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Optical and electrical properties of sol–gel derived thin films of $PbTiO_3$

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Abstract

Thin films of polycrystalline $PbTiO_3$ were prepared by sol–gel process—spin coating method. The substrates used were fused silica and stainless steel. The effect of post-deposition annealing on the electrical properties was analysed. Crystalline phase of $PbTiO_3$ can only be obtained when the annealing temperature was higher than 500 °C. The electrical measurements were conducted on metal-film-metal capacitors. Films annealed at 600 °C exhibited crystallinity with perovskite phase, a dielectric constant of 125 and a dissipation factor of 0.035 at 1 kHz. Current–voltage (*I*–*V*) characteristics were found to be ohmic at lower fields and space charge limited current (SCLC), controlled by traps at higher fields. Transmission spectra of the films deposited on fused silica were recorded and from this, refractive index, extinction coefficient and thickness of the films were calculated. The refractive index was found to be in the range 1.90–2.25 for different wavelengths (300–900 nm).

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Keywords: C. Electrical properties; Sol–gel; $PbTiO_3$ thin film; Dielectric constant; Dielectric loss; Refractive index; Extinction coefficient

1. Introduction

Ferroelectric (FE) materials are of high interest for a number of applications, including non-volatile memories, dynamic random access memories, electro optic switches, pyro-electric detectors, etc. [1–3]. Presently, the usage of an optically transparent substrate in combination with transparent ferroelectric thin film transistor offers interesting opportunity for optical applications [2].

Thin films of lead titanate based materials like lead zirconium titanate (PZT) and lead lanthanum zirconium titanate (PLZT) have been studied extensively in the recent past for optical memory, wave guiding applications, etc. [2–4]. Lead titanate is well known to have good ferroelectric and pyroelectric properties [2] such as high Curie temperature, large pyroelectric properties and is one of the most promising materials with wide applicability. $PbTiO_3$ thin films have been prepared by using various techniques like; flash evaporation, chemical vapour deposition, magnetron sputtering, sol–gel [5], etc. Sol–gel method has been recognized as one of the major materials processing technology in the recent years due to its versatility in synthesizing new materials for a variety of applications. In this paper, the electrical and optical properties of sol–gel derived lead titanate thin films on fused silica and stainless steel substrates are reported.

2. Experimental details

Thin films of lead titanate were fabricated by sol–gel method using titanium isopropoxide and unhydrated lead acetate as precursors. The sol was prepared by dissolving 3.61 g of $[Pb(CH_3COO)_2]$ in 15 ml of methoxy ethanol at about 68 °C. The solution was then heated to around 115 °C in a reaction flask fitted with a reflex condenser and cooled down to 90 °C. Then titanium isopropoxide (2.94 ml) was added drop wise to the mixture to yield 1:1 molar ratio of lead to titanium. The isopropyl acetate thus formed was eliminated and lead titanate precursor solution was obtained. This clean solution was filtered through Whatman's glass micro fibre filters GF/C and stored in a sealed clean bottle.

Stainless steal plates and fused silica were used as substrates. After spinning the precursor solution at 2500 rpm for 30 s on substrates, the films were kept at hot plate in air at around 400 °C for 30 min to eliminate solvents and other organics. Films coated on the fused silica were then annealed at different temperatures for 30 min with a heating rate of 200 °C/h. Single coated films thickness was found to be approximately 1200 Å. Repeated coatings were done to get thicker films by repeating the same process. For making films on stainless steel, post deposition rapid annealing was carried out at various temperatures from 400 to 700 °C for 2 min. Variation of the methoxy ethanol content

