CHAPTER - 5

EFFECT OF Er CONCENTRATION ON SURFACE AND OPTICAL PROPERTIES OF K DOPED ZnO SOL-GEL THIN FILMS

5.1 Introduction

ZnO is a very interesting material for many different applications in both microelectronic and optoelectronic devices. It is a wide band gap metal oxide semiconductor with a direct energy gap of about 3.37 eV. As a consequence, ZnO absorbs UV radiation due to band-to-band transitions; hence it can be used as transparent electrode in solar cells and flat panel displays as well as for the fabrication of grating in optoelectronic devices [281]. Surface topography of ZnO film may be described in terms of its fractal geometry, which is a part of modern mathematics that uses fractional dimensions to describe disordered objects. The concept of fractal dimension is used to explore the surface morphologies of ZnO thin films generated under various sputtering powers. The fractal dimensions were estimated by applying the structure function method [282]. The evaluation of refractive indices in optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, where the refractive index of a material is the key parameter for device design. The knowledge of real and imaginary parts of complex refractive index as a function of wavelength is necessary to make effective use of these materials for optoelectronic devices [283–285], particularly as an antireflective coating [286]. The variation of refractive index with doping also provides the means to tailor the refractive index to any desired value which is required for its use in filters [287].

Recently, group-I elements such as Li and Na have been explored, both of which can substitute Zn$^{2+}$ and give rise to a hole in the ZnO matrix. Wang et al. [289] reported that group-I elements were identified to be shallow acceptors to create p-type conduction in ZnO.
compared with group-V elements. In group-I dopants, Li has been studied for a long time [290]. However, as Li ion has a small radius, it tends to stay in the interstitial position and acts as a donor. Recent investigations have suggested that doping of Na into ZnO is a promising p-type conversion method [91, 89]. Very few works are available for the optical properties of K doped ZnO films. Little attention has been paid to another important element K in group-I and its related alloys [291, 292, 94], which behaves analogously to Na. Erbium (Er) doped semiconductors have been reported to be promising optical materials for optoelectronic devices [293]. ZnO has been considered as a candidate host material for Er doping. Er doped ZnO thin films have been intensively studied and fabricated by various methods [294–297]. Also, many scientific and technological efforts have been made in these fields aiming at obtaining single crystal thin films for 1.54 μm minimum loss region in fiber optic applications. In previous study, codoping methods have been tried to realize p-type ZnO conversion by using Al–N, In–N, Na–H, Mg–Li, Li–N, etc., and the goal is to facilitate the solubility of acceptor and improve the p-type stability [224, 298-301].

Many different deposition techniques, such as spray pyrolysis [302], pulsed laser deposition [303], sputtering method [304], metal organic chemical vapor deposition (MOCVD) [305], molecular beam epitaxy (MBE) [306] and sol-gel [307, 308] have been developed to prepare undoped, doped and codoped ZnO thin films. Among them, the sol-gel method is one of the most commonly used techniques due to several advantages, such as low cost, simple deposition procedure, easier composition control, low processing temperature and easier fabrication of large area films. However each method has its relative advantages for certain applications. To the best of our knowledge, no work has been carried out on the structural and optical properties of K doped and (K, Er) codoped ZnO. Hence, this chapter is devoted to analysis the above said properties of K doped and (K, Er) codoped ZnO thin films.
5.2 Experimental procedure

The K doped and (K, Er) codoped ZnO thin films were deposited on glass substrate by sol-gel spin coating method. Zinc acetate dihydrate, potassium chloride, erbium chloride, 2 – methoxyethanol and monoethanolamine (MEA) were the precursors used. Zinc acetate dihydrate and potassium chloride were first dissolved in a mixture of 2-methoxyethanol and MEA for K doping and erbium chloride is varied with respect to Zn and K for codoped films. Here we have chosen the sol-gel method because in this process it is possible for us to estimate the exact stoichiometric ratio of the dopant erbium for different doping levels as it is prepared in the solution / molecular level. 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 advantage of this method is that the sol-gel has been precisely optimized for its stoichiometry before being coated on the substrate. Procedure outlined in the 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 450°C and 550°C 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 Nanoscope-E AFM (Digital Instruments, USA). The incorporation of dopant was analyzed by energy dispersive X-ray spectra. The absorption and transmission spectra were recorded from JASCO V-670 UV – VIS-IR Spectrometer.
5.3 Results and Discussions

5.3.1 XRD analysis

The XRD patterns of K doped and (K, Er) codoped ZnO thin films with temperatures 450°C and 550°C are presented in Fig.5.1.

