7. OPTICAL STUDIES OF PULSED LASER DEPOSITED PZT THIN FILM BY SPECTROSCOPIC ELLIPSOMETRY

7.1 INTRODUCTION

The studies on the optical properties of PZT thin film are scarce compared to its studies on the ferroelectric property. When there are considerable reports on the optical properties of this material using the transmittance spectrum, only a few studies have been reported for the optical studies by spectroscopic ellipsometry (SE). Daniel Franta et al. [61] have prepared the sol-gel deposited Pb(Zr<sub>0.5</sub> Ti<sub>0.5</sub>)O<sub>3</sub> PZT thin film on the Pt/Ti/SiO<sub>2</sub>/Si substrate and studied the spectral dependencies of the optical constants using SE. Jiang et al. [62] have obtained the refractive index n, and the extinction coefficient k of the spin coated Pb(Zr<sub>0.53</sub> Ti<sub>0.47</sub>)O<sub>3</sub> PZT thin film prepared on the Pt/Ti/SiO<sub>2</sub>/Si substrate using SE. Tang et al. [63] have reported the SE studies of refractive index n, and the extinction coefficient k of the spin coated Pb(Zr<sub>0.4</sub> Ti<sub>0.6</sub>)O<sub>3</sub> and Pb(Zr<sub>0.6</sub> Ti<sub>0.4</sub>)O<sub>3</sub> thin film deposited on the Pt/Ti/SiO<sub>2</sub>/Si substrate. Huang et al. [64] investigated the optical properties of Pb(Zr<sub>0.3</sub> Ti<sub>0.7</sub>)O<sub>3</sub> thin film grown on Pt/Ti/SiO<sub>2</sub>/Si substrate by infrared spectroscopic ellipsometry. Galca et al. [65] studied the Substrate–target distance dependence of structural and optical properties of Pb(Zr,Ti)O<sub>3</sub> films (20/80 Zr/Ti ratio) obtained by pulsed laser deposition using ellipsometer.

From the above discussion, it is clear that many studies on the optical properties of the PZT with different Zr/Ti ratio have been carried out by spectroscopic ellipsometry (SE), mostly for the thin films prepared by sol-gel method and spin-coating method. In all these studies, Pt/Ti/SiO<sub>2</sub>/Si substrate is used. A thorough literature survey showed that spectroscopic ellipsometry (SE) study of optical properties of PZT thin films prepared by pulsed laser deposition (PLD) is rarely reported [65]. Moreover, SE studies of the optical properties of PZT with Zr/Ti composition 52/48 is scarcely reported [66]. Hence, the optical properties using spectroscopic ellipsometry (SE) for nanostructured Pb(Zr<sub>0.52</sub> Ti<sub>0.48</sub>)O<sub>3</sub> thin film prepared by PLD on a Si(100) substrate have been studied and analyzed. The growing interest in graded refractive index films for applications in
optical devices and applications in space environment, make it imperative to study the optical properties of the PZT thin films.

In the present study, the optical characterization of Pb(Zr\textsubscript{0.52}Ti\textsubscript{0.48})O\textsubscript{3} thin film coated on SiO\textsubscript{2}/Si (100) substrate prepared by pulsed laser deposition method have been reported. This Pb(Zr\textsubscript{0.52}Ti\textsubscript{0.48})O\textsubscript{3} composition lies in the tetragonal part of the PbZrO\textsubscript{3}-PbTiO\textsubscript{3} system phase diagram and near to morphotropic phase boundary (MPB). The optical properties of Pb(Zr\textsubscript{0.52}Ti\textsubscript{0.48})O\textsubscript{3} thin film have been investigated by spectroscopic ellipsometry (SE) in the UV-vis-NIR wavelength range of 200 – 900 nm. The optical properties such as refractive index, extinction coefficient, absorption coefficient, band gap and dielectric constant obtained from the ellipsometric parameters have been presented and compared with the other experimental values.

