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Preparation of transparent ferroelectric $Pb_{0.92}La_{0.08}Ti_{0.96}O_3$ thick films on ITO-coated glass substrates by a sol–gel route

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Abstract

$Pb_{0.92}La_{0.08}Ti_{0.96}O_3$ films with thickness between 580 nm and 1830 nm were deposited on ITO-coated glass substrates using a sol–gel process under a relative low temperature of 580 °C. The films are crystallized well and of pure perovskite polycrystalline structure, and the surface of the films was smooth and condense. With the increase of the film thickness, the grain size and dielectric constants of the films increase. The dielectric constant-voltage curves are symmetric about a zero-bias axis and showed the hysteresis for all the films. In addition, the coercive field E_c decreases with the film thickness. All the films are transparent and the absorption edges were found to shift to longer wavelength with increasing thickness of the films. The refractive index (n) and extinction coefficient (k) of 1830 nm thick film are 2.39 and 0.009, respectively, at 633 nm wavelength.

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Keywords: Ferroelectric thick films; Dielectric properties; Optical properties; Sol–gel

1. Introduction

Ferroelectric thin films are being studied with renewed interest because of their possible application in various integrated electronic and optoelectronic devices. The optically transparent lanthanum (La)-doped lead titanate (PLT) thin films are attractive candidates for non-volatile memory [1], pyro-electric detectors [2], electro-optic modulators [3], and microwave devices [4]. Thin films offer the potential of increased speed, reduced operating voltages and enhanced efficiency, and they are especially attractive for monolithic optoelectronic integration circuits [5]. In recent years, the PLT thin films have been studied extensively [6–8]. Most research focused on the dielectric properties of PLT thin film with different La doping concentration and the thicknesses of the films were usually below 1 μm. In the field of optoelectronics, however, the ferroelectric films with thickness above 1 μm are required [9,10]. So far, there have been few reports on the dielectric and optical properties of the thick PLT films. In addition, the ferroelectric thin films were usually deposited on $Pt/Ti/SiO_2/Si$ substrates, while for the application in the optical field, the transparent substrates are needed. Indium tin oxide (ITO)-coated glass substrate is a good choice since it is cost-effective, easy to fabricate and capable of large area. The main problem is that the ITO-coated glass substrate is not sustainable to the process temperature higher than 600 °C. Thus, annealing temperatures below 600 °C should be used during making the films, while an annealing temperature much lower than 600 °C cannot crystallize the films well. Thus, an annealing temperature of 580 °C was selected in this study to deposit PLT film on ITO-coated glass substrates by a sol–gel method. The aim of this work is to prepare 8 mol% La-doped $PbTiO_3$

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($Pb_{0.92}La_{0.08}Ti_{0.96}O_3$, PLT8) films in the phase-pure perovskite phase at low temperature and to study the dielectric and optical properties. The composition of PLT8 was chosen due to the fact that the PLT films with La concentration near 8% show good optical transmittance [11,12], although there are many reports that high dielectric properties were obtained at 28 mol% La concentration [13,14].

2. Experiments

The PLT8 films with thickness ranging between 580 nm and 1830 nm were deposited on ITO-coated glass substrates using a sol–gel process. Titanium propoxide was firstly mixed with acetic and stirred for 5 min. Secondly, lead acetate and lanthanum acetate were dissolved in glacial acetic acid and heated to 110 °C to remove the associated water of crystallization. When the temperature of complex La–Pb solution decreased to 90 °C, the Ti sol was added to La–Pb solution while stirred continuously for approximately 1 h. This complex PLT8 sol is termed as the parent sol. For coating, the parent sol was diluted to 0.4 mol L^{-1} with acetic acid. The ITO-coated glass substrates were cleaned thoroughly in a series of organic solvents by ultrasonication and finally absolute alcohol. The diluted sol was spin-coated on the substrates at 4000 rev min^{-1} for 20 s. After each spin-coating, the film was fired on the furnace at 120 °C and then inserted into a preheated tube furnace at 400 °C for 10 min in ambient air. The film was coated and heated several times to increase the film thickness. After the last coating, the tube furnace temperature was increased at a rate of 3–4 °C min^{-1} up to 580 °C and held for 1 h before cooling to room temperature. Using this method, we successfully obtained four PLT films of different thicknesses, sample a (580 nm, coating 6 times), sample b (1012 nm, coating 10 times), sample c (1390 nm, coating 15 times) and sample d (1830 nm, coating 20 times).