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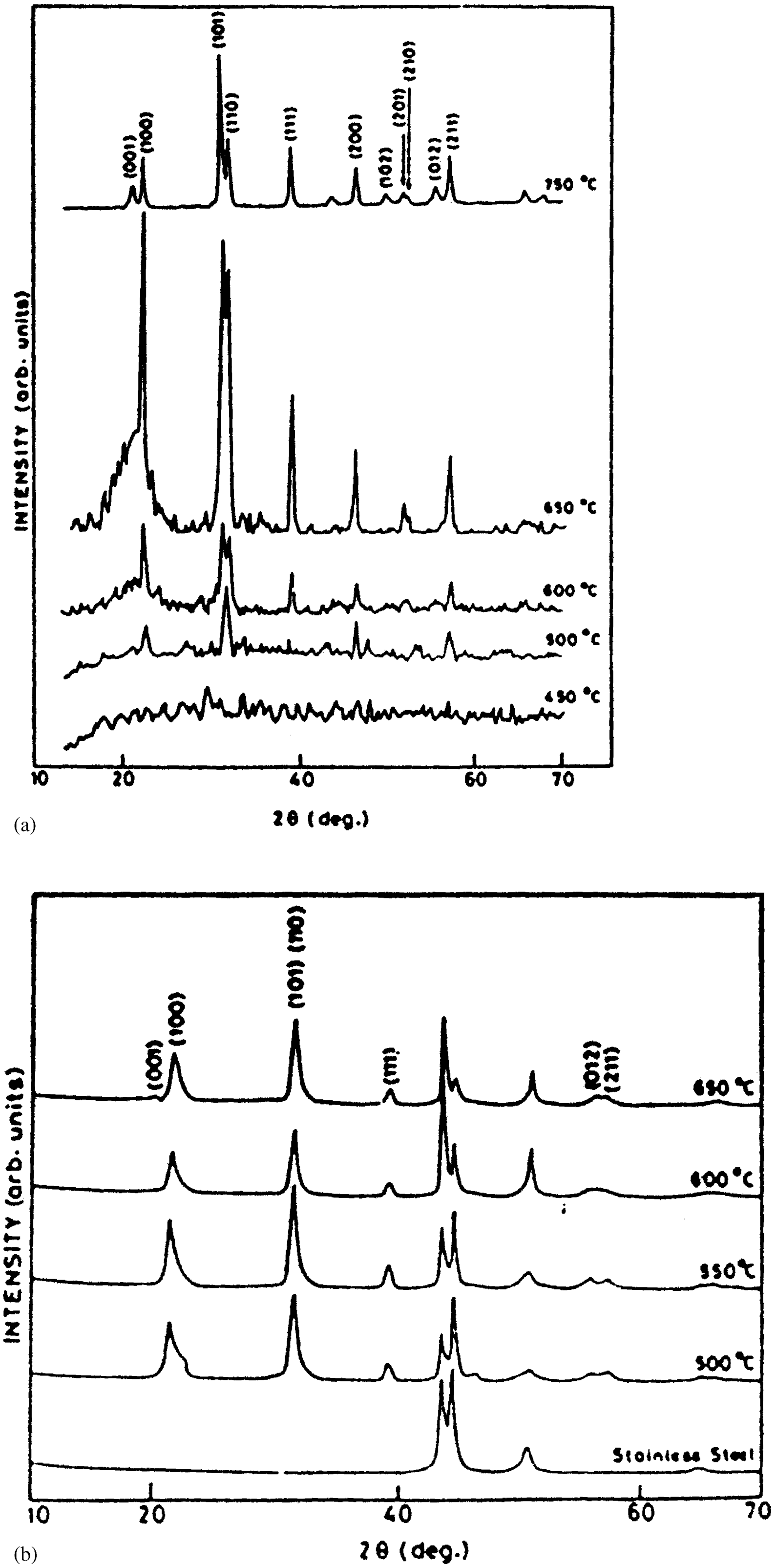

Fig. 1. (a) X-ray diffraction pattern of $PbTiO_3$ films annealed at various temperatures on fused silica. (b) X-ray diffraction pattern of $PbTiO_3$ films annealed at various temperatures on stainless steel.