![XRD patterns of K doped and (K, Er) codoped ZnO films.](image)

From the patterns, it can be seen that all the films have diffraction peaks corresponding to the (100), (002) and (101) plane and among these (002) plane has a strong orientation. This indicates that all the doped and codoped ZnO thin films are preferentially oriented along the c axis perpendicular to the substrate. No secondary phase is observed in all the films. The K doping and (K, Er) codoping almost does not affect the position of (002) diffraction peak, but it strongly affects the peak intensity. When the doping concentration is 2 mol. %, the diffraction peak intensity is the strongest one. With the increase of K and Er doping concentration, there is a drop in (002) diffraction peak intensity. It coincides with the previous result [309]. Many experimental results show that deposition conditions and annealing treatment are the two major factors affecting the growth orientation of ZnO thin films. In ZnO thin films prepared by sol-gel method, the sol stabilizer and annealing treatment are the two major factors affect the oriented growth of the films.
Fig. 5.1. indicates that the annealing treatment has an important effect upon the intensity of (002) peak of 1 and 2 mol. % of K doped ZnO but not in the (K, Er) codoped ZnO films. The variation of intensity in (002) peak is mainly connected with the position of K and Er atoms in ZnO. Kim et al. [291] from their experimental result suggest that K atoms are mostly located in the interstitial site of ZnO matrix when K doping concentration is below 2 at %. The theoretical calculation results of Park et al. [76] are also in support of the above experimental results. However, when the annealing temperature is relatively high (≥ 600°C), there is a possibility that most of the K atoms are substituted in the Zn site. Here, the doped and codoped films are prepared below 600°C, so the K atoms could have occupied interstitial position in the K doped ZnO films. The crystallinity has been improved in the present case. But in the codoped (K, Er) ZnO films K and Er atoms are substituted in the interstitial position of Zn site in the ZnO films where there is a decrease in the crystalline nature. The particle size of the deposited films are calculated using equation (3). In both annealing temperatures, the particle size is decreased with the increase of K and Er doping concentration. The average particle size of doped and codoped ZnO films is 31.32 and 19.99 nm respectively. The calculated structural parameters are listed in Table 5.1.

**Table 5.1** Calculated structural and morphological parameters.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle Size (XRD) nm</th>
<th>Particle Size (AFM) nm</th>
<th>Surface Roughness (nm)</th>
<th>Fractal Dimension (D₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% K doped ZnO</td>
<td>31.26</td>
<td>31.45</td>
<td>8.96</td>
<td>1.44</td>
</tr>
<tr>
<td>2% K doped ZnO</td>
<td>32.48</td>
<td>32.09</td>
<td>10.71</td>
<td>1.54</td>
</tr>
<tr>
<td>3% K doped ZnO</td>
<td>30.24</td>
<td>33.43</td>
<td>9.71</td>
<td>1.52</td>
</tr>
<tr>
<td>1% K &amp; 1% Er codoped ZnO</td>
<td>21.05</td>
<td>49.56</td>
<td>25.75</td>
<td>1.49</td>
</tr>
<tr>
<td>1% K &amp; 2% Er codoped ZnO</td>
<td>20.04</td>
<td>19.71</td>
<td>6.91</td>
<td>1.26</td>
</tr>
<tr>
<td>1% K &amp; 3% Er codoped ZnO</td>
<td>18.90</td>
<td>16.32</td>
<td>11.75</td>
<td>1.43</td>
</tr>
</tbody>
</table>
5.3.2 Surface and Elemental composition analysis

Surface morphology and elemental composition of K doped and (K, Er) codoped ZnO films are shown in Fig.5.2.