The phases of the films were evaluated using an X-ray diffractometer (XRD) with Ni filtered CuK_{α}. The surface morphology of the films was studied using a Hitachi S-5750 scanning electron microscopy (SEM). The transmissions were record by a JASCO V-570 UV/VIS/NIR spectrophotometer. The refractive index (n) and extinction coefficient (k) of all samples were measured by the method of spectroscopic ellipsometry. In order to evaluate the dielectric properties of the films, the Pt metal was sputtered on the surface of the films as a top electrode, with diameter of 0.4 mm. Therefore, the sandwich oxide–insulator–metal structure, ITO–PLT–Pt, was formed on the glass substrate. The dielectric properties, as a function of the frequency (100 Hz–1 MHz) or DC bias, were measured by a HP4294 impedance analyzer. Film thickness was measured by an ET350 Talysurf profilometer (Kosaka Laboratory Ltd.).

3. Results and discussions

Fig. 1 shows the XRD patterns of the PLT films with various thickness on ITO-coated glass substrates. It can be found that, under a relative low annealing temperature of 580 °C, all the PLT films were crystallized well into pure polycrystalline structure and free of other phases. The relative intensity of the (110) and (111) diffraction peak increases as the film thickness increase, illustrating the improvement of the film crystallization as the increase of the film thickness. The splitting of the (200)/(002) and (201)/(210) doublets can be obviously observed in Fig. 1, which indicates that the films are in tetragonal phase at room temperature. The surface morphology of the films corresponding to Fig. 1 is shown in Fig. 2. Dense, smooth, and crack-free surface morphologies can be observed for all the films. With the increase of the film thickness, the average grain size was obviously increased from about 50 nm (sample a) to 150 nm PLT (sample d). Lee and Joo reported that there is a seed layer existing between the substrate and the film [15]. It can be assumed that the lower PLT layer played the role of a nucleation site or a seeding layer for the formation of the upper PLT layer, resulting in the increase of the grain size as the increase of the film thickness.

The dielectric constant and dissipation factor measurements were made at room temperature as a function of frequency. The dielectric constants of all samples decrease with the increasing of frequency, as shown in Fig. 3. This is due to the fact that some dipole or domains cannot switch with increasing frequency, which have no contribution to dielectric constants [8]. From Fig. 3, it can also be seen that the dielectric constant of the samples increases from 220 to 550 at 1 kHz when the film thickness increases from 580 nm to 1830 nm. It is similar to the results reported by Udayakumar et al. and Chen et al. [16,17]. They attribute this phenomenon to the action of thin layer between the film and the substrate, whose dielectric constant is very low. Because this low dielectric constant layer is very thin, its effect becomes less and less when the films thickness increases greatly. This can explain our experimental result that the dielectric constants just change a little when the film thickness is above 1390 nm, as compared with curves c and d in Fig. 3. From Fig. 3, it can be noted that the dissipation factor keeps 0.05 approximately at 1 kHz irrespective of the film

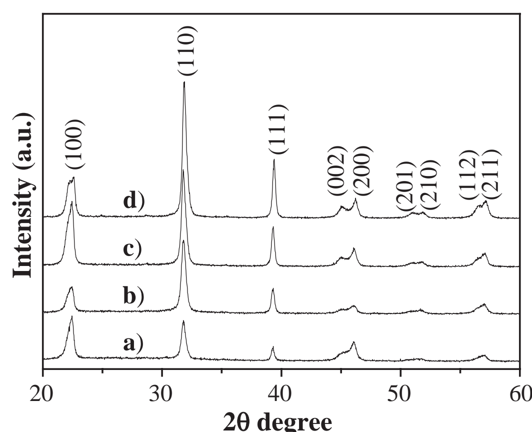

Fig. 1. XRD patterns of PLT films with different film thicknesses, (a) 580 nm, (b) 1012 nm, (c) 1392 nm, and (d) 1830 nm.

