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**Optical Constants and Band Gap Determination of $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$ Thin Films
Using Spectroscopic Ellipsometry and UV-Visible Spectroscopy**

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ABSTRACT

We report the structural evolution and optical properties of lanthanum doped lead zirconatetitanate (PLZT) thin films prepared on Pt/TiO₂/SiO₂/Si substrates by chemical solution deposition. X-ray diffraction demonstrates the post-deposition annealing induced crystallization for PLZT films annealed in a temperature (T_a) range of 550-750 °C. PLZT films annealed at higher temperature exhibit polycrystalline structure along with larger grain size. Optical band gap (E_g) values determined from UV-visible spectroscopy and spectroscopic ellipsometry (SE) for PLZT films were found to be in the range of 3.5-3.8 eV. E_g decreases with increasing T_a . The optical constants and their dispersion profiles for PLZT films were also determined from SE analyses. PLZT films show an index of refraction in the range of 2.46-2.50 ($\lambda=632.8$ nm) with increase in T_a . The increase in refractive index at higher T_a is attributed to the improved packing density and crystallinity with the temperature.

Keywords: PLZT, chemical solution deposition, annealing, band gap, optical constants.

1.Introduction

Ferroelectric lanthanum-doped lead zirconatetitanate (PLZT) of perovskite type crystalline structure is an interesting material due to its large remnant polarization and electro-optic effects, near the morphotropic phase boundary (MPB). The excellent optical and electrical properties make it material of choice for applications in MEMS, optical modulators/transducers and smart sensors [1], [2], [3], [4], [5] and [6]. Recent studies revealed that this material possesses great potential for use in future photovoltaic (PV) devices in which combination of optical transparency and ferroelectric properties are utilized [7] and [8]. Owing to the ability of ferroelectric materials to produce photo-voltage above bandgap without the need of p-n junction [9] as required in traditional semiconductor solar cells and the existence of bulk PV effects, PLZT films are considered to be promising candidates for solar cells applications. However, for practical realization of these devices, a thorough understanding of optical properties is essential.

Many studies on the optical properties such as electro-optic effect, optical wave-guiding, optical storage, photo-refractivity of PLZT films are reported [6], [10] and [11]. However, very limited reports exist on the dispersion profiles of refractive index, extinction coefficient and optical nonlinearities of these films. All reported work on optical characterization is based on films of various compositions [12], [13], [14] and [15] than the one reported in this work. Okuyama et al and Nordesh et al [16] and [17] studied the optical properties of sputter deposited PLZT (7/65/35 and 8/40/60) films on single crystal $\text{SrTiO}_3/\text{MgO}$ substrates. Leng et al used sputtered PLZT (8/65/35) films on ITO/quartz substrates to obtain the optical properties as a function of crystal structure [18] whereas Zhang et al used pulsed laser deposited PLZT (5/53/47) thin films on quartz substrates to perform such studies [19]. Sun et al reported the influence of La content (x ranging from 10-25%) on optical properties using sol-gel deposited

PLZT (x/52/48) films [20]. Sato et al focused on the influence of crystal orientation on electro-optic effect in epitaxial PLZT films where various orientations were achieved using oriented substrates [21].

In our most recent work, we reported the influence of post deposition annealing temperature on the electrical and photovoltaic properties of $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$ films [22], [23] and [24]. This particular composition is close to the MPB and lies in the tetragonal part of the PbZrO_3 - PbTiO_3 system phase diagram. There exists a particular temperature range which results in proper crystallization of the PLZT films into perovskite phase without the formation of unwanted pyrochlore phase. The optical properties of ferroelectric thin films are also known to be strongly influenced by annealing temperature [25]. Moreover, the crystallization temperature also affects the grain size which in turn affects the optical properties of the films. Thus, it is important to investigate the optical properties of the PLZT (5/54/46) films as a function of crystallization temperature.

In this work, we report the effect of annealing temperature on the optical properties of PLZT thin films prepared using chemical-solution-deposition method. The effect of annealing temperature on the crystal structure and crystallite size is discussed. The optical properties affected by crystallite size are investigated using UV-Visible (in the wavelength range of 300-1000 nm) and ellipsometric spectroscopies. The results of this study indicate that the annealing temperature impacts the optical properties of PLZT thin films. To the best of our knowledge, a detailed account of optical properties of chemical solution deposited PLZT thin films of 5/54/46 composition is missing at this time. Therefore, the present work on the optical properties using UV-Visible and spectroscopic ellipsometry shed light in this direction and will be useful as a road-map for tuning the applications of such PLZT films in device applications.

