CHAPTER – 7

OPTICAL CONSTANTS AND NEAR INFRARED EMISSION OF Er DOPED ZnO
SOL-GEL THIN FILMS

7.1 Introduction

Present-day scientific and technological developments demand the use of novel optical materials which exhibit unique optical properties not observed in conventional materials. Investigations have focused on developing new optical materials and efficient ways of tailoring the properties of existing ones within the scope of the available preparation techniques. Studies on wide band gap semiconductors (WBGS) such as ZnSe, GaN and ZnO based materials have made substantial progress. Among these ZnO has attracted enormous interest, because of its higher energy gap (3.24 eV) and exciton binding energy (60 meV) at room temperature, which is approximately three times as large as those of ZnSe and GaN [353]. It has been investigated extensively in the optoelectronic field, such as surface acoustic wave devices [354, 355], ultraviolet light emitting diodes [88, 356 and 357], photo detectors [358, 359] laser diodes [360] and so on. Among optoelectronic materials, devices designed using Er doped semiconductors have attracted much interest for applications in optoelectronic fields. Numerous studies have been devoted to investigate various Er doped semiconductors, such as GaAs, Si, GaP, SiC, GaN, and so on [361 – 366]. The researches based on these semiconductors suggest that the codoping of Er and O could increase its luminescence intensity greatly. It has already been realised that ZnO is an ideal host material of Er$^{3+}$ ions due to the more easily realization of the coexistence of Er and O.
The Er doped semiconductors are promising optoelectronic materials due to the Er intra 4f shell transition with a photoemission at a wavelength of 1.54 μm, which lies in the minimum loss region of silica based optical fibres [367–371]. Chen et al [372] reported that there is a shift of band gap due to the presence of oxygen deficiency in Er doped ZnO films. The Er doped ZnO films were studied by pulsed laser deposition, sputtering, spray pyrolysis, thermal evaporation method and sol-gel method. Little progress has been made on the optical constant of Er doped ZnO thin films by sol-gel. In this chapter, we present the optical constant of Er doped ZnO thin films at different annealing temperatures and characterized by Raman, photoluminescence and UV-Visible analysis.

7.2 Experimental procedure

The Er doped ZnO thin films were deposited on glass substrate by sol-gel spin coating method. Zinc acetate dihydrate, erbium chloride, 2 – methoxyethanol and monoethanolamine (MEA) were the precursors used. Zinc acetate dihydrate and erbium chloride were first dissolved in a mixture of 2-methoxyethanol and MEA. The molar ratio of MEA to zinc acetate dihydrate was maintained at 1.0 and the concentration of zinc acetate at 0.5 M. The resulting mixture was stirred at 60°C for 1 hr. Finally, a clear and transparent homogeneous solution was formed. The concentration of erbium chloride as a dopant was 1-5 mol. % with respect to zinc. The samples have been named EZ1, EZ2 and so on upto EZ5 depending on the concentration of the dopant from 1 to 5%. Procedure as said in chapter-3 has been adopted for cleaning and coating of thin films on the substrate. The grown film was then kept in a furnace and annealed in air atmosphere at 500°C and 600°C for 1 h respectively.

X-ray diffraction (XRD) studies of the films were performed using monochromatic CuKα1 radiation. Surface morphology of the films was studied by scanning electron microscope
(Hitachi, Model: S-3400N) and the incorporation of dopant is analysed by energy dispersive X-ray spectra. The μ-PL measurements were performed on the Jobin Yvon LabRAM HR 800UV micro-Raman system at room temperature, using the 325 nm line of a He–Cd laser as excitation source. The absorption and transmission spectra are taken from JASCO V-670 UV – VIS-IR Spectrometer.

7.3 Results and Discussions

7.3.1 Structural properties

![X-ray diffraction patterns of various percentages of Er doped ZnO films.](image)

Fig.7.1 X-ray diffraction patterns of various percentages of Er doped ZnO films.

The XRD spectra at two different temperatures and various doping concentrations are given in Fig.7.1. The peak positions of (100), (002), and (101) planes are blue shifted and their intensities show variations in the doped films when compared to pure ZnO. The high intense (002) peak of ZnO has decreased while the usual low intensity peaks of ZnO at the other two positions increased in intensity in the doped samples leading to a change in the crystalline size as
measured from Scherrer formula. The average crystalline size is 27.44 nm for 500°C and 29.28 nm for 600°C for all doping percentages which confirms the good crystalline quality of the deposited films. Formation of single phase of ZnO with wurtzite structure (JCPDF No. 79 – 0206) [373] is evidenced from the XRD spectra.