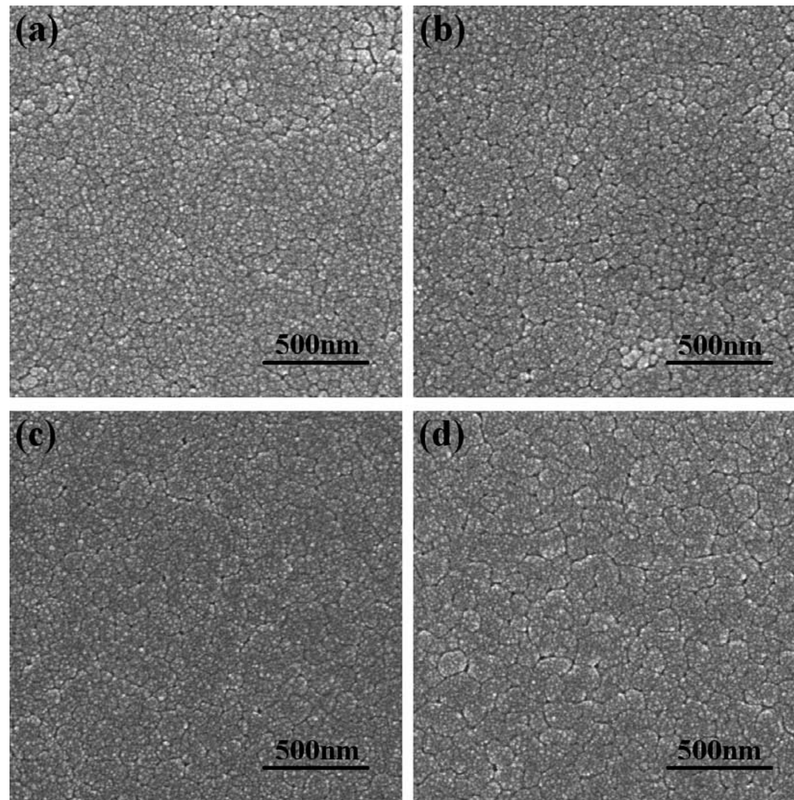

Fig. 2. SEM micrographs of PLT thick films corresponding to Fig. 1.

thickness. This phenomenon is similar to that found in the barium strontium titanate films, where the increase of dielectric constant was observed as the increase of the film thickness, while the dissipation factor keeps almost unchanged [18,19]. The dissipation factor of the films is influenced by many factors. Grained films have many grain boundaries and any low-resistivity material within the boundaries forms a parallel conduction path contributing to the measured dielectric loss. Also, the magnitude of the density of oxygen vacancies in the perovskite oxide contributes to the loss [20]. In addition, the Schottky barrier effect cannot be excluded as a contribution to the loss [21]. The present study indicates that the combining effect of the above mechanism on the dielectric loss keeps almost unchanged when the film thickness increases from 580 nm to 1830 nm. We note that the value of the dissipation factor in this study is a little higher than that of the samples deposited on $Pt/Ti/SiO_2/Si$ substrates [22]. This may be due to the fact that Sn and In elements in the ITO bottom electrode is more diffusive and easier to diffuse into the PLT film than Pt, which may accumulate in the grain boundaries, leading to the increase of the dissipation factor.

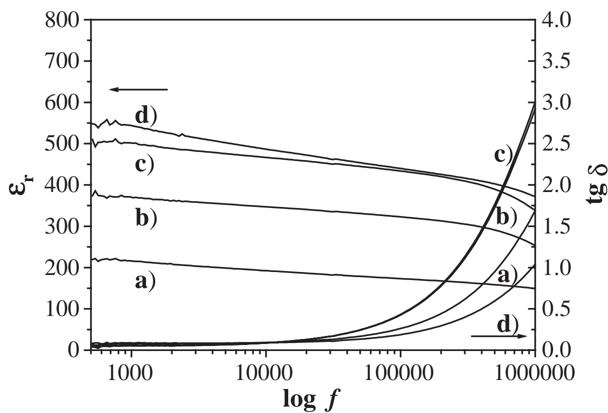

Fig. 3. Frequency dependence of dielectric constant and loss of the PLT films corresponding to Fig. 1.