![SEM images and EDX spectra doped and codoped films.](image)

Fig.5.2 SEM images and EDX spectra doped and codoped films.

From the figure, we observe that the surfaces of the doped and codoped films composed of small grains and form a rod like wrinkle structures. The presence of the constituent elements of the K doped and (K, Er) codoped ZnO films are confirmed by the occurrence of their own respective peaks. A detailed analysis of surface and optical properties of the doped and codoped films are undertaken for better clarity at one annealing temperature 450°C.
The AFM measurements could provide information regarding the surface morphology of the films and this capability might be used to investigate the nature of the deposited thin films like the surface roughness and particle size. A careful analysis of roughness can yield information regarding the kind of growth that is taken place during the formation of films. The typical AFM surface images of the doped and codoped films are shown in Fig.5.3 (a-f).

![Fig.5.3 Two dimensional surface morphology images of different K and Er doped films (a & d = 10 & 12 µm, b & e = 5 µm, c & f = 1 µm).](image)

A light and dark area is found in Fig.5.3 indicating greater height and friction. These predict that a strong dependence between the slope of the surface asperity and the friction coefficient on nanometer scale. Micrographs at 5 µm × 5 µm shows a wrinkle structure formation on the surface of the films. The following reasons are responsible for the wrinkle structure formations. (i) It occurs in the whole film as a result of the relaxation of stress due to various type of instabilities [310]. These wrinkle patterns, although have a certain dominant wavelength associated with them, often exhibit isotropic wave patterns. (ii) The rigid coating buckles which yield distinct wrinkling patterns ranging from homogeneous to
hierarchical wrinkles [311], (iii) fiber like streaks or wrinkles could be induced by shortness of OH and OR groups during the annealing process [312]. In our previous work, we have reported the wrinkle structure formation in the Al and N codoped ZnO films prepared by so-gel method. Xu et al. [313, 265] have reported that the K doped ZnO films surfaces contains no wrinkle structures. Unlike in our case, there is wrinkle structure formation at 1 mol.%, however wrinkle structures disappear with the increases of K concentration and its surface is composed of spherical grains. That is why we kept 1 mol.% doping of K in ZnO and varied our codoping percentage to probe the wrinkle structure formation. The calculated width and distance between the two wrinkle structures is 0.3 – 0.5 µm for K doped ZnO films. It is directly proportional to the Er concentration. The width and distance between two wrinkle structures is 0.5 – 0.7 µm which may arise due to the particle aggregation.

The average particle size and surface roughness of doped and codoped ZnO films are calculated and listed in Table 5.1. There is no abrupt change in the particle size of the K doped ZnO films but it decreases with the increases of Er concentration. The possibility of bonding of oxygen atoms leading to the formation of O₂ gas and a subsequent pumping out of the gas during deposition might be the reason for the reduction in particle size.

It is also reported that the oxygen gets re-evaporated from the surface at higher substrate temperatures [314]. Because of the oxygen deficiency during the growth, excess zinc is produced which occupies the interstitial positions in the crystal lattice and formed as native defects. It is known from earliest literatures that ZnO has a tendency to grow with native defects such as zinc interstitials (Zn_i) and oxygen vacancies (V_O). Here, interstitial zinc atoms migrating at the grain boundaries act as a barrier for further growth of grain boundaries which in turn decreases the particle size. Density functional theory calculations show that intrinsic defects, most likely zinc interstitials, are migrating in the vicinity of grain boundaries [315]. More excess zinc interstitial sites have been created at higher substrate
temperatures because of the lower ionization energy [316] and the grain size of particles are reduced further. The calculated average surface roughness value is 9.79 nm for K doped ZnO films and 14.80 nm for (K, Er) codoped ZnO films. The increase of surface roughness indicates that the deorientation of crystallinity and it is well matched with the XRD results. The histogram variation of surface roughness with respect to the K and Er concentrations are shown in Figs.5.4 (a & b).