Fig.7.2 (a) SEM images of Er doped ZnO film at different resolutions.

The observed scanning electron microscope (SEM) images of Er doped ZnO thin films are given in Fig.7.2 (a). Images at different nano meter scale show that the surface of the film is composed of small grains. Sphere like grains are observed from all the films at 2 μm scale and also show dense packing. Degradation in the grain size occur on Er doping as they create more nucleation centres during the deposition process and coalescence of grains during the annealing process increases the grain size.
The element compositions of the Er doped ZnO films were analysed by energy dispersive X-ray (EDX) spectra and are shown in Fig.7.2 (b).

Fig.7.2 (b) EDX spectrum of Er doped ZnO films.

The presence of the constituent elements for the Er doped ZnO films was confirmed by the occurrence of their respective peaks. To confirm the absence of the secondary phase formation in Er doped ZnO thin films, Raman spectra was taken at the back scattering geometry \( z(xx)\bar{z} \). Looking at the Raman spectra of Er doped ZnO (Fig.7.3 (a)) it is almost the same as the bulk ZnO materials. The main structure of ZnO has not changed after doped with Er, when the size of particle reduces to nanoscale. The \( k=0 \) selection rule for the first order Raman scattering is relaxed, therefore the phonon scattering will not be limited to centre of the Brillouin zone and the phonon dispersion near the centre of the Brillouin zone should also be considered as well.
Fig. 7.3 (a) Micro Raman spectra of undoped, 4 and 5% Er doped ZnO films at two different temperatures.

The predicted optical modes by group theory for the space group $C_{6h}^4$ [252, 374] are $A_1 + 2B_1 + E_1 + 2E_2$ at the $\Gamma$ point of the Brillouin zone; $B_1$ (low) and $B_1$ (high) modes are normally silent; $A_1$ and $E_1$ are both Raman and IR active while $E_2$ modes are only Raman-active. Thus, $A_1$ and $E_1$ modes are split into longitudinal (LO) and transverse (TO) optical components. The Raman active modes in Er doped ZnO thin films are listed in Table 7.1. The LO phonon modes up to fifth order were observed starting from the first order $A_1$ LO phonon peak from 574 cm$^{-1}$ agreeing with the previous literature values [375].

**Table 7.1** Observed Raman active modes in Er doped ZnO films at different concentration and temperatures.

<table>
<thead>
<tr>
<th>Raman active modes</th>
<th>Ref.[24] (cm$^{-1}$)</th>
<th>500°C (cm$^{-1}$)</th>
<th>600°C (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2E$_2$ (low)</td>
<td>208</td>
<td>201</td>
<td>201</td>
</tr>
<tr>
<td>E$_2$ (high) – E$_2$ (low)</td>
<td>322</td>
<td>321</td>
<td>321</td>
</tr>
<tr>
<td>E$_2$ (high)</td>
<td>443</td>
<td>465</td>
<td>465</td>
</tr>
<tr>
<td>A$_1$ (1LO)</td>
<td>573</td>
<td>574</td>
<td>574</td>
</tr>
<tr>
<td>A$_1$ (2LO)</td>
<td>-</td>
<td>1145</td>
<td>1149</td>
</tr>
</tbody>
</table>
The integrated intensity ratio of each Gaussian line nLO to 1LO as a function of n (number of LO phonons) for different concentrations of erbium and different annealing temperatures are presented in Fig.7.3 (b).