7.2 RESULTS AND DISCUSSION
7.2.1 Structural and morphological studies

The XRD pattern of the PZT thin film is shown in Figure. 7.1 and it shows the clear formation of a single phase perovskite structure in the tetragonal phase which was confirmed by the JCPDS data. Formation of the unwanted pyrochlore phase was eliminated in the film through a careful selection of deposition parameters. The XRD pattern reveals a prominent peak with high orientation of PZT thin films along (211) direction along with the four low intense peaks along the (100), (101), (111) and (200) direction.
Figure. 7.1: XRD pattern of the PZT (52/48) thin film coated on SiO$_2$/Si(100) substrate.
Figure. 7.2: SEM images of the nanostructured PZT thin film coated on SiO$_2$/Si(100) substrate (a) low-magnification and (b) high-magnification.

The surface morphology of the PZT thin film prepared by the PLD process was investigated by the scanning electron microscope and it is shown in Figure 7.2 (a) and (b). The SEM image which shown in Figure. 7.2 (a) reveals the presence of many clusters. In Figure 7.2 (b) which is the magnified SEM image, the well-developed nano-grain structure with dense and uniform distribution is seen and the grain sizes are in the range of 50-100 nm. From Figure. 7.2 (b), it is seen that the surface consists of some voids.

7.2.2 Optical studies of PZT thin films

Spectroscopic ellipsometry (SE) is nondestructive, noninvasive, and noninvasive, contactless optical technique, applied not only for the optical characterization of bulk materials and thin films, but also for in situ real-time measurement of multilayered film structures, interfaces, surfaces, and composites, during fabrication and processing. SE is used to measure the film thickness and the
dielectric functions of multilayer thin films. In the present work, SE was used to study
the optical properties of the pulsed laser deposited PZT thin film coated on SiO$_2$/Si(001)
substrate. The optical characteristics were measured using a SOPRA ESVG model
rotating polarizer ellipsometer in the energy range 1.5 - 5 eV for an angle of incidence of
75° at room temperature. In spectroscopic ellipsometry, the change in the amplitude
and the phase difference between the parallel (p) and perpendicular (s) components of
the reflected light polarized with respect to the plane of incidence are measured as the
ellipsometric parameters. The change in the reflected light is measured by the ratios of
their amplitudes and phase differences. The complex reflectance ratio, ρ is given by
\[ ρ = \frac{r_p}{r_s} = \tan \psi \exp (i\Delta) \] (7.1)
where \( r_p \) and \( r_s \) are the Fresnel reflection coefficients for the light polarized parallel and
perpendicular to the plane of incidence respectively. The ellipsometric parameters \( ψ \)
and \( Δ \) are ellipsometric angles. The \( \tan ψ \) gives the ratio between the absolute values of
these two electric field components and \( Δ \) represents the phase difference between
them.

From the ellipsometric parameters, the optical pseudo-dielectric function \( ε(E) \)
was deduced using the following relation:
\[ ε (E) = N_o^2 \sin^2 \theta + \left[ \frac{1 - ρ}{1 + ρ} \right]^2 \sin^2 \theta \tan^2 \theta ] \] (7.2)
where \( \theta \) is the angle of incidence and \( N_o \) is the refractive index of the ambient.

Figure. 7.3 shows the measured ellipsometric parameters \( ψ \) and \( Δ \) of the PZT
film as a function of incident energy. In the lower energy region, the multiple reflections
of light within the film lead to oscillations due to interference. This indicates that the
material is transparent to the light for energies less than 3 eV. It is to be noted that the
number of oscillations depends on the thickness of the thin film.
In order to extract the refractive indices of the films, a four layer model consisting of ambient/PZT/SiO$_2$/Si(100) was used. The thickness of the sample and the refractive index are obtained by employing a Bruggemen effective medium approximation [85]. The standard reference for the SiO$_2$ [86] and Si [87] were taken from literature, while Cauchy dispersion relation was employed to evaluate the refractive index. A linear regression analysis was used to vary the model parameters until the mean square deviation ($\chi^2$: defined below) between the computed and experimental values of $10^{-3}$ is achieved. The mean square deviation ($\chi^2$) is defined as

$$\chi^2 = \frac{1}{N - M - 1} \sum_{j=1}^{N} \left[ (\tan\Psi_{j,\text{expt}} - \tan\Psi_{j,\text{comp}})^2 + (\cos\Delta_{j,\text{expt}} - \cos\Delta_{j,\text{comp}})^2 \right]$$  \hspace{1cm} (7.3)

where, $N$ is the number of data points and $M$ is the number of parameters to be fitted. The $\tan\Psi_{j,\text{comp}}$, $\cos\Delta_{j,\text{comp}}$ were computed for the assumed model, and $\tan\Psi_{j,\text{expt}}$, $\cos\Delta_{j,\text{expt}}$ are the experimentally obtained ellipsometric parameters. The complex refractive index ($N$) is given by the equation

$$N = n + ik$$  \hspace{1cm} (7.4)
where \( n \) and \( k \) are the refractive index and the extinction coefficient respectively. The refractive index of the films was extracted using Cauchy dispersion model given by [88]

\[
    n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}
\]  

(7.5)

A, B and C are the Cauchy parameters and \( \lambda \) is the wavelength of the incident light.