Fractal analysis is used to investigate the surface science that significantly simplifies the surface morphology properties of ZnO thin films. It has been established in previous research that roughness parameters based on conventional theories depend on the sampling interval of the particular measuring instrument used [317]. In addition, the fractal surface maintains the characteristics of continuity, non-differentiability, self-similar and self-affine. By definition, a fractal is a set for which the so-called fractal dimension (D_s), always exceeds the topological dimension. If the fractal dimension D_s = 2 [318, 319], it denotes a flat surface and an increasing value of ‘D_s’ represents an increasing surface roughness. The structure
function and variation methods are performed successfully with images containing a few hundred pixels and optimally describe the surface topography of ZnO thin films. Here, we have adopted the structure function method to analyze the fractal dimension of ZnO thin films. In this methodology, the fractal dimension is calculated from the least-square degeneration line using a log–log plot of structure function $S(\tau)$ vs a large vector ‘$\tau$’ [320]. The fractal dimension ‘$D_s$’ determines the relative amounts of the surface irregularities for different distance scales. The results of fractal dimension analysis are shown in Fig.5.5 (a & b).

![Fractal analysis of surface](image)

**Fig.5.5** Fractal analysis of surface (a) K doped ZnO, (b) K, Er codoped ZnO

Fractal dimension is calculated based on the intervals between consecutive wrinkles on the surface. The calculated fractal dimension value is 1.50 for K doped ZnO films and 1.394 for (K, Er) codoped ZnO films and it indicates lesser surface roughness and confirms the patterns formations. The codoped films fractal dimension values are decreased compared to doped films and it shows an increase of surface smoothness by the addition of Er in the K doped ZnO films.
5.3.3 Optical properties

A ZnO thin film is a transparent conductive thin film in the visible region, so it can be used as a window material and transparent electrode. Transmittance spectra of K doped and (K, Er) codoped ZnO thin films annealed at 450°C as a function of wavelength in the range of 300 – 850 nm are presented in Fig.5.6. All the films show high transmittance in the visible region and the observed average transmittance is ≤ 85%.

![Transmittance spectrum](image)

**Fig.5.6** Transmittance spectrum different K and Er concentrations.

The transmittance of the doped and codoped ZnO films peaks much about the crystallization quality. The energy gap and refractive index of semiconductors represent two fundamental physical aspects that characterize their optical and electronic properties. The optical energy gap (E_g) determines the threshold for absorption of photons in semiconductors. The absorption spectrum of K doped and (K, Er) codoped ZnO thin films are displayed in
Fig. 5.7. It is blue shifted with increase of Er concentration in K doped ZnO films. Fundamental absorption edge is observed at 365 nm for K doped ZnO films and at 360 nm for (K, Er) codoped ZnO films, which is correlated to the change of the optical band gap value. The optical band gap ($E_g$) can be determined from the absorption co-efficient ($\alpha$), which can be calculated from the transmittance spectra of doped and codoped ZnO films.

Near the absorption edge, $\alpha$ can be expressed as [321],

$$\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right)$$  \hspace{1cm} (19)

Where ‘$d$’ is the film thickness and ‘$T$’ is the transmittance. ZnO is a wide band gap semiconductor material with direct band gap. The optical band gap $E_g$ is given in equation (6) and the functional relationship between $(ahv)^2$ and photon energy for K doped and (K, Er) codoped ZnO are presented in Fig. 5.8.
The $E_g$ value can be obtained by extrapolating the linear portion to the zero absorption co-efficient. The observed band gap values are listed in Table 5.2.

