical measurements. Dielectric properties of the films at various temperatures are measured using an impedance analyzer (HP4192 A).
3. Results and discussions

The crystallographic structure of the PCT films for various compositions and annealing temperatures has been studied by XRD. Fig. 1 shows the effect of varied Ca concentrations (0.20, 0.24, and 0.28) on the diffraction patterns of the films. The patterns show well-resolved peaks in each case. 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 using $hkl$ values for PCT films ($x = 0.20, 0.24,$ and $0.28$) are $4.03$ and $3.83$, $4.02$ and $3.86$, and $3.97$ and $3.89$, respectively. It is observed that as Ca-doping amount increases, $c$-value decreases and $a$-value increases. It may be explained on the basis of Ca ions occupying Pb ion sites with smaller ionic radius ($\text{Ca}^{2+} = 0.99 \text{Å}, \text{Pb}^{2+} = 1.20 \text{Å}$) [22]. The $c/a$ ratio of various compositions (0.20, 0.24, and 0.28) is $1.05, 1.04,$ and $1.02$, respectively, and suggests that the films have perovskite phase with tetragonal structure. As is clear, the tetragonality decreases with increase of Ca content.

The effect of changing annealing temperature (450, 550, and 650 °C) on the crystallinity of PCT films has been shown in Fig. 2. Film crystallization is partial at the heat treatment of 450 and 550 °C. As the annealing temperature is increased to 650 °C, the peaks in the XRD patterns become sharper and more intense, and the full-width at half-maximum (FWHM) decreases, indicating better crystallinity and increased grain size.

The effect of varying Ca content on the microstructure of PCT films has been studied by taking AFM images (3-D), as shown in Fig. 3. AFM images are
Fig. 3. AFM images (3-D) of PCT films on ITO coated corning glass substrates for: (a) $x = 0.20$; (b) $x = 0.24$; and (c) $x = 0.28$. 
Fig. 4. AFM images (3-D) of PCT (x = 0.24) films on ITO coated corning glass substrates for annealing temperature: (a) 450; (b) 550; and (c) 650 °C.
characterized by slight surface roughness with a uniform crack-free, densely-packed microstructure. The surface roughness (RMS) of the films is calculated by using the equipment's software routine. The surface roughness of PCT thin films for the three compositions (0.20, 0.24, and 0.28) is 4.86, 3.65, and 2.3 nm, respectively. Thus, surface roughness of PCT thin films, measured by AFM, decreases as Ca concentration increases. This is due to the fact that with an increase in Ca concentration, the grain size decreases [23] and surface morphology becomes smoother. The change in surface microstructure with increase in Ca concentration is considered due to the change of lattice parameters and the volume of the unit cell.

The effect of changing the annealing temperature on the microstructure of PCT films has been studied by taking AFM images (3-D), as shown in Fig. 4. The surface roughness of PCT films (x = 0.24) for three annealing temperatures (450, 550, and 650 °C) is 1.5, 2.42, and 3.65 nm, respectively. This shows that as annealing temperature is increased, the surface roughness increases. These values are lower than the values of Martin et al. [24] and Pontes et al. [25]. As the annealing temperature is increased, grain-growth occurs which results in increased grain size. This is due to an increase in the surface mobility with the increasing temperature, thus allowing the film to lower its total energy by the growth of grains and decreasing the grain boundary area. Thus, thin film becomes more granular with rise in temperature which results in increased surface roughness.

FT-IR spectra of the as deposited film and the film annealed at 650 °C on silicon substrates are shown in Fig. 5. The broadband around 3350 cm⁻¹ corresponds to the (O-H) stretching vibration of hydroxyl groups of alcohols. The bands present around 1410 and 1560 cm⁻¹ can be ascribed to ν.sym (–COO⁻) and ν.asym (COO⁻) of acetyl groups respectively. The band around 1110 cm⁻¹ may have contribution from two factors: due to the Ti-O-C vibration of propoxy groups directly bonded to titanium and due to the presence of native oxide prior to deposition. The small bands around 1050 and 1010 cm⁻¹ are the C-H rocking modes. The small band at 650 cm⁻¹ is attributed to the O-C-O vibration. After annealing the film at 650 °C for 2 h, the broadband around 3350 cm⁻¹.
The band at 1100 cm$^{-1}$ is from the substrate. C-H rocking modes at 1050 and 1010 cm$^{-1}$ disappear completely. In addition, no O-C-O vibrations are observed indicating complete removal of organics. The bands in the region 500-800 cm$^{-1}$ have contributions from M-O bonds. These observations suggest that PCT crystallizes at annealing temperature of 650 °C.

The observed variation of dielectric constant with temperature for all the compositions is shown in Fig. 6. Dielectric constant increases with temperature due to interfacial polarization becoming more dominant, as compared to the dipolar polarization. After Curie temperature is reached, the dielectric constant decreases due to the phase transition from ferroelectric phase to paraelectric phase. The increase in dielectric constant with calcium addition is due to the decrease of tetragonality and ease of 90° domain orientation. Dielectric peaks observed indicate that the Curie temperature $T_c$ of PCT 80/20, PCT 76/24, and PCT 72/28 films is about 190, 135, and 120 °C, respectively. It turns out that $T_c$ decreases with an increase in Ca-doping. The dielectric peaks are fairly broad as commonly observed in ferroelectric ceramics in thin films form and the broadening can be mainly attributed to the compositional fluctuations and structural disorders. Most of the diffuse phase transitions studied in oxide ferroelectrics have occurred at temperature (<400 °C) where the disorders are likely to be frozen [26]. Thus, one would not expect to find this type of behaviour at a high temperature where the defects are more mobile in the lattice.

4. Conclusions

Calcium modified lead titanate thin films have been successfully prepared by chemical deposition technique. Perovskite phase of PCT films is formed with a polycrystalline tetragonal structure. The effect of increasing calcium content in lead titanate reveals the decrease of the surface roughness of the PCT films. AFM studies on the films heat-treated at different temperatures reveals that the surface roughness increases with the increase in annealing temperature, suggesting an increase of crystallization with temperature. Crystallization of the films at 650 °C is also supported by the analysis of FT-IR spectra. Dielectric studies indicate the ferroelectric to paraelectric phase transition of PCT films.

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References