The dielectric response of the films under the same maximum dc bias field of 200 kV/cm is shown in Fig. 4. As the measurement voltage increases from zero, switching occurs, and the apparent capacitance increases to a maximum at the coercive voltage. From an examination of Fig. 4, it is evident that the coercive field of PLT8 films decreases from 70 kV/cm to 45 kV/cm when the thickness increases from 580 nm to 1830 nm. Udayakumar et al [16] reported the similar phenomenon in their work about PZT film. We proposed that this is due to the improved crystallization with the increase of the film thickness. The detail dielectric parameters of all samples are listed in Table 1.

Fig. 5 shows the optical transmission spectra of the weakly absorbing PLT thick films on ITO-coated glass substrate annealed at 580 °C. The observed fringes were a result of the interference of light beams from air–film and film–substrate interfaces. The transparency of all samples increases sharply at the wavelength of about 320 nm. The maximum transparency reaches 90% in the range of communication wave band. With the increase of film thickness, the transparency decreases, and the absorption edge of the PLT films shifts towards longer wavelength (i.e., lower energy). This implies a decrease in the electron gap energy with the increase of film thickness. Zhou et

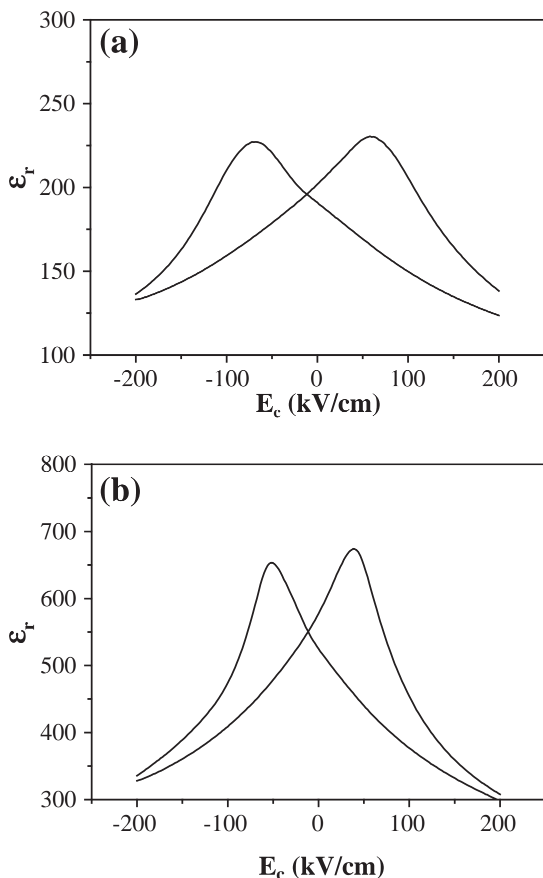

Fig. 4. Dielectric permittivity as a function of dc bias for the PLT films with thicknesses of (a) 580 nm and (b) 1830 nm.

al [23] reported that the absorption edge shifts to longer wavelength with increasing crystalline size for the PLT films deposited on the fused quartz substrates. Gu et al [24] observed that in the case of $Bi_4Ti_3O_{12}$ films, E_g for films with smaller grain size was larger than that for films with larger grain size. We proposed that the present result originated from the same reason, since the increased grain size is observed as the film thickness increases, as shown in Fig. 2.

The refractive index (n) and extinction coefficient (k) of all the samples were derived from model fitting the experimental spectroscopic ellipsometric data. The refractive index (n) of PLT8 films increases from 2.28 to 2.39 at 633 nm with the increasing of the film thickness from 580 nm to 1830 nm. In comparison, the refractive index (n) of single crystal PLT is 2.44 at 633 nm wavelength [25]. Refractive index are related to the

Table 1
The detail parameters of samples with different thicknesses

Sample name	Thickness (nm)	Dielectric constant (f=1 kHz)	Dielectric loss (f=1 kHz)	Coercive field (kV/cm)
a	580	218	0.06	70
b	1012	370	0.05	55
c	1390	498	0.05	51
d	1830	550	0.05	45