2. Experimental section

PLZT thin films were deposited on Pt(111)/TiO₂/SiO₂/Si(100) substrate via chemical solution deposition process. The PLZT precursor was obtained by dissolving lead acetate trihydrate (Pb[CH₃COO]₂·3H₂O), lanthanum acetate (La[CH₃COO]₃), zirconium propoxide (Zr[OCH₂CH₂CH₃]₄), titanium butoxide (Ti[OCH₂CH₂CH₂CH₃]₄) in the solvent 2-methoxyethanol. The concentration of the precursor solution was 0.4 M. The prepared solution was spin coated on the substrate at room temperature with a spin speed of 3000 rpm for 30 sec. After each deposition, the film was hydrolyzed at 120 °C for 2 minutes and pyrolyzed at 350°C for 2 minutes, using hot plate. This process was repeated three times to achieve the film thickness of 210 nm. After triple coating and heating cycles, the films were annealed in flowing oxygen-gas (2000 sccm) in a rapid thermal annealing (RTA) furnace for 2 minutes in the temperature range of 550-750 °C.

The phase identification and crystal structure measurements on the films were made using Philips X'pert X-ray diffractometer (XRD) with Cu K α radiation at 45 kV and 40 mA. The (111) and (001)/(100) peaks from the observed diffraction patterns were used to determine the grain size of the films crystallized at different temperatures, using Scherrer formula [27]. Optical properties of these films were investigated using UV-Visible (UV-Vis) spectroscopy and spectroscopic ellipsometry (SE). The UV-Vis reflectance spectra of the films were obtained using a Shimadzu UV 1800 UV-VIS spectrophotometer in the reflectance mode in the wavelength range of 300-1000 nm **with a step size of 1 nm. The resolution of the spectrophotometer is 1 nm.** SE measurements were carried out using a J.A. Woollam VB-250 Variable Angle Spectral Ellipsometer (VASE) in the spectral range of 300-1000 nm **with a step size of 10 nm** and at incidence angles of 65 and 75°. **The number of resolutions was set at 100.** The ellipsometric

spectra (Ψ and Δ) collected for all the films were fitted with appropriate model to extract optical properties of the films annealed at different temperatures. Additionally, the UV-VIS and ellipsometric reflectance data were employed to determine the band gap energies of these films using Kubelka-Munk function.

3. Results and discussion

Figure 1 shows the XRD patterns of PLZT thin films annealed at various temperatures ($T_a=550-750$ °C). The diffraction patterns show that the films annealed at 650 and 750 °C are polycrystalline in nature, exhibiting only perovskite peaks without the formation of pyrochlore phase. However, a pyrochlore phase is observed in the film annealed at 550 °C, indicating that films enter the intermediate cubic pyrochlore phase before transforming into ferroelectric perovskite phase [18]. The absence of pyrochlore phase in the films annealed at higher temperatures is a clear manifestation of the role of annealing temperatures in the proper crystallization of the films. The XRD patterns of as-deposited films (not shown) are diffuse without any indication of diffraction peaks confirming their amorphous nature. The effect of annealing temperature is remarkable as is evident in Fig. 1; the intensity of perovskite peaks is observed to increase with increasing annealing temperature due to crystallization and grain growth. It can be said that the annealing at 550 °C is not very effective in promoting structural order or achievement of complete crystallization of the films is not observed compared to those annealed at higher temperatures, $T_a = 650-750$ °C. For instance, all of the XRD peaks can be noted for the films annealed at 650 °C and higher temperatures. XRD data also demonstrates that the high quality films annealed at higher temperatures (650 °C and 750 °C) exhibit (001) and (110) peaks whereas the film annealed at lower temperature shows (100) peak. The intensity of (110) diffraction peak is observed to increase with the increasing temperature. As reported by

Ramana et al for several of the oxide films, the preferred orientation of the films is a result of the growth or rearrangement process, which will favor those crystallographic orientations with low strain energy density [26].

