Determination the dispersion parameters and urbach tail of ZnO and ZnO:Co thin films prepared by The chemical Spray pyrolysis technique

Zain A.Muhammad
Al-Mustansiriyah University, College of Education, Physics Department

Abstract
Undoped and Co doped ZnO samples with two different percentage of Co content (1 %, 5 % ) were prepared by a chemical Spray pyrolysis technique. Transmission and absorptance spectra have been recorded in the wavelength range (300-900) nm. From The refractive index data for infinite wavelength we have calculated single oscillator energy and dispersion energy proposed by Wemple -DiDomenico model which was found to be decrease from (2.42 - 1.47) eV as the doping percentage increase. the optical energy gap which was found according to Tauc model were (3.17-3.29) eV. The obtained values for Urbach energies was found increasing from (0.757-0.902) eV upon doping.

Keywords: (ZnO-Co) thin films, Chemical Spray Pyrolysis, dispersion parameters
والتي وجدت أن قيمتها تتناقص من $(2.42 - 1.47)$ بزيادة نسبة التشويب. تم حساب قيمة فجوة الطاقة طبقا لنموذج Tauc وكانت قيمتها تتراوح ما بين $(3.29 - 3.17)$ eV، كما تم حساب طاقة اورباخ ووجد أن قيمتها تزداد نتيجة التشويب $(0.902 - 0.757)$ eV.

**NTRODUCTION**

ZnO is one of the few metal oxides which can be used as a transparent conducting oxide. It has some advantages over other possible materials such as In$_2$O$_3$, Cd$_2$SnO$_4$ or SnO$_2$ due to its unique combination of interesting properties: non-toxicity, good electrical, optical and piezoelectric behavior, and its low cost. [1] It is used as window layers in solar cells, field emitters, ultraviolet laser emission, photodetectors, piezoelectricity, bio-sensors, short wavelength light emitting diode and information technology [2]. The device application of micro and nanostructure of ZnO is one of the major focuses among researchers to diminish the size of the device in order to achieve higher speeds in its electrical transport and also to study the effect of confinement on optical properties [3]. The interest in doping ZnO is to explore the possibility of tailoring its electrical, magnetic and optical properties. [4] ZnO films have been deposited using many methods of deposition techniques such as low temperature chemical bath method, magnetron sputtering, thermal evaporation, and chemical spray pyrolysis. [5], pulsed laser deposition. [6], hydrothermal method. [7], sol-gel [8], pulsed enhanced chemical vapor deposition. [9], reactive plasma deposition [10], electrochemical deposition [11], RF- magnetron sputtering. [12]. In the present investigation, some dispersion parameters of ZnO films are studied as a function of cobalt concentration.

**EXPERIMENTAL DETAIL**

The spray pyrolysis was done with a laboratory designed glass atomizer, which has an output nozzle of 1mm in diameter. The volume of the solution used for the deposition was 100 ml. The starting solution was sprayed onto a preheated glass slide, using compressed air, the solution flow rate was 10ml/min, the nozzle to substrate distance was 29cm. The process involve spraying cycle of 10 sec, followed by 2min wait to avoid a too strong cooling of the substrate. The substrate was mounted on a heater, their temperature was controlled with a thermocouple (Chromel- alamal, the optimized temperature of the substrate was kept on 400°C. An homogeneous was prepared by dissolving ZnCl$_2$ of 0.1 M in distilled water. One to two
drops of HCl was added to prevent the formation of zinc hydroxide. Similarly, aqueous solution of CoCl$_2$.6H$_2$O was used to obtain Co doped films. the Cobalt concentration was (1.5%) weight. After deposition, films are allowed to cool at ambient temperature slowly. The deposited films are stable at room temperature, well adhered to the substrate and free from pin hole. Thickness measurement for the as deposited thin films were carried by weighting method and was found around 300nm. Optical measurement were recorded using Double beam spectrophotometer in the wavelength range (300-900)nm.

**Results and Discussion**

The investigation of the spectrum of the absorption coefficient near the fundamental edge was calculated using the following relation [13]

$$\alpha = \frac{2.303 A}{d} \quad ...... \quad (1)$$

Where (A) is the absorption and (d) is the film thickness. Which provides us with a valuable information about the energy band structure of the material and is shown in Fig. (1). the relationship between the absorption coefficient and the photon energy is given by Tauc relation[14].

$$\alpha h\nu = B(h\nu - E_{opt})^n \quad ...... \quad (2)$$

where (B) is an energy independent constant, $E_{opt}$ is the optical band gap, $h\nu$ is the photon energy and (n) is an index that characterizes the optical absorption process depending on the kind of transition .Since ZnO thin films are direct transition type than an index (n) =1/2, the optical energy gap can be estimated by plotting ($\alpha h\nu$)$^2$ versus $h\nu$, then extrapolating the straight line part of the plot to the photon energy axis, Figures (2),(3) and (4) show the variation of the optical energy gap for pure and Co doped ZnO with different amount of Co content. As the Co content increased from (0, 5%) we obtained optical energy gap of 3.17,3.328, 3.29 eV, respectively, the observed increase in the band gap is explaind on the basis of quantum size effects.