### Table 5.2 Calculated optical constants.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Band Gap $(E_g)$ eV</th>
<th>Refractive Index</th>
<th>$E_U$ (meV)</th>
<th>$E_0$ (eV)</th>
<th>$E_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% K doped ZnO</td>
<td>3.306</td>
<td>1.56</td>
<td>30</td>
<td>3.33</td>
<td>7.75</td>
</tr>
<tr>
<td>2% K doped ZnO</td>
<td>3.300</td>
<td>1.62</td>
<td>27</td>
<td>3.31</td>
<td>8.97</td>
</tr>
<tr>
<td>3% K doped ZnO</td>
<td>3.281</td>
<td>1.69</td>
<td>26</td>
<td>3.30</td>
<td>16.78</td>
</tr>
<tr>
<td>1% K &amp; 1% Er codoped ZnO</td>
<td>3.361</td>
<td>1.66</td>
<td>43</td>
<td>3.32</td>
<td>7.55</td>
</tr>
<tr>
<td>1% K &amp; 2% Er codoped ZnO</td>
<td>3.350</td>
<td>1.31</td>
<td>47</td>
<td>3.34</td>
<td>9.81</td>
</tr>
<tr>
<td>1% K &amp; 3% Er codoped ZnO</td>
<td>3.339</td>
<td>1.54</td>
<td>50</td>
<td>3.35</td>
<td>14.21</td>
</tr>
</tbody>
</table>

From these observed energy gap values we infer two things. The absorption spectrum of pure ZnO is largely altered by the doping resulting in degenerated energy levels which causes the Fermi level to push above conduction band edge. This shift is known as doping induced band filling called Burstein Moss shift and so the band gap increases from doped to
codoped thin films. The second one is the decrease of band gap values with the increase percentage of K doping in ZnO and percentage of Er codoping in K doped ZnO. It is caused by the increase in the band tail states that arise due to increase in the doping level resulting in the shrinkage of band gap. Such a decrease in the band gap can also be explained by the formation of charged defect centers with the metal additives thereby enhancing the conductivity. Refractive index of the semiconductor is a measure of its transparency to incident spectral radiation. Assessment of the refractive index of the optical material is notably important for the applications in integrated optic devices [322].

The refractive index (n) and extinction co-efficient (k) of thin films are calculated from the expressions [323] given below,

\[
n = \left(\frac{1+R}{1-R}\right) + \sqrt{\left(\frac{4R}{(1-R)^2} - k^2\right)} \tag{20}
\]

\[
k = \frac{\alpha \lambda}{4\pi} \tag{21}
\]

The plot of refractive index (n) and extinction co-efficient (k) for the K doped and (K, Er) codoped ZnO thin films are shown in Fig.5.9.

![Fig.5.9 Refractive index and Extinction co-efficient of doped and codoped ZnO films.](image-url)
From the graph, it is found that the refractive index of the K doped and (K, Er) codoped ZnO films decreases when compared to pure ZnO \( (n = 2) \). For instance at 360 nm, the refractive index values range from 1.31 – 1.69 for the doped and codoped ZnO films. Lv et al., [324] gave an explanation for the decreases in the refractive index in terms of voids on the surface and Li et al. [325] suggested that it is due to the increase in the carrier concentration which is an indication that most of K ions occupy the interstitial positions as donors rather than occupying the substitutional sites replacing the Zn ions, as acceptors.

In our study, the SEM and AFM images reveal that the voids are not present on the surface of the films. Hence the observed decrease of the refractive index with the increases of doping level is attributed mainly due to the increase in carrier concentration. The extinction co-efficient of all the films initially decrease in the absorption region (UV) and then show an increasing trend with the increase of wavelength. The observed extinction co-efficient values are in the range 0.02 – 0.03 and this very low value indicates the smoothness of the surface and homogeneity of the films.

Dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and also in designing the devices for spectral dispersion. The result of refractive index dispersion below the interband absorption edge corresponds to the fundamental electronic excitation spectrum. The dispersion parameters of various materials are investigated by using the model available in the literature [326–329]. This model describes the dielectric response for transitions below the optical gap. It plays an important role in determining the behavior of the refractive index. The refractive index of K doped and (K, Er) codoped ZnO films can be analyzed by single oscillator model proposed by Wemple-DiDomenico (WDD) [330, 331]. The dispersion relation of refractive index is,
\[ n^2 = 1 + \frac{E_d E_0}{E_0^2 - (h\nu)^2} \]  \hspace{1cm} (22)

where ‘\( n \)’ is the refractive index, ‘\( h \)’ is Planck’s constant, ‘\( \nu \)’ is the frequency, ‘\( h\nu \)’ is the photon energy, ‘\( E_0 \)’ is the average excitation energy for electronic transitions. ‘\( E_d \)’ is the dispersion energy, which is a measure of the strength of interband optical transitions and can be considered as a parameter having very close relation with the charge distribution within the unit cell through chemical bonding. These parameters can be easily obtained by plotting of \((n^2-1)^{-1}\) versus \((h\nu)^2\).