![Integrated intensity ratio](image)

**Fig.7.3 (b)** Integrated intensity versus number of LO phonons.

The separation between first LO phonon to second LO phonon is 70.8 meV at 500°C and 71.2 meV for 600°C. The ratio of integrated intensity of second order LO phonon to first order LO phonon gives rise to the electron phonon coupling. It clearly demonstrates how well the integrated intensity ratio viz., electron phonon coupling increases with the crystallite size. The crystallite sizes were found to increase upon doping and temperatures (500°C to 600°C) from the XRD calculations. The Frohlich type of interaction essentially has a size dependence on electron phonon coupling [376]. To be more precise the electron phonon coupling parameter increases with increasing particle size [308]. Hence strong coupling between electron and LO phonon is established here confirming the Frohlich type of interaction in the present case.
7.3.2 Exciton binding energy

The exciton binding energy (EBE) of Er doped ZnO films is calculated using the hydrogenic model [377], from which the parameters exciton Bohr radius (a*) and exciton binding energy (E_b) are given by

\[
a^* = \frac{m}{m^*} \varepsilon a_0
\]

(26)

\[
E_b = \frac{a^2}{\varepsilon a^*} = \frac{e^2a_0}{(m^*/m)(a^*)^2}
\]

(27)

Where, ‘m’ and ‘m*’ is the electron effective and reduced masses, ‘a_0’ is the Bohr radius for the hydrogen atom, ‘e’ is the electron charge and ‘\varepsilon’ is the dielectric constant. The calculated exciton binding energies are listed in Table 7.2. The decrease of EBE value with concentration may due to the internal field which arises in consequence of the spontaneous and the piezoelectric polarizations [378-381]. The increase in the carrier density screens the electron-hole Coulomb interaction and reduces the exciton binding energy [347] and it is essential for exciton based device applications. EBE value is found to increase with the increase of annealing temperature. For Er doped ZnO films the observed highest EBE value is 72 meV at 600°C. Though the binding energy decreases further on doping concentration, all the doped samples have greater binding energy than undoped ZnO.

Table 7.2 Comparison of observed and calculated values of optical parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E_g (eV)</th>
<th>E_b (meV)</th>
<th>Calculated value of n</th>
<th>Observed value of n from UV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Eqn. (5)</td>
<td>Eqn. (6)</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.27</td>
<td>60 60</td>
<td>2.40</td>
<td>2.74</td>
</tr>
<tr>
<td>EZ1</td>
<td>3.32</td>
<td>67 72</td>
<td>2.39</td>
<td>2.73</td>
</tr>
<tr>
<td>EZ2</td>
<td>3.31</td>
<td>64 68</td>
<td>2.39</td>
<td>2.73</td>
</tr>
<tr>
<td>EZ3</td>
<td>2.46</td>
<td>64 66</td>
<td>2.70</td>
<td>2.90</td>
</tr>
<tr>
<td>EZ4</td>
<td>3.29</td>
<td>61 66</td>
<td>2.40</td>
<td>2.74</td>
</tr>
<tr>
<td>EZ5</td>
<td>2.49</td>
<td>60 63</td>
<td>2.69</td>
<td>2.90</td>
</tr>
</tbody>
</table>
7.3.3 Optical properties

The micro PL of Fig.7.4 has three notable peaks; a green emission peak usually occurs as a cause of oxygen related vacancies, Zn interstitials and Zn vacancy; occurrence of a near band emission peak as a consequence of exciton formation and its population; a near infrared (NIR) peak arising due to oxygen related defects.

![Room temperature photoluminescence spectra of Er doped ZnO films.](image)

In the present case when erbium is doped, the localized levels may get modified as the localized levels depend on the following situations. The impurity atoms themselves may create localized levels. The perturbing influence/ association of impurity atom in the vicinity of the host atoms or their association with lattice defects say vacancies whose existence is tied up with the incorporation of impurity. These situations prompt a modification of green luminescence here.
Green luminescence efficiency is enhanced when excitons are localized in the vicinity of green emitting defects [348]. The band edge luminescence/near band edge emission occurs at 3.24 eV corresponds to donor acceptor pair combination. The decrease in the intensity of this peak upon increasing temperature is due to thermal quenching. The occurrence of NIR mode (1.62 eV) may be due to the creation of oxygen vacancies. Another reason may be due to the occurrence of deep acceptor transition by the electrically active oxygen interstitial defects. The optical constants play an important role in the optical communication and designing of the optical devices, because they are closely related to the electronic polarizability of ions and the nature of the materials inside the local field [382]. The absorption spectra of Er doped ZnO films at different annealing temperatures are presented in Fig.7.5 (a).

**Fig.7.5 (a)** Absorption spectrum of Er doped ZnO films.
The transmission spectra of Er doped ZnO films at different annealing temperatures are presented in Fig.7.5 (b).