Figure 7.4 shows the dependence of \( n \) and \( k \) on the incident wavelength. The refractive index at 633 nm is 2.239. The value of the refractive index determined by SE for the PZT (50/50) deposited on sapphire by sol-gel method is 1.9 at 650 nm as reported in reference-89 and our result at this wavelength 650 nm is 2.2 which is found to be closer to this report.

![Figure 7.4: Wavelength dependence of the refractive index \( n \) and the extinction coefficient \( k \) of PZT (52/48) thin film.](image)

The refractive index of the PZT thin films prepared by different growth techniques such as spin coating, sol-gel coating, sputtering, PLD for different compositions [56, 57, 61-63, 66, 89, 90] along with the refractive index values of the bulk ceramics PbZrO\(_3\) and PbTiO\(_3\) are presented in the Table. 7.1 and are compared with the refractive index values of the present work. As seen from the table 7.1, the technique used to determine the refractive index in these studies is different. For instance, in some reports
transmittance and in some reports ellipsometry is used for the study of optical properties. So, this table helps to compare the refractive index values reported in this work with that of other reports. In the table 7.1, all these refractive index values are reported for the wavelength of 633 nm except the S.No.3 which is for 650 nm. In Table 7.1, serial numbers 1 and 2 are for the ceramics and from 3-6 are for the Zr/Ti composition of 50/50. Numbers 7 and 8 are for 60/40 composition and 9-11 are for 40/60 composition. The last three from 12-14 are for 52/48 (No:12-present work) and 53/47 (No:13,14) compositions which can considered to be the same for the comparison that follows.

The values of bulk ceramics indicate that the refractive index for the PZT lies between 2.42-2.668. When 50/50 composition is considered, Table. 7.1 shows that refractive index value is between 2.44-2.54 except that correspond to reference 88 (S.No.3). For compositions 60/40, the refractive index values are 2.376 and 2.45 and for 40/60 are between 2.45-2.544 as seen from the Table 7.1. From the last two reports (S.No:13, 14), it is seen that the refractive index values are 2.55 [62] and 2.567 [56] which are for 53/47 composition (near MPB) and they are in good agreement with each other. For nearly the same composition (52/48), refractive index value for the PZT thin film presented in this work is 2.239 which is less than that given by reference 62 and 56 mentioned above. It is known that the refractive index in the transparent region is dependent on several characteristics of the deposited material such as the crystalline quality, the porosity and stoichiometry. So, our low refractive index values are attributed to the voids present in the film as the voids will decrease the refractive index. This is also evident from the magnified SEM image of PZT thin film (Figure. 7.2(a)). It is inferred from the reported refractive index values given in the Table. 7.1 that the refractive index values vary slightly with the composition of Zr/Ti of the PZT.

Table. 7.1: Comparison of refractive index values of ceramics and thin films with the pulsed laser deposited PZT (52/48) thin film.
The above discussion suggests that as refractive index does not vary much due to the substrate also. Galca et al. [65] reported the refractive index of the PZT (20/80) thin film prepared by the PLD process for the target-substrate distance of 5 cm as 2.61 at 630 nm. The refractive index value presented in this work is found to be lower than their value (Table 7.1) and this may be due to the difference in the composition and also due to the existence of voids in our films. The XRD pattern and low values of the $k$

