4. INFLUENCE OF K-DOPING ON THE OPTICAL PROPERTIES OF ZnO THIN FILMS

4.1 INTRODUCTION

ZnO thin films have been prepared by different techniques such as pulsed laser deposition [89 and 90], Magnetron sputtering [91 and 92], Molecular beam epitaxy [93] and Sol-gel method [94]. Many works have been reported on the doping of ZnO with various elements. The synthesis of potassium doped ZnO nano films by sol – gel dip-coating method has been reported by Xu et al. [95-97] and they have studied the optical properties and the evolution behavior under different annealing temperatures. But the preparation of K-doped ZnO thin films using the chemical method such as the chemical bath deposition (CBD) method has not been reported yet. The CBD technique has many advantages such as simplicity, large area films with good uniformity, low cost etc. Moreover, so far, there are no reports on the optical constants of the K-doped ZnO thin films. It is known that measured parameter of material properties may vary depending upon the different approaches of synthesis and different methods of fabrication of thin films. So, the thin films prepared by CBD method may lead to tailoring of the materials properties.

Hence, the focus is to synthesize potassium doped zinc oxide thin films by chemical bath deposition technique and to study effect of K-doping on the surface morphology and optical properties such as optical energy band gap, refractive index, extinction coefficient, dielectric constant, absorption coefficient and photoluminescence of ZnO thin films. The synthesized materials were subjected to various characterizations such as X–ray diffraction analysis (XRD), FESEM, energy dispersive X ray (EDAX) analysis, optical and photoluminescence (PL) studies and the results have been discussed in detail.
4.2 RESULTS AND DISCUSSION

4.2.1 Powder X-ray diffraction studies

XRD patterns of K-doped and undoped ZnO thin films were obtained using Cu-Kα1 radiation for the wavelength of 1.5406 Å at the scan rate 4°/min and XRD patterns are shown in Figure. 4.1. All the films are polycrystalline and exhibit the hexagonal wurzite structures which are in very good agreement with JCPDS card number PDF # 891397, PDF # 890510. No other phases are observed in the XRD pattern.

![XRD patterns of K-doped and undoped ZnO thin films](image)

Figure. 4.1: XRD patterns of (a) 1%, (b) 2%, (c) 4% K-doped and (d) undoped ZnO thin films.

In the XRD patterns, there are three prominent peaks of (100), (002) and (101) planes and this reveals that the thin films have hexagonal wurzite structure. The (100) peak is very strong for 2% doped thin film. The angle of diffraction of (002) plane for the undoped ZnO thin film is (34.30°), and for 1%, 2%, and 4% doped films are 34.39°, (34.45°) and (34.35°) respectively. After doping, the (002) peak shifts towards the higher angle side and this suggests that the lattice constant of the crystal decreases which may be due to the occupation of some K atoms on the Zn site [98].
4.2.2 Surface morphology and EDAX

The surface morphologies of the undoped and K-doped ZnO thin films were studied by field emission scanning electron microscope (FESEM) and the SEM micrographs are shown in Figure. 4.2. The SEM images show that the doped thin films comprise single crystalline nano sized grains whereas the surface of undoped ZnO thin film exhibits a rod like structure. The K-doped ZnO thin films have small grains of almost uniform shape and the surface of these thin films is very smooth.

Figure 4.2: Surface morphology of (a) 1%, (b) 2%, (c) 4% K-doped and (d) undoped ZnO films.

From the micrograph, it is observed that undoped ZnO film exhibits in the form of rods but the doped ZnO films exist in circular shape. This change in the shape is due to the presence of the doping concentrations [99-107]. The grain size of the doped samples measured from the SEM images ranges from 6 nm to 11 nm. The element compositions of the undoped and all the K-doped ZnO films were analyzed by energy dispersive X ray (EDAX) analysis and are shown in Figure. 4.3.
The presence of the constituent elements for the undoped and K-doped ZnO crystal was confirmed by the occurrence of their respective peaks. In Figure 4.3 (a, b and c), the sharp peaks that lies between 1.5 and 2 eV corresponds to Si (Substrate). This peak is indicated in the EDAX of undoped ZnO.

4.2.3 Optical studies

Transmission spectra of the undoped and K-doped ZnO thin films as a function of wavelength in the range 300 – 800 nm are shown in Figure. 4.4. The transmission spectra have 40 to 50% of transmittance in the visible region for the thin films. The transmittance of the thin films shows variation with increasing doping concentrations of ZnO thin film.
The energy gap and the 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 photon in semiconductor. The energy gap of all the films is determined from the absorption coefficient ($\alpha$) which can be calculated from the transmittance ($T$) of the doped ZnO thin films. The absorption coefficient ($\alpha$) is calculated from equation 4.1.