in the solution could control the thickness of the film. The films were found to be transparent and polycrystalline. The film thickness was measured by optical nano-scope (Model 911-9150, Anelva, Japan). The crystal structure was studied with Rigaku Geigerflex X-ray diffractometer. For electrical measurements, top electrode was vacuum evaporated aluminium dots. Dielectric properties and ac conductivity were measured by using HP 4284 precision LCR meter and *I–V* characteristics were done with Keithley 617 Programmable Electrometer. Optical properties were done with thin films grown on fused silica. Transmission spectra were recorded with Perkin-Elmer UV-Vis Spectrophotometer. Refractive indices were calculated from the transmission spectra by the technique reported by Manifacier et al. [6].

3. Results and discussion

X-ray diffraction (XRD) analysis was carried out on the films made on fused silica. The pyrolised films (400 °C) were found to be amorphous, and post-deposition annealing was required to develop crystallinity. Fig. 1(a) shows the XRD patterns of the films deposited on fused silica and annealed at different temperatures by conventional process, keeping the annealing time constant (30 min). It is clear from the figure that 30 min time was enough to attain perovskite phase at 500 °C. The polycrystalline nature and absence of preferred orientation is evident from the XRD pattern. Fig. 1(b) shows the XRD pattern of rapid annealed lead titanate thin films grown on stainless steel substrate. Films annealed below 500 °C were found to be amorphous and crystallized films were obtained at an annealing temperature of 500 °C and above.

3.1. Electrical measurements

The electrical properties of $PbTiO_3$ were measured on the films deposited on stainless steel substrates. The top electrode of the metal–insulator–metal (MIM) structure was vacuum deposited Al dots.

The dielectric properties of the thin films deposited are improved by heat treatment in the furnace between 400 and 750 °C. The annealing effect on the dielectric constant of lead titanate films is shown in Fig. 2 at different frequencies. It can be seen from the figure that relative dielectric constant (ϵ') increased in the annealing range of 450–750 °C. This trend is due to the increased grain size and higher crystallinity with annealing temperatures. The decreased ϵ' for films annealed at 800 °C could be due to the loss of Pb by evaporation [7,8] or due the formation of low dielectric constant interface layer because of the reaction between the films and substrate. Similar observation of decrease in ϵ' has been observed by other authors [7].

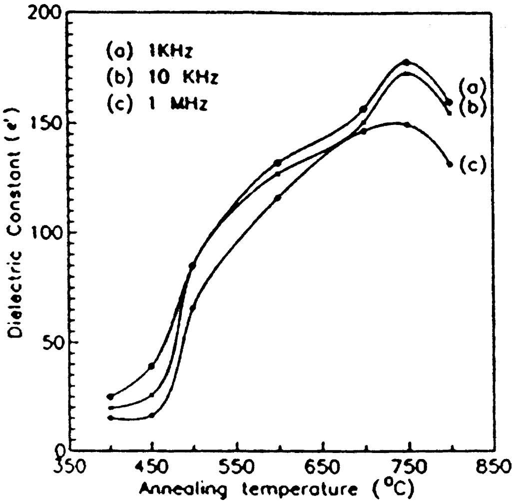

Fig. 2. Dielectric constant as a function of annealing temperature for a 6500 Å thick $PbTiO_3$ film.

Fig. 3 depicts the variation of dielectric constant, ϵ' and dielectric loss, ϵ'' against frequency of lead titanate films at 25, 100 and 200 °C. At the first two temperatures, ϵ' shows very low dispersion with frequency, whereas at third temperature, the dispersion is larger. At 25 °C, the variation of ϵ'' shows high dispersion in the low frequency region. This may be due to the increase in the thermally generated charge carriers in the sample. The low dispersion in the ϵ' and the absence of any relaxation peaks in ϵ'' indicate the absence of any interfacial polarization of the Maxwell–Wagner (MW) type as well as due the electrode barrier in the sample.