The grain size of the films post annealed at different temperatures is determined from (110) and (001)/(100) peaks obtained from each diffraction pattern using Scherrer formula given as [27]:

$$\beta = \frac{0.9 \lambda}{\Delta \cos \theta} \quad (1)$$

where β is the average grain size, λ is the wavelength of Cu K α radiation, Δ is the full width at half maximum of the peak and θ is the angle of incidence. **Instrumental broadening effects are considered to determine the size to the best possible accuracy [27].** The grain size of the films at different annealing temperatures for (110) and (001)/(100) peaks are summarized in Table I. The grain size of films is observed to increase with the increase in annealing temperature. It is to be noted that the highest annealing temperature causes (001)/(100) grain size to increase from 4.82 nm to 6.43 nm ($T_a = 550-750^\circ\text{C}$) and (110) grain size to increase from 4.96 to 5.13 nm ($T_a = 650-750^\circ\text{C}$). Thus, the annealing temperature significantly affects the morphology of the films.

Spectral characteristics of the films were used to determine their optical behavior and band gap. Figure 2 shows the UV-vis reflectance of PLZT thin films annealed at various temperatures. Reflectance decreases slightly in the lower wavelength region with increasing annealing temperature. The increase in reflectance could be attributed to the increase in grain size and surface roughness with the increase in annealing temperature. The high temperature annealing not only enhances the electrical characteristics of the films [22], [23], [24] and [28], but

also leads to the formation of highly dense, crystalline films with larger grain size. The increase in densification and the surface roughness significantly affects the scattering of incident light in thin films[29] and [30].As already mentioned the diffraction patterns of films revealed that the films annealed at 750 °C were crystallized more in the perovskite phase as compared to the films annealed at lower temperatures. The films show higher reflectance due to scattering of light at the grain boundaries. The reflectance spectra of the films annealed at higher temperatures show drop in reflectance values at around 350 nm whereas the 550 °C annealed film shows the drop at around 320 nm, corresponding to the wavelength at which the absorption coefficient becomes maximum. The drop in reflectance is ascribed to the transition from wavelengths for which the absorption is weak to the wavelengths at which the absorption is strong. Further, the change in reflectance is used to determine band gap energies of optical transition in these films.

Figure 3 shows the transformed Kubelka-Munk spectra of PLZT thin films crystallized at various temperatures. The optical absorption coefficient (α) calculated from the reflectance data using Kubelka-Munk equation[31], [32], [33] and [34] is expressed as:

$$\alpha = \frac{(1 - R)^2}{2R} = \frac{K}{S} \quad (2)$$

where R is the measured reflected light, K is the absorption coefficient and S is the scattering coefficient. Further analysis of the absorption data was carried out to understand the broad energy feature(s) and determine band gap of PLZT films. Band gap values for these films can be measured by employing the power law of the form [29] and [30]:

$$\alpha h\nu = B(h\nu - E_g)^n \quad (3)$$

where ' $h\nu$ ' is the incident photon energy, α is the absorption coefficient, B is the absorption edge width parameter, E_g is the band gap, and ' n ' is the exponent dependent on direct or indirect transitions across the band gap [35], [36] and [37]. In this work, the plots of $(\alpha h\nu)^2$ versus photon energy yield linear plots in the high absorption region. The $(\alpha h\nu)^2$ versus incident photon energy for PLZT films are shown in Figure 3. Extrapolating the linear region of the $(\alpha h\nu)^2$ plot to zero and regression analysis with best confidence provide accurate direct- E_g values. The E_g values of PLZT films are summarized in Table I. **The E_g values reported for PLZT films in this work are within an accuracy of ± 0.01 eV.** Note that the direct band gap in PZT corresponds to the electronic transitions from valence bands formed by O $2p$ states to the conduction bands formed by mixed d -states of Ti and Zr. The E_g values determined in the present work are in good agreement with those reported in the literature [18] and [38]. However, it can be observed that the annealing temperature affects the bandgap energy value of PLZT thin films. The E_g values decrease from 3.80 eV to 3.51 eV for increasing annealing temperatures from 550 to 750 °C. The lower band gap energies observed at higher annealing temperature are due to larger grain size [39].