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film</th>
<th>$\lambda$ (nm) : n</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PbZrO$_3$ Ceramic</td>
<td>632.8:2.42</td>
<td></td>
<td>91</td>
</tr>
<tr>
<td>2.</td>
<td>PbTiO$_3$ Ceramic</td>
<td>632.8:2.668</td>
<td></td>
<td>91</td>
</tr>
<tr>
<td>3.</td>
<td>Sol-gel: PZT (50/50) on Platinized Si</td>
<td>650:~1.9</td>
<td>Ellipsometry</td>
<td>88</td>
</tr>
<tr>
<td>4.</td>
<td>Sputtered: PZT (50/50) on sapphire</td>
<td>633:2.54</td>
<td>Ellipsometry</td>
<td>92</td>
</tr>
<tr>
<td>5.</td>
<td>Sol-gel: PZT (50/50) on Platinized Si</td>
<td>633:2.45</td>
<td>Ellipsometry</td>
<td>61</td>
</tr>
<tr>
<td>6.</td>
<td>Sputtering: PZT (50/50) on sapphire</td>
<td>633: 2.44-2.54</td>
<td>Ellipsometry</td>
<td>92</td>
</tr>
<tr>
<td>7.</td>
<td>Spin coating: PZT(60/40)</td>
<td>633:2.376</td>
<td>Ellipsometry</td>
<td>63</td>
</tr>
<tr>
<td>8.</td>
<td>MOCVD PZT (60/40)</td>
<td>633:2.45</td>
<td>Ellipsometry</td>
<td>63</td>
</tr>
<tr>
<td>9.</td>
<td>MOCVD: PZT(40/60)</td>
<td>633:2.5</td>
<td>Ellipsometry</td>
<td>66</td>
</tr>
<tr>
<td>10.</td>
<td>Spin coating: PZT(40/60)</td>
<td>633:2.544</td>
<td>Ellipsometry</td>
<td>63</td>
</tr>
<tr>
<td>11.</td>
<td>Sol-gel: PZT (40/60)</td>
<td>633: ~2.45</td>
<td>Transmittance</td>
<td>90</td>
</tr>
<tr>
<td>12.</td>
<td>PZT (52/48) (PLD on Si(100) substrate)</td>
<td>633:2.239</td>
<td>Ellipsometry</td>
<td>Present work</td>
</tr>
<tr>
<td>13.</td>
<td>Sputtering: PZT (53/47) (Spin coating, Platinized Si)</td>
<td>633:2.55</td>
<td>Ellipsometry</td>
<td>62</td>
</tr>
</tbody>
</table>
reveals the good crystalline quality and good surface smoothness of prepared PZT thin film.

![Absorption coefficient α as a function of wavelength for PZT (52/48) thin film.](image)

Figure. 7. 5: Absorption coefficient $\alpha$ as a function of wavelength for PZT (52/48) thin film.

The absorption coefficient ($\alpha$) of the films as a function of wavelength is expressed as [93]

$$\alpha = \frac{4\pi k}{\lambda}$$  \hspace{1cm} (7.6)

where $\lambda$ is the wavelength of light and $k$ is the extinction coefficient. The absorption coefficient of the PZT thin films as a function of wavelength is shown in Figure. 7.5. The absorption coefficient is found to decrease with the increase in the wavelength and this trend is in agreement with that reported by Tang et al. [63] who studied the optical properties of spin coated PZT thin films (Zr/Ti ratio = 40/60) deposited on Pt-coated Si substrate. The value of the absorption coefficient at 633 nm (1.95 eV) is $4.02 \times 10^4$ cm$^{-1}$. The absorption coefficient is greater than $1 \times 10^5$ cm$^{-1}$ for the wavelength below 410 nm and this indicates that absorption coefficient is higher for the shorter wavelength. The thickness of the PZT thin film as estimated by the SE data is 524 nm.
Figure 7.6: Plot of \((\alpha h \nu)^2\) vs. photon energy, the bandgap energy is deduced from the extrapolation of the straight line to \((\alpha h \nu)^2 = 0\).

The relation between the energy gap \(E_g\) and absorption coefficient \(\alpha\) is given by the Tauc equation

\[
(\alpha h \nu)^2 = A(h \nu - E_g)
\]

(7.7)

where, \(h \nu\) is the incident photon energy and \(A\) is a constant which does not depend on photon energy. Equation (7.7) corresponds to the allowed direct transition between occupied and empty states. PZT exhibits a direct band gap \(E_g\) at the symmetry point X of the Brillouin zone [94].