The effect of applied bias field on the capacitance of lead titante film on stainless steel is given in Fig. 4. The measurements were performed by superimposing an ac signal of amplitude 100 mV and frequency 1 kHz with dc bias on a 1 μm thick film. The nature of the *C–V* curve indicates hysteresis and non-linear behaviour of ferroelectric lead titanate with applied field. Further, it also confirms the tetragonal structure of lead titanate film. Similar results for PZT were reported by Uhlmann et al. [9].

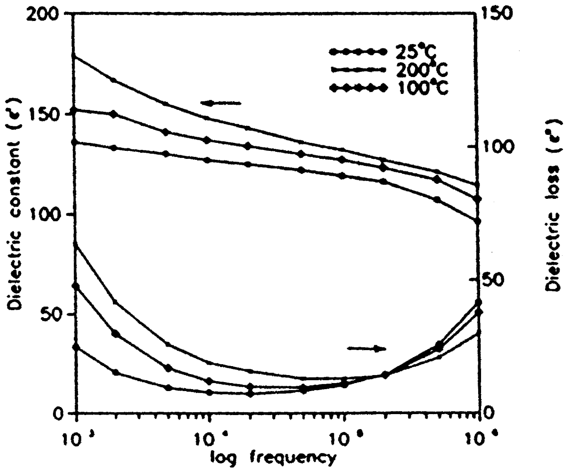

Fig. 3. Variation of ϵ' and ϵ'' with frequency at various temperatures for a 6500 Å thick $PbTiO_3$ film annealed at 600 °C.

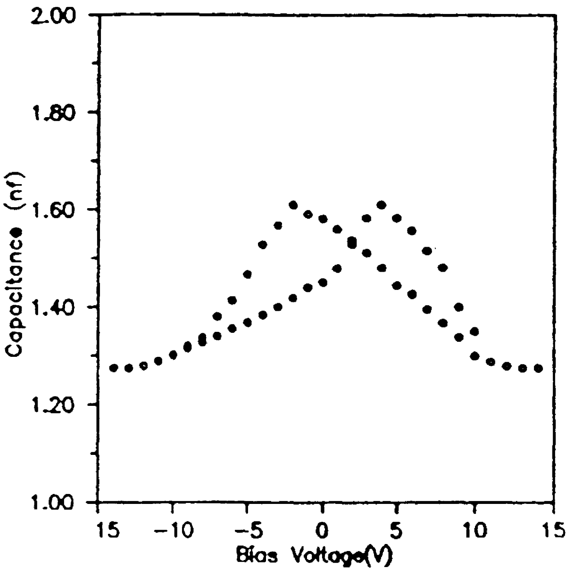

Fig. 4. The effect of applied bias field on the capacitance of a sol–gel derived $PbTiO_3$ film on a stainless steel substrate.

The current–voltage characteristics (log I versus log V) of MIM capacitors employing lead titanate films are shown in Fig. 5. It may be noted from this figure that at low voltages, an exponential increase of current with applied voltage was observed, followed by a saturation region at high voltages. Similar non-linear I–V characteristics were obtained for barium titanate [10]. In these kinds of resistively films, the possible dominant conduction mechanisms may arise due to tunnelling. Schottky effect, Poole Frankel effect and/or space charge limited current (SCLC). As the thickness of the film was well above 500 Å, the tunnelling process can be ruled out. To understand the type of conduction mechanism, semi log plot of I versus $V^{1/2}$ and I versus V were drawn and are shown in Fig. 5(a) and (b), respectively. For conduction mechanism either by Schottky or Poole Frankel emission over a single metal insulator barrier I/V versus $V^{1/2}$ should be linear one. The absence of linearity in our case [Fig. 5(b)] clearly rules out this as the possible conduction mechanism. Also, we noticed the polarity reversal of the applied field caused no asymmetry in the I–V behaviour, indicating the absence of any Schottky type barrier at the film and metal electrode interface. There was no change in the conductivity with change in the polarity of the applied field, which is an indication for conduction process to be bulk limited not electrode limited. Low dispersion of ϵ' and absence of relaxation peaks in ϵ'' also confirms this; space charge limited current conduction therefore seems to be the possibility. Similar results on PZT were reported by Scott et al. [11] and Krupanidhi and Roy [12] indicate the dominance of space charge limited current.