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

where, $d$ is film thickness. The thickness of the undoped and 1%, 2% and 4% doped ZnO films are found to be 1880, 4180, 3180 and 2680 nm respectively. The absorption edge was analyzed by the following equation [108].

Figure 4.4: Optical transmittance spectrum of undoped and K-doped ZnO thin films.
Figure 4.5: Plot of $(\alpha h\vartheta)^2$ vs photon energy for the undoped and K-doped ZnO thin films.

$$(\alpha h\vartheta)^2 = A (h\vartheta - E_g)$$  \hspace{1cm} (4.2)

where $A$ is a constant, $h\vartheta$ is the incident photon energy and $E_g$ is the optical energy band gap. Based on the equation 4.2, the plots of $(\alpha h\vartheta)^2$ as a function of incident photon energy ($h\vartheta$) were obtained for the undoped and doped thin films and are shown in Figure 4.5. The linear portions of these plots are extrapolated to meet the energy axis and the energy value at $(\alpha h\vartheta)^2 = 0$ gives the values of the energy gap $E_g$ for the thin films. The $E_g$ values are 3.8, 3.94, 3.89 and 3.86 eV for the undoped and 1%, 2%, and 4% of K-doped ZnO thin films respectively. From these energy gap values two points are inferred. One is from the undoped to doped thin film, it is observed that $E_g$ value increases. The second is with the increase in the doping concentration from 1 % to 4 %, $E_g$ value decreases.

The first one can be explained as follows. It is known that the absorption spectrum of pure semiconductor is largely altered by doping resulting in degenerate energy levels which causes the Fermi level to push above
conduction band edge. This shift is known as doping induced band-filling called as Burstein - Moss shift and so the band gap increases from the undoped to doped thin film. The second one 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. Xu et al. [97] have also reported that for the K-doped ZnO thin films (1 %, 2 % and 3 % doping) prepared by the sol-gel dip coating method on the glass substrate, the $E_g$ value initially increases and then slightly decreases as the doping level is increased. In our study, the band gap reduces from 3.94 eV to 3.86 eV for the different doping concentrations, which is due to increase in the grain size [109 and 110].

### 4.2.4 Determination of optical constants

The optical constants of materials are important parameters for the designing of the optical devices. The refractive index of the semiconductor is a measure of its transparency to incident spectral radiation. The assessment of the refractive index of optical materials is notably important for the applications in integrated optic devices [111].

The refractive index (n) and extinction coefficient (k) of the thin films were calculated from the equation 4.3 and 4.4 [112] given below.

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

\[
k = \frac{\alpha \lambda}{4\pi}
\]
Figure 4.6: Refractive index (n) and extinction coefficient (k) for (a) 1%, (b) 2%, (c) 4% K doped and (d) undoped ZnO thin films.

where, R is reflectance, n is refractive index, k is extinction coefficient, α is absorption coefficient and λ is wavelength. The plot of refractive index (n) and extinction coefficient (k) for the K-doped and undoped ZnO films are shown in Figure 4.6. For the undoped thin film, the refractive index remains almost constant around 2 for the entire spectral range. From the graph, it is found that the refractive index of all the K-doped thin films decreases with increase in the wavelength showing the same trend. The n values range from 2 to 3.3 for the thin films. When the refractive index values for various doping levels are compared, the refractive index values are found to decrease with the increase of the doping content. For instance, for 400 nm, the values of the refractive index are 3.26, 3.05 and 2.6 for the 1%, 2% and 4% concentrations respectively. Liu et al. [113] explained the reason for the decrease in the refractive index as due to voids on the surface. For the decrease of the refractive index Li et al. [114] suggested that it is due to the
increase in the carrier concentration which is the 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 photoluminescence spectra (shown in the later section) of all the thin films show that the interstitial defects are very low and the level of defects also remains the same indicating that the interstitial donors do not vary with the increase in the doping. So, the observed decrease of the refractive index with increase in the doping level is not attributed to the increase in the carrier concentration. So, in our study, the decrease of the refractive index is due to the voids in the ZnO thin films. The variation of refractive index with K-doping suggests that the optical properties can be controlled by changing the dopant level and this is important for the optoelectronic applications.

The extinction coefficient (k) of all the thin films initially decreases in the absorption region (UV) and then shows an increasing trend with the increase in wavelength. In the range from 400 nm to 800 nm, as the K-doping is increased, the k value of the thin films increases. For instance, in the case of 400 nm, the k values are 0.0088, 0.0116 and 0.0135 respectively for 1%, 2% and 4% K-doping. The k values vary from 0.001 to 0.0163 for the thin films. For the undoped thin film, the k value is 0.001. The extinction coefficient of all the thin films is of very low order for the entire studied wavelength. This very low value of k indicates the smoothness on the surface and homogeneity of the films [115]. Using the obtained values of refractive index and extinction coefficient, the real and imaginary parts of the dielectric constant are calculated by the following equations 4.5 and 4.6 [116].