The dependence of \((n^2-1)^{-1}\) versus \((h\nu)^2\) is given in Fig.5.10. The ‘\( E_d \)’ and ‘\( E_0 \)’ values are calculated from the slope \((E_dE_0)^{-1}\) and intercept \((E_0/E_d)\) of Fig.5.10. The calculated parameters are listed in Table 5.2. The calculated values ‘\( E_0 \)’ and ‘\( E_d \)’ increases upon increasing the K and Er concentration.

![Plot of \((n^2-1)^{-1}\) versus \((h\nu)^2\) of doped and codoped ZnO films](image-url)
It is inferred that the excitation energy for electronic transitions increases and it confirms the interband formation between the valence and conduction band simultaneously increases the strength of the interband optical transitions. Using the obtained values of refractive index and extinction co-efficient, the real and imaginary parts of the dielectric constant are calculated from the following expressions [321],

\[ \varepsilon_r = n^2 - k^2 \]  
\[ \varepsilon_i = 2nk \]

The variation of \( \varepsilon_r \) and \( \varepsilon_i \) with respect to the wavelength for doped and undoped ZnO films are shown in the Fig.5.11. The plots of \( \varepsilon_r \) are similar to that of refractive index because of the smaller values of ‘k’. The values of \( \varepsilon_i \) depend mainly on the ‘k’ values and it initially decreases and then increases. The real and imaginary dielectric constant values are in the range 2 - 3 and 0.04–0.07 respectively for the thin films.

Fig.5.11 Real and imaginary part of dielectric constants with different K and Er concentrations.
Urbach band tail calculation can be performed to confirm the change in bandgap energy and the interband formation in Er codoping. The optical band structure and optical transitions are affected by the width of the localized states available in the bandgap. This width is called the Urbach tail, which is generally related to a similar exponential tail for the density of states. The Urbach tail of the films can be determined from the following relation [332],

\[
\alpha = \alpha_0 \exp \left( \frac{h \nu}{E_U} \right)
\]

where \((\alpha_0)\) is a constant, \((h \nu)\) is the photon energy and ‘\(E_U\)’ is the Urbach energy from which the width of the band tail as well as the width of the localized states can be estimated. The plot of \(\ln (\alpha)\) versus photon energy is shown in Fig.5.12 which should be linear. Urbach energy is obtained from the inverse of the slope of Fig.5.12 and is listed in Table 5.2. It increases with the increase of Er concentration and confirms the increased width of the localized states.

![Fig.5.12 ln (α) as a function of photon energy.](image)
5.4 Conclusions

The as prepared K doped and (K, Er) codoped ZnO films whose surface morphology and optical properties are deeply analyzed. The X-ray diffraction analysis confirms the exceptional crystalline quality of the doped films without any degradation of the wurtzite structure of ZnO. The addition of Er codopant into K doped ZnO films reduces the crystalline quality without any secondary phase formation. In both Scherrer method and AFM studies, a decrease in particle size is observed for doped to codoped films due to the presence of Zn, defects. The presence of doping elements is confirmed from their respective peaks in the EDX spectra. The wrinkle structures are observed on the surface of the doped and codoped ZnO films from SEM and AFM images. The effect of Er concentration has increased the width and distance between the two wrinkle structures. The formation of wrinkle pattern is also confirmed from the fractal dimension analysis and the calculated value is 1.5 for K doped ZnO films and 1.39 for codoped films. A blue shift of absorption edge and an increase of bandgap after codoping is explained by Burstein – Moss effect. Both films show decreased refractive index and it is explained by the increasing of carrier concentration. The width of interband localized states are calculated from Urbach tail energy.