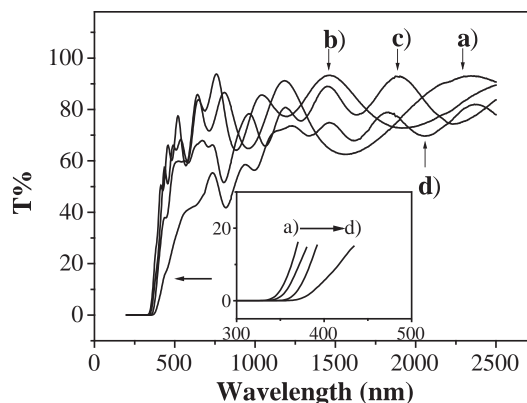

Fig. 5. Transmittance spectra for the samples corresponding to Fig. 1.

crystallinity, density, electronic structure, and the defects in the materials [23]. From Figs. 2 and 3, it can be noted that the crystallinity of PLT8 films were improved greatly with the increase of the film thickness, which may cause the increase of refractive index of the PLT8 films to a value approaching to that of the PLT crystal. Fig. 6 show the dependence of refractive index (n) and extinction coefficient (k) of samples a and d on wavelength, which show the typical shape of a dispersion curve. The n and k value of sample d are 2.39 and 0.009, respectively, at 633 nm. This is comparable to the results reported by Chopra et al [11], where the PLT8 films were annealing under 650 °C.

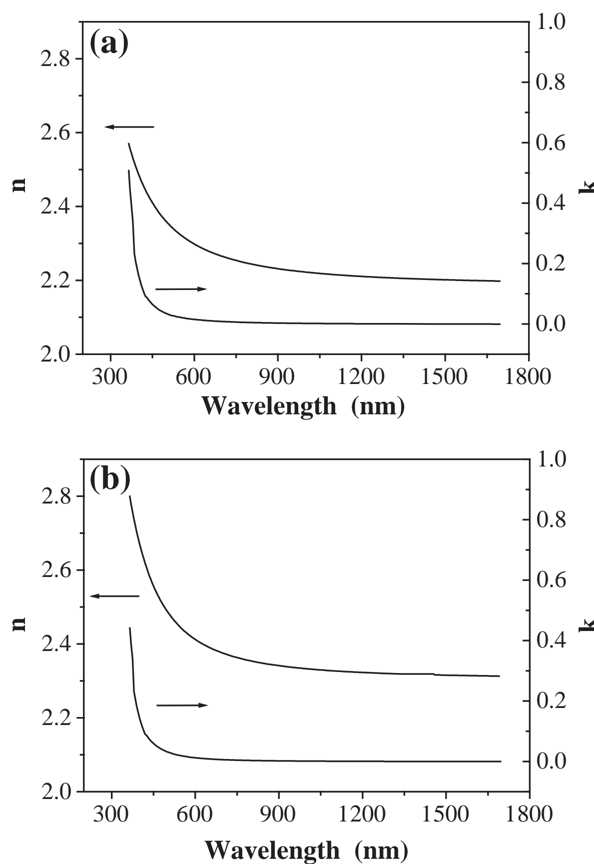

Fig. 6. Dependence of refractive index n and extinction coefficient k of PLT8 film on the wavelength for the samples of (a) 580 nm and (b) 1830 nm.

4. Conclusions

In summary, the PLT8 thick films were deposited successfully on the ITO-coated glass substrates by a sol–gel technique. The dielectric and optical properties of PLT8 thick films (580 nm–1830 nm) were studied. With the increase of film thickness, the relative dielectric constant increases from 220 (for 580-nm film) to 550 (for 1830-nm film) at 1 kHz, while the coercive field decreases with the increase of film thickness. The refractive index (n) and extinction coefficient (k) of the 1830-nm-thick PLT8 are 2.39 and 0.009, respectively, at 633 nm wavelength. The maximum transparency reaches about 90% in the range of communication wave band. The absorption edge of the PLT8 films shifts towards longer wavelength (i.e., lower energy) with the increase of film thickness. This study indicates that the PLT8 films can be deposited on the glass substrates, and the good dielectric and optical properties could be attractive combinations for the films to be used in the optoelectronics field.

Acknowledgements

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