The variation of $\varepsilon_r$ (real part of dielectric constant) and $\varepsilon_i$ (imaginary part of dielectric constant) with respect to wavelength for the doped and undoped ZnO films are shown in Figure. 4.7. 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 so $\varepsilon_i$ initially decreases and then increases. The real and imaginary dielectric constant values are in the range 3.5 - 11 and 0.055 – 0.085 respectively for the thin films.
Figure. 4.7: Real and imaginary parts of dielectric constant for (a) 1%, (b) 2%, (c) 4% K-doped and (d) undoped ZnO thin films.

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

The variation of absorption coefficient as a function of wavelength in the range 400 nm - 800 nm is shown in Figure. 4.8 for all the thin films. For all the doped thin films, the variation absorption coefficients with the increase in the wavelength show the similar trend. As the doping concentration is increased, the value of absorption coefficient increases.
Figure. 4.8: Absorption coefficient as a function of wavelength for the undoped and K doped ZnO thin films.

For 400 nm, the values of absorption coefficient are 2.75x10^5 cm\(^{-1}\), 3.7x10^5 cm\(^{-1}\) and 4.26x10^5 cm\(^{-1}\) respectively for 1%, 2% and 4% K-doping. For the undoped thin film, the absorption coefficient slightly decreases in the lower wavelength and then it is almost the same around 3.25x10^5 cm\(^{-1}\). All the thin films show the high absorption coefficient greater than 3.25x10^5 cm\(^{-1}\) in the absorption region. Hence, these thin films are suitable as absorber layers in solar cell.

4.2.5 Photoluminescence studies

The photoluminescence study is a powerful tool for investigating the effect of doping in nanostructures. The photoluminescence (PL) spectra of undoped and K-doped ZnO thin films are shown in Figure 4.9. The PL spectra of the thin films show the UV emission and blue emission (deep level emissions) as previously reported by Xu et al. [97] who studied the PL spectra of the K doped ZnO thin film prepared by dip-coating method on the glass substrate.
In this work, the PL spectra of the doped and undoped films show that the UV emission peaks centered at 393 nm and 389 nm respectively. This change in the shift for the doped films is due to the presence of doping concentrations. When doped, the energy gap has increased compared to the undoped thin films and so the doped films show a emission at lower wavelength (λ) compared to undoped. The two weak blue emissions (deep level emissions) are in the range from 465-487 nm for all the films. The UV emission originates from free exciton recombination [117 and 118] and the blue emission is attributed to the presence of defects such as Zn interstitial. Different defects are different centers of radiative recombination and are related to different transitions. According to Xu et al. [97] and Zheng et al. [119 and 120] the blue emission is due to the Zn interstitial defects.

It is observed from the PL spectra of the doped films that the UV emission intensity decreases from the undoped to 1 % doped thin film. Then it increases from 1 % doped thin film to 2 % doped followed by the decrease for 4 % doped thin films. The variation in the UV intensity may be due to the structural defects as the intensity of the luminescence depends on the nature
of the exposed surface of the material. The intensity of the blue emission is very low for all the doped thin films compared to that of UV emission which indicates that the Zn interstitial defects are very low for all the doped thin films. The intensity of the blue emission are almost similar for all the doping levels suggesting that the level of Zn interstitial defects do not vary significantly with the rise in the K-doping concentration.

4.3 CONCLUSION

Potassium doped and undoped zinc oxide thin films with different doping concentrations were synthesized using chemical bath deposition technique. The powder X-ray diffraction analysis confirms the crystalline quality of the doped ZnO nano films without any degradation of the wurtzite structure of the zinc oxide. The grain size of the doped thin films is in the range from 6 nm to 11 nm as measured from FESEM analysis. The optical studies reveal that the band gap of K doped ZnO thin films decreases with the rise in the doping level with grain sizes and the values are 3.94, 3.89 and 3.86 eV respectively for 1%, 2% and 4% concentrations. Various optical investigations such as refractive index, extinction coefficient, dielectric constant and absorption coefficient were obtained from the transmittance studies and the optical constants confirms its suitability for the optical device fabrication. All the thin films show high absorption coefficient greater than $3.25 \times 10^5$ cm$^{-1}$ in the absorption region. The PL spectra of the doped thin films for various concentrations contains two emission peaks namely strong UV emission and weak blue emission. The intensity of the blue emission is very low for all the doped thin films suggesting the presence of low Zn interstitial defects. All these studies reveal that the potassium doped ZnO nano films are suitable for the fabrication of optoelectronic and various sensing devices.