The ac conductivity (σ_{ac}) of lead titanate films is shown in Fig. 6 at different temperatures. It shows that σ_{ac} increases as the frequency and temperature increase. σ_{ac} is proportional to the out of phase part of the polarization produced

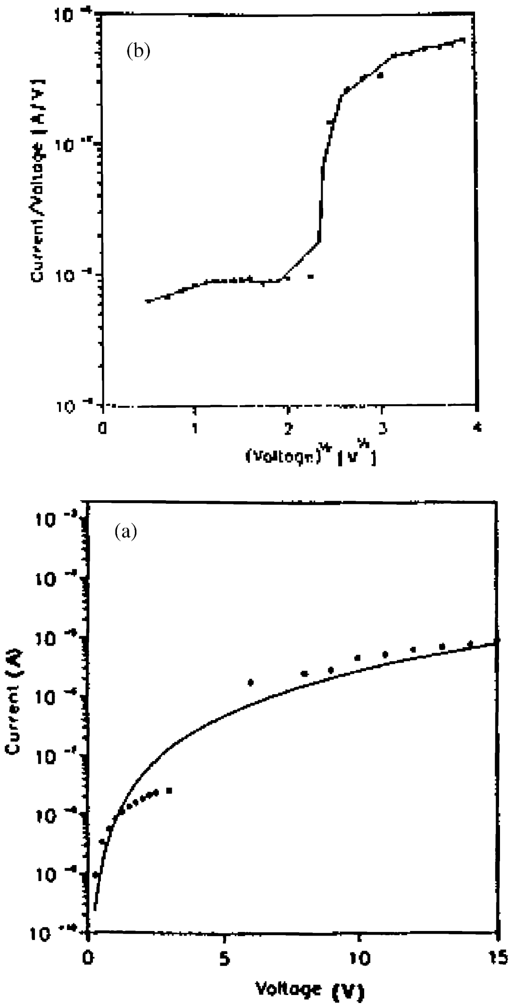

Fig. 5. (a and b) Typical current–voltage for stainless steel–$PbTiO_3$–Al capacitors on a semi log plot and semi log plot of I/V vs. $V^{1/2}$, for the same data.

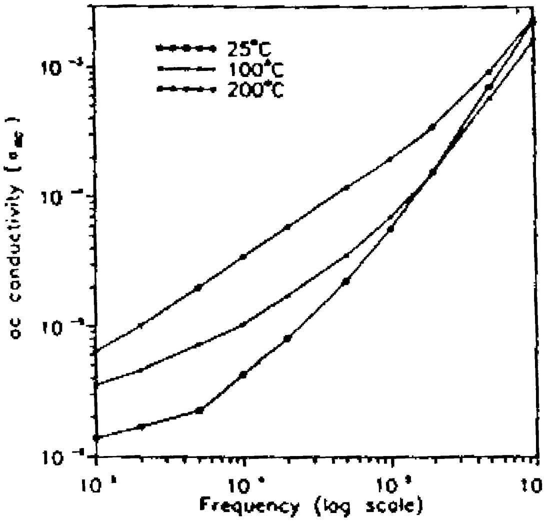

Fig. 6. Variation of ac conductivity with frequency for various temperatures.