![Fig.7.5 (b) Transmittance spectrum of Er doped ZnO films.](image)

The fundamental absorption edge occurs at 360 nm in pure ZnO and is slightly red shifted with increasing Er doping concentration. On an average nearly 80% transmission is observed in the films. From the transmittance spectra the absorption coefficient (α) can be calculated using equation (19) [322]. Using the functional relationship of \((\alpha h\nu)^2\) and photon energy \((h\nu)\), a Tauc plot (Fig.7.6) has been drawn for various percentage of Er doping on ZnO. Extrapolation of the linear portion to the zero absorption gives rise to the value of the optical band gap ‘\(E_g\)’. The obtained band gap varies from 3.26 eV to 3.32 eV confirming the red shift of the absorption edges. The refractive index is found to increase with annealing temperature on the Er doped samples (Fig.7.7).
Fig. 7.6 Tauc plot.

Fig. 7.7 Effect of Er concentration on refractive index in ZnO films at two different temperatures.
Probably the additional thermal energy helps to incorporate more Er ions to occupy the substitutional site of ZnO lattice, which might have caused changes in the refractive index. Empirical relationships modelled by a theoretical numerical analysis have been used to calculate the refractive indices of semiconductors using their energy gaps. This model is based on the fact that there is a strong correlation between the energy gap and the refractive index of the semiconducting materials. This physical relationship remains strictly intrinsic and specific to the material considered. Duffy et al [383] and Annai et al [384] used the following equation to calculate refractive index (n),

\[ n(E_g) = 0.05E_g^2 - 0.65E_g + 4 \] \hspace{1cm} (28)

\[ n = \frac{17 - E_g}{5} \] \hspace{1cm} (29)

Where, ‘Eg’ is the band gap. The calculated refractive indices are listed in Table 7.2. They agree with the experimental values. The higher refractive value (above 2) when compared to glass suggest that the material is suitable for antireflection coatings. Frequency dependence on the complex dielectric constant is a parameter which gives information about the electronic excitation and the real and imaginary parts are calculated using the equations (23 & 24) [351]. The real and imaginary dielectric constant of Er doped ZnO films as a function of wavelength are shown in Fig.7.8. Both real and imaginary part of dielectric constants decrease with the increase of annealing temperature while it increase with the increase of Er concentration. The optical conductivity as a function of photon energy of Er doped ZnO films at 500°C and 600°C from visible to UV region is given in Fig.7.9.
Fig. 7.8 Variation of dielectric constant versus wavelength of Er doped ZnO films.

Fig. 7.9 Dependence of optical conductivity on photon energy in Er doped ZnO films.
Tiny changes are observed in the visible region might be due to the trapping of free carriers in this region. Optical conductivity increases exponentially with respect to the photon energy and maximum conductivity is realized in the UV region. This confirms the increase of free carriers in the UV region.

7.4 Conclusions

The effect of erbium concentration and annealing temperature on optical constant of ZnO sol-gel thin films are investigated using spin coating method. The Er doped ZnO films retain the hexagonal wurtzite structure and no extra peak is observed. The EZ4 and EZ5 films show better crystalline nature. Sphere like grains are observed in the surfaces of the films and the presence of Er ions doping in ZnO matrix has been confirmed by EDX measurement. The wurtzite structure mode $E_2$(high) is slightly changed due the reorientation in the crystalline nature. The additional peaks $A_1$(LA + LO) (longitudinal acoustic + longitudinal optical), $A_1$(2 TO + 1 LO) and $2E_2$(low) + 4 LO are observed in EZ films. An observed reduction in the near band edge emission (NBE) peak intensity with respect to increase in temperature shows thermal quenching effect. The modification of localized levels on doping has enhanced the green luminescence. The increase in exciton binding energy on doping substantiates the modified localized levels. The presence of oxygen related defects are responsible for the appearance of near infra-red emission peak in doped ZnO. All the doped films have higher exciton binding energy than the undoped ZnO. The fundamental absorption edge at 360 nm is red shifted on Er doping. The average transmission of the films is above 80% in the visible region. Theoretical and experimental values of refractive index nearly coincide and the films with higher value of refractive index confirm surfaces with lesser voids. It is also evidenced from SEM images. The optical conductivity of the EZ films is mainly in the UV region and hence can be used for the UV detector applications.