The absorption coefficient near the fundamental absorption edge is exponentially dependent on the incident photon energy and obeys the empirical Urbach relation. The Urbach energy($E_U$)(which is considered as a parameter that includes all possible defects) is usually used to describe the width of the localized states in the band gap (but not their positions).The Urbach energy can be calculated by the following relation [15].

$$\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_U} \right) \quad .......... \quad (3)$$
Taking the natural logarithm of equation (3) gives

$$\ln(\alpha) = \ln(\alpha_o) + \frac{h\nu}{E_U} \quad \text{(4)}$$

where \( (\alpha_o) \) is constant, \( E_U \) is the Urbach energy. Thus the plot of \( \ln(\alpha) \) versus photon energy should be linear. From Fig.(5) we can determine the Urbach energy which equal to the inverse of the slope of straight line. The obtained \( E_U \) values are shown in Table (1). Urbach energy values of the films increase with increasing Co content. The increase in \( E_U \) is attributed to the increase of disorder of the material occurred by doping. The dispersion of refractive index for ZnO:Co and ZnO films was analyzed using the concept of the single oscillator and can be expressed by Wemple and Di-Domenico (WD) model[16]. In this model, the refractive index data have been examined below the inter-band absorption edge, where the normal dispersion of the optical dielectric constant of the material and the energy dependence of refractive index satisfy the relation[17],

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \quad \text{(5)}$$

Equation (5) can be written as

$$(n^2 - 1)^{-1} = \frac{E_d}{E_o} - \frac{1}{E_o E_d} (h\nu)^2 \quad \text{(6)}$$

where \( E_o \) is the average oscillator energy (an average of the optical band gap) and \( E_d \) is the dispersion energy parameter of the material that measures the average strength of inter-band optical transitions and can be considered as a parameter having very close relation with the charge distribution within unit cell and therefore with the chemical bonding[16]. Plotting of \((n^2 - 1)^{-1}\) against \((h\nu)^2\) as shown in Fig. (6) allows us to determine the oscillator parameters, by fitting a linear function to the data, \( E_o \) and \( E_d \) can be determined from the intercept,

\((E_o / E_d)\) and the slope \((1/E_o E_d)\), the dependence of single effective oscillator parameters on Co is shown in Table (1). The static refractive index \( n_0 \) is evaluated using this equation \( n_0^2 = n^2 (h\nu = 0) = 1 + E_o / E_d \), and the value of the infinite wavelength dielectric constant given by \( \varepsilon_0 = n_0^2 \), their values show in Table (1). The moments of optical dispersion spectra \( M_{-1} \) and \( M_{-3} \), can be evaluated using the relations[18]

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad \text{and} \quad E_d^2 = \frac{M_{-1}}{M_{-3}} \quad \text{...............(6)}$$
The obtained $M_{-1}$ and $M_{-3}$ moments changes with dopants. The evaluated values of $M_{-1}$ vary from 4.88 to 1.16 (dimensionless) and $M_{-3}$ lies between 0.53 and 0.89 (eV)$^{-2}$ as shown in Table 1.

Table (1): The optical parameters of Co doped ZnO and ZnO thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{opt}$ (eV)</th>
<th>$E_0$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$E_U$ (eV)</th>
<th>$\varepsilon_0$</th>
<th>$n_0$</th>
<th>$M_{-1}$ (eV)$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>3.17</td>
<td>3.02</td>
<td>14.74</td>
<td>0.757</td>
<td>5.88</td>
<td>2.42</td>
<td>4.88</td>
</tr>
<tr>
<td>ZnO:1%Co</td>
<td>3.27</td>
<td>3.27</td>
<td>6.40</td>
<td>0.791</td>
<td>2.95</td>
<td>1.71</td>
<td>1.95</td>
</tr>
<tr>
<td>ZnO:5%Co</td>
<td>3.29</td>
<td>3.60</td>
<td>4.19</td>
<td>0.902</td>
<td>2.16</td>
<td>1.47</td>
<td>1.66</td>
</tr>
</tbody>
</table>

Conclusions:

Pure and Co doped ZnO thin films were deposited onto preheated glass substrate by spray pyrolysis at a temperature 400°C. The results show remarkable shifts in the values of the infinite wavelength refractive index, energy band gap, urbach energy, spectra moments and the infinite wavelength dielectric constant between the ZnO and Co doped ZnO samples. These constitute important factors in possible areas of application of Co doped ZnO thin films.

References


Fig.(1) $\alpha$ as a function of $h\nu$.

Fig.(2) $(\alpha h\nu)^2$ versus photon energy for pure ZnO.
Fig. (3) \((\alpha h\nu)^2\) versus photon energy for ZnO:1\%Co.

Fig. (4) \((\alpha h\nu)^2\) versus photon energy for ZnO:5\%Co.
\[ y \text{(pure)} = 1.32x + 8.7247 \]
\[ y(1\%) = 1.2631x + 7.797 \]
\[ y(5\%) = 1.1082x + 7.7181 \]

**Fig.(5) \( \ln(\alpha) \) as a function of \( h\nu \).**

\[ y(5\%) = -0.0663x + 0.8593 \quad \text{R}^2 = 0.9885 \]
\[ y(1\%) = -0.0477x + 0.5112 \quad \text{R}^2 = 0.9679 \]
\[ y \text{(pure)} = -0.0224x + 0.2053 \quad \text{R}^2 = 0.9868 \]

**Fig.(6) \((n^2-1)^{-1}\) as a function of \((h\nu)^2\)**