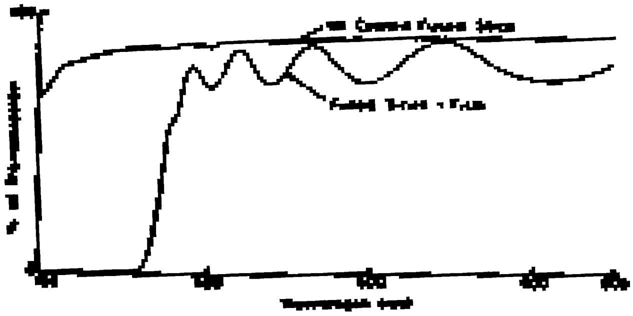

Fig. 7. Optical transmittance spectrum of $PbTiO_3$ film on fused silica substrate with that of uncoated substrate.

by an electrical field applied to the solid. When the conductivity is dominated by thermally excited carriers in the band, the ac conductivity is frequency independent to the first approximation. Also if ac conductivity is due to free carriers than σ_{ac} decreases with increase in frequency according to the relation [13]

$$\sigma_{ac} = \frac{\sigma_{dc}}{1 + \omega^2\tau^2}$$

where τ is the relaxation time, ω the frequency and σ_{dc} is the dc conductivity. In our samples, the σ_{ac} increases with frequency. Hence the conductivity arises from bound carriers trapped in the sample. This frequency and temperature dependent σ_{ac} behaviour is strongly suggestive of impurity state dominated conduction [14], i.e. donor like impurity present in the sample act as shallow traps as already explained in *I–V* characteristics.

3.2. Optical properties

The optical properties of lead titanate thin films were carried out to investigate the dispersion of refractive index (n) and extinction coefficient (k). The n, k and their dispersion is similar to each material, and is influenced by the electronic structure and/or crystallinity. The transmittance spectrum of lead titanate films deposited on fused silica was obtained and is shown in Fig. 7. The film had good transmittance above 75% in the visible region. The optical band gap E_g was determined by extrapolating the linear portion of the plot (Fig. 8) relating $(\alpha h\gamma)^2$ versus $h\gamma$ to $\alpha^2 = 0$. The value of E_g is 3.6 eV, which is approximately equal to the reported value of 3.59 for lead titanate films [15] and depends on the films processing parameters.

Knowing the thickness and the refractive index at different wavelengths, extinction coefficients of lead titanate film as function of wavelength were calculated [6] and are shown in Fig. 8. Flat behaviour of k is observed beyond 450 nm and k increases rapidly towards short wavelength. This may be because of the fact that, in Manifacier method, the calculated k value actually includes the total optical losses caused by the absorption and scattering. Hence, the higher scattering in the shorter wavelength region causes drastic increase in k in that region.

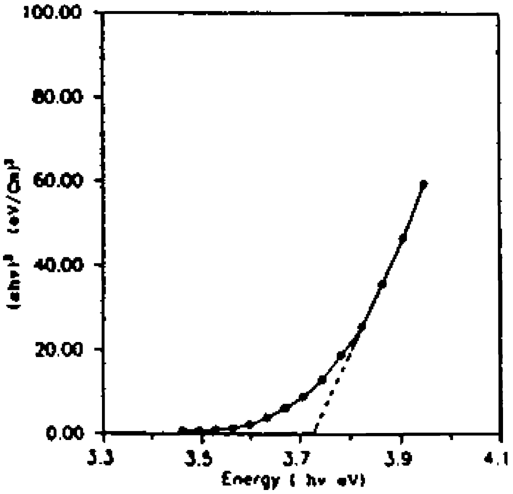

Fig. 8. Determination of bad gap from optical data.

4. Conclusion

Polycrystalline and transparent films of lead titanate of high crystallinity were grown on fused silica and stainless steel substrates by using sol–gel method. The value of dielectric constant depended on film thickness and annealing temperature. Ferroelectric nature of the film was evident from the non-linear dependence of capacitance with bias voltage. The films exhibited ohmic behaviour at low fields and SCLC at higher fields for electrical conduction controlled by trap levels. Optical band gap energy, extinction coefficient and refractive index were also obtained.

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