Optical constants of these films were primarily probed by spectroscopic ellipsometry (SE), which measures the relative changes in the amplitude and phase of the linearly polarized monochromatic incident light upon oblique reflection from the sample surface. The experimental parameters obtained by SE are the angles Ψ (azimuth) and Δ (phase change), which are related to the microstructure and optical properties, defined by [40]:

$$\rho = R_p/R_s = \tan \Psi \exp (i\Delta) \quad (4)$$

where R_p and R_s are the complex reflection coefficients of the light polarized parallel and perpendicular to the plane of incidence, respectively [36], [40], [41], [42] and [43]. In general, the fundamental equation of ellipsometry that relates the measurable with the accessible optical information is:

$$\rho = \tan \psi \exp(i\Delta) = \rho(N_0, N_1, N_2, L_1, \Phi_0, \lambda) \quad (5)$$

where the middle term contains the measurable and the last term on the right contains all the accessible parameters of the measurement, namely, film thicknesses, optical properties, the wavelength of light, and the angle of incidence [40] and [41]. The spectral dependencies of ellipsometric parameters Ψ (azimuth) and Δ (phase change) can be fitted with appropriate models to extract film thickness and the optical constants i.e., the refractive index (n) and extinction coefficient (k), based on the best fit between experimental and simulated spectra [36], [40] and [41]. In the present case, the Levenberg-Marquardt regression algorithm was used for minimizing the mean-squared error (MSE) [40], [41]:

$$(6) \quad MSE = \frac{1}{2N - M} \sum_{i=1}^n \left[\left\{ \frac{(\Psi_{\text{exp.}} - \Psi_{\text{calc.}})}{\sigma_{\Psi_i}^{\text{exp}}} \right\}^2 + \left\{ \frac{(\Delta_{\text{exp.}} - \Delta_{\text{calc.}})}{\sigma_{\Delta_i}^{\text{exp}}} \right\}^2 \right]$$

where $\Psi_{\text{exp.}}$, $\Psi_{\text{calc.}}$ and $\Delta_{\text{exp.}}$, $\Delta_{\text{calc.}}$ are the measured (experimental) and calculated ellipsometry functions, N is the number of measured Ψ , Δ pairs, M is the number of fitted parameters in the optical model and σ are standard deviations of the experimental data points [36] and [41].

Figure 4 shows the spectral dependence of the ellipsometric parameters, Ψ and Δ , of PLZT thin films annealed at various temperatures, measured at incidence angles of 65° and 75° . In order to extract optimal data from SE experimental and simulated measurements, the construction of a meaningful, multilayer optical model is essential. The model representation accounts for a number of distinct layers with individual optical dispersions and the interfaces

between these layers are optical boundaries at which light is refracted and reflected according to the Fresnel relations. The dispersion relations of the optical constants of PLZT films are derived using a stack model (Figure 5) composed of the Si substrate, interfacial SiO₂ layer, TiO₂ layer, Pt layer and PLZT film. **Combined with reasonable optical model, the best MSE values of the fitting of ellipsometry functions provide the best accuracy in determining the optical constants. In general, the precision of oxide films using such procedure is 0.1 Å for thickness and is 0.001 for index of refraction. Thus,** succeeding the construction of the optical layer model, the PLZT films were modeled with a conventional Cauchy dispersion model, because the films are transparent in the visible region the Cauchy model is optimal. The Cauchy equation can be expressed approximately as a refractive index n as a function of wavelength λ :

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 \quad (7)$$

where A , B , and C are the Cauchy coefficients and specific to the material, A is the constant that dominates $n(\lambda)$ for long wavelengths, B controls the curvature of $n(\lambda)$ in the middle of the visible spectrum, and C influences $n(\lambda)$ to a greater extent in shorter wavelengths[36], [43], [44] and [47]. Note that this principle behind Cauchy's polynomial is also used for the dispersion function $k(\lambda)$:

$$k(\lambda) = D + E/\lambda^2 + F/\lambda^4 \quad (8)$$

where D , E , and F are constants specific to the material[36], [44] and [45].

The dispersion profiles of $n(\lambda)$ determined from SE data for the films are shown in Figure 6. The $n(\lambda)$ dispersion curves indicate a sharp increase at shorter wavelengths corresponding to fundamental absorption of energy across the band gap. However, the effect of annealing temperature is evident in the dispersion curves, where there is an increase in ' n ' values

with temperature. The significant decrease in refractive index at higher wavelengths shows a typical dispersion curve near an electronic interband transition. The refractive index of PLZT films at 632.8 nm is determined to be 2.496 (Figure 6a). For wavelength greater than 400 nm, the extinction coefficient values of all the films are close to zero indicating low optical losses due to absorption. Such low losses are quite important for considering the PLZT films for optoelectronic applications [29], [30] and [46]. **In the context of recent observation and demonstration of temperature anomalies of elastopoticty of PbZrO₃ single crystals [47], it is important to comment on such effects on the optical constants of PLZT films in this work. PZT, being solid solution of PbZrO₃ and PbTiO₃, is supposed to combine the properties of PbZrO₃ and PbTiO₃. Thus, it is reasonable to expect that the temperature anomalies in the elastopoticty of PbZrO₃ might have some influence on the optical constants of PLZT films. However, we believe that the effect is not pronounced in the present case of PLZT films due to the fact that post-deposition annealing is to introduce changes in the crystal structure and packing density, which improves the index of refraction as noted.**