Table 7.2: Comparison of energy gap \((E_g)\) of ceramics and thin films with the pulsed laser deposited PZT (52/48) thin film.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film</th>
<th>Band gap (eV)</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sol-gel: PZT (40/60)</td>
<td>3.6</td>
<td>Transmittance</td>
<td>90</td>
</tr>
</tbody>
</table>
To calculate the energy gap $E_g$, $(\alpha h \nu)^2$ was calculated and the plots of $(\alpha h \nu)^2$ as a function of photon energy $(h \nu)$ was plotted for the PZT thin film coated on Si substrate by the PLD method and are shown in Figure. 7.6. From this plot, the energy gap $E_g$ was obtained by extrapolating the linear portion to meet the energy axis. The energy value at $(\alpha h \nu)^2 = 0$ gives the energy gap value and it is 3.65 eV for the prepared PZT thin film. Table 7.2 presents the energy gap values of the present work along with the values reported by other work [53, 62, 56, 92, 95]. The measured energy gap value of PZT thin film is in reasonable agreement with Ref. 90 (ratio 60/40) and differs from Ref. 56 (ratio 53/47) slightly.

<table>
<thead>
<tr>
<th></th>
<th>Process: PZT (Ratio)</th>
<th>Energy Gap ($E_g$)</th>
<th>Method</th>
<th>Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Sol-gel: PZT (60/40)</td>
<td>3.65</td>
<td>Transmittance</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>Sol-gel: PZT (65/35)</td>
<td>3.4</td>
<td>Transmittance</td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>Spin coating (80/20)</td>
<td>3.73</td>
<td>Ellipsometry</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>Spin coating (70/30)</td>
<td>3.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spin coating (50/50)</td>
<td>3.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spin coating (40/60)</td>
<td>3.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Spin coating: PZT (53/47)</td>
<td>~3.42</td>
<td>Transmittance</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>PLD: PZT (52/48)</td>
<td>3.65</td>
<td>Ellipsometry</td>
<td>Present work</td>
</tr>
</tbody>
</table>

To calculate the energy gap $E_g$, $(\alpha h \nu)^2$ was calculated and the plots of $(\alpha h \nu)^2$ as a function of photon energy $(h \nu)$ was plotted for the PZT thin film coated on Si substrate by the PLD method and are shown in Figure. 7.6. From this plot, the energy gap $E_g$ was obtained by extrapolating the linear portion to meet the energy axis. The energy value at $(\alpha h \nu)^2 = 0$ gives the energy gap value and it is 3.65 eV for the prepared PZT thin film. Table 7.2 presents the energy gap values of the present work along with the values reported by other work [53, 62, 56, 92, 95]. The measured energy gap value of PZT thin film is in reasonable agreement with Ref. 90 (ratio 60/40) and differs from Ref. 56 (ratio 53/47) slightly.
Using the obtained values of refractive index and extinction coefficient, the real and imaginary parts of the dielectric constant were calculated by the following expression [91]

\[ \varepsilon_r = n^2 - k^2 \]  \hspace{1cm} (7.8)
\[ \varepsilon_i = 2nk \]  \hspace{1cm} (7.9)

The real and imaginary parts of the dielectric constants were plotted as a function of incident wavelength and are shown in Figure. 7.7. From Figure. 7.7, it is observed that \( \varepsilon_r \) and \( \varepsilon_i \) values of the films decreases with wavelength. The plot of \( \varepsilon_r \) is similar to that of refractive index because of the smaller values of k. The plot of k is similar to that of \( \varepsilon_i \).

7.3 CONCLUSION

Pb\((Zr_{0.52}Ti_{0.48})O_3\) (PZT) thin film was grown on SiO\(_2\)/Si(100) substrate by pulsed laser deposition method. The XRD pattern of the PZT thin film reveals the formation of a single phase perovskite structure in the tetragonal phase. The scanning electron
microscope image demonstrates the well-developed nano-grain structure with dense and uniform distribution of grain size in the range of 50-100 nm. The thickness of the thin films determined by the ellipsometer data is 524 nm. The refractive index of the thin film is 2.239 and it is slightly less than the values reported for the same composition. This is due to the voids present in the thin film. The low value of the k indicates the good smoothness of the thin film. The absorption coefficient is large for shorter wavelength and it is in the order of $10^5$ cm$^{-1}$. The value of the absorption coefficient at 633 nm is $4.02 \times 10^4$ cm$^{-1}$. The energy gap of the PZT thin film was estimated to be 3.65 eV which is in reasonable agreement with the other reported value.