The band gap values were also determined from SE measurements and compared with those determined from UV-vis spectrophotometry. The spectral data obtained from ellipsometry was transformed to obtain absorption coefficient using equation (2) which was further used to determine band gap energies. Plots of $(\alpha h\nu)^2$ vs $(h\nu)$, for PLZT films are shown in the Figure 7. The energy band gaps, E_g , obtained from linear extrapolation of plots to $(\alpha h\nu)^2 = 0$ are listed in Table I. It can be seen that the band gap obtained from UV-Vis and SE are in good agreement with each other. Further, the energy band gaps of low temperature annealed film shows a slight change in the values obtained using two different spectroscopic methods. Similar trend i.e., E_g increase with increasing temperature, as seen in both the

independent optical characterization methods is indicative of the effect of crystallization and increased grain size with increasing annealing temperature.

4. CONCLUSIONS

Nanocrystalline, ferroelectric perovskite phase of chemical-solution-deposited PLZT films can be obtained by post-deposition annealing at 750°C. PLZT films annealed at lower temperature 550°C exhibit an intermediate pyrochlore phase. Corroborating with structural transformation, UV-visible spectral reflectance and spectroscopic ellipsometry measurements indicate that E_g of PLZT film increases from 3.5 to 3.8 eV with decreasing T_a from 750 to 550 °C. All the PLZT films demonstrated a high optical quality as evidenced by extinction coefficient profiles obtained from SE measurements. Refractive index (n) of the PLZT films increase from 2.46 to 2.50 ($\lambda=632.8$ nm) with increasing T_a from 550 to 750 °C. The changes in E_g and n are attributed to the thermally-induced improvement in the crystal structure and packing density of PLZT films upon annealing.

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TABLES

Table I Grain size, band gap energies for direct optical transition determined from UV-Visible and ellipsometry reflectance spectra of the PLZT films deposited on Pt/TiO₂/SiO₂/Si post-annealed at various temperatures.

<i>Crystallization Temperature (°C)</i>	<i>Grain size (nm)</i>		<i>Direct energy band gap $E_{gd}(eV)$</i>	
	<i>Peaks</i>		<i>UV-Visible spectroscopy</i>	<i>Spectroscopic Ellipsometry</i>
	<i>(110)</i>	<i>(001)/(100)</i>		
550	--	4.82	3.80	3.82
650	4.96	5.89	3.53	3.53
750	5.13	6.43	3.51	3.51

Table II Cauchy parameters of PLZT films used to obtain optical constants from ellipsometry.

<i>Crystallization Temperature (°C)</i>	<i>A</i>	<i>B (μm)²</i>	<i>C (μm)⁴</i>	<i>D</i>	<i>E (μm)</i>	<i>F (μm)</i>
550	2.3912	0.00439	0.00897	0.06519	1.5634	0.4
650	2.4123	0.00987	0.00924	0.05825	1.6320	0.4
750	2.4391	0.00297	0.00998	0.04980	1.4820	0.4

FIGURES

Figure 1: XRD patterns of $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$ thin films annealed at (a) 550 °C, (b) 650 °C, and (c) 750 °C.

Figure 2: UV-Visible reflectance spectra of PLZT thin films on platinized silicon substrates crystallized at different temperatures.

Figure 3: $(\alpha h\nu)^2$ versus $h\nu$ curves of PLZT thin films crystallized at 550⁰C, 650⁰C, and 750⁰C.

Figure 4: Spectral dependence of Ψ and Δ for PLZT thin films annealed at (a) 550⁰C, (b) 650⁰C, and (c) 750⁰C.

Figure 5: Stackmodel of PLZT thin film on Pt/TiO₂/SiO₂/Si used for optical measurements.

Figure 6: Wavelength dependence of (a) refractive index and (b) extinction coefficient of PLZT films post annealed at various temperatures.

Figure 7: Plots of $(\alpha h\nu)^2$ versus $h\nu$, obtained from ellipsometric reflectance of the films post annealed at 550 - 750 °C.