Indium doped ZnO Urbach energy and dispersion parameters of thin films

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Abstract
The characterization of ZnO and ZnO:In thin films were confirmed by spray pyrolysis technique. The films were deposited onto glass substrate at a temperature of 450°C. Optical absorption measurements were also studied by UV-VIS technique in the wavelength range 300-900 nm which was used to calculate the optical constants. The changes in dispersion and Urbach parameters were investigated as a function of In content. The optical energy gap was decreased and the wide band tails were increased in width from 616 to 844 eV as the In content increased from 0wt.% to 3wt.% The single–oscillator parameters were determined also the change in dispersion was investigated before and after doping.

Key words
Spray pyrolysis, transparent conductor, ZnO, Dispersion Parameters.

Introduction
Zinc oxide (ZnO) is one of the most multifunctional semiconductor material used in different areas for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) region [1]. Furthermore, it is one of the most potential materials for being used as a transparent conducting oxide (TCO) because of its high...
electrical conductivity and high transmission in the visible region [2]. Doping ZnO with selective elements can recognize appropriate optical, electrical, and magnetic properties, which is important for their practical application.

ZnO can be doped with a wide variety of ions to meet the demands of several application fields. Among the various dopants for ZnO films always group III elements such as Al [3], In [4], and Ga [5] are usually used as Dopants, and In have been determined to be the most suitable materials. In particular, indium-doped ZnO (IZO) nanostructures are regarded as a promising candidate for transparent conductors [6], gas sensors [7], and photo detectors [8], due to their good physical properties. It is well known that the physical properties of a film are strictly controlled by the deposition conditions, even though in the case of spray pyrolysis the solution conditions are very important as well [9].

In the present study, pure and In-doped ZnO thin films were prepared by spray pyrolysis technique, it is simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings [10]. Therefore, the invention provides very cheap and simple method, compared to alternative methods, for manufacturing zinc oxide films. The optical characterization of ZnO films were investigated for a better understanding of its physical properties.

Experimental details
Thin films of zinc oxide have been prepared by chemical pyrolysis method. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at temperature of 450°C, the starting solution was achieved by an aqueous solutions of 0.1M Zn (CH₃COO)₂·2H₂O and 0.1M InCl₃ which was used as a doping agent with a concentration of 1wt.% and 3wt.%. These materials were diluted with de-ionized water and ethanol formed the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 10 s and the spray interval (3min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 10⁵ Nm⁻², distance between nozzle and substrate was about 29 cm ±1 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 0.3μm. Optical absorption spectra were recorded in the wavelength range (300-900nm) using UV-visible spectrophotometer (Shimadzu Company Japan) in order to investigate the effect of Indium doping on the parameters under investigation.

Results and discussion
Study of the optical absorption for the investigated films, particularly the absorption edge has proved to be very useful for elucidation of the electronic structure of these materials. The optical absorption spectra of the tested films as a function of doping concentration are shown in Fig.1. These spectra indicate that the films have low absorbance in the visible and near infrared regions. However, absorbance in the ultraviolet region is high. It has been observed that the maximum absorption peak shifts towards the longer wavelength with increasing the InCl₃ concentration. This suggests the decrease in the band gap which is an indication that the introductions of shallow donor level due to doping of indium, and it have been created in the region between the conduction and the valance band.
The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [11], the absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient on photon energy $\hbar \nu$ takes the following form:

$$\alpha = \alpha_0 \exp \left( \frac{\hbar \nu}{E_U} \right)$$  \hspace{1cm} (1)

where $\alpha_0$ is a constant and $E_U$ is interpreted as the width of the tails of localized states in the gap region. To evaluate the values of $\alpha_0$ and $E_U$, the plot of $\alpha$ in logarithmic scale as a function of photon energy $\hbar \nu$ is shown in Fig.2. The reciprocal of the slope of each line yields the magnitude of $E_U$ and its values for different In concentrations of the films are listed in the Table 1. It is clear that In dopant increases the width of the tail of localized states and decreases the energy gap of ZnO films. Using Eq.(1) at a constant temperature, a graph representing $\ln(\alpha)$ on the y-axis and $\hbar \nu$ on the x-axis in the range of the Urbach tail would yield a straight line with a slope equal to $\sigma/kT$, where $\sigma$, known as the steepness parameter, is a temperature-dependent parameter characterizing the broadening of the absorption edge due to electron–phonon or exciton–phonon interactions [12,13].

$$\sigma = \frac{\alpha \cdot n \cdot c}{4 \cdot \pi}$$  \hspace{1cm} (2)

where $c$ is the velocity of light. Fig. 3 shows the conductivity values of the ZnO and ZnO:In films at room temperature. It was observed that the optical conductivity increases as the percentage of In in the PVA increase to 3wt.%.
Fig. 3: Optical conductivity versus wavelength.

The refractive index dispersion data were evaluated according to the single-effective-oscillator model [15, 16] using the following relation:

\[ n^2 = 1 + \frac{E_d E_o}{E_o^2 - E_d^2} \]  

(3)

where \( E_d \) and \( E_o \) are single oscillator constants, \( E_o \) is the energy of the effective dispersion oscillator, \( E_d \) the so-called dispersion energy, which measures the intensity of the inter band optical transitions. The oscillator energy \( E_o \) is an average of the optical band gap, \( E_{opt} \), can be obtained from the Wemple–Didomenico model. This model describes the dielectric response for transitions below the optical gap. Experimental verification of Eq. (3) can be obtained by plotting \( (n^2 - 1)^{-1} \) versus \( (h\nu)^2 \) as illustrated in Fig. 4 which yields a straight line for normal behaviour having the slope \((E_d E_o)^{-1}\) and the intercept with the vertical axis equal to \( E_o/E_d \). \( E_o \) and \( E_d \) values were determined from the slope, \((E_d E_o)^{-1}\) and intercept \((E_o/E_d)\) on the vertical axis. \( E_o \) values decreased as the optical band gap decreases. According to the single-oscillator model, the single oscillator parameters \( E_o \) and \( E_d \) are related to the imaginary part of the complex dielectric constant, the moments of the imaginary part of the optical spectrum \( M_{-1} \) and \( M_{-3} \) moments can be derived from the following relations [17]:

\[ E_o^2 = \frac{M_{-1}}{M_{-3}} \]  

(4)

\[ E_d^2 = \frac{M_{3} - 1}{M_{-3}} \]  

(5)

The values obtained for the dispersion parameters \( E_o, E_d, M_{-1} \) and \( M_{-3} \) are listed in Table 1. For the definition of the dependence of the refractive index \( n \) on the light wavelength \( (\lambda) \), the single-term Sellmeier relation can be used [18]:

\[ n^2(\lambda) - 1 = S_o \lambda_o^2 / 1 - (\lambda_o/\lambda)^2 \]  

(6)

where \( \lambda_o \) is the average oscillator position and \( S_o \) is the average oscillator strength. The parameters \( S_o \) and \( \lambda_o \) in Eq.(6) can be obtained experimentally by plotting \((n^2 - 1)^{-1}\) against \( \lambda^{-2} \). From Fig.5, the slope of the resulting straight line gives \( 1/S_o \), and the infinite-wavelength intercept gives \( 1/S_o \lambda_o^2 \). The calculated values of \( S_o \) and \( \lambda \) is shown in Table 1. \( E_o \) is an average energy gap and can be related to the optical band gap \( E_g \) in close approximation \( E_o \approx 2 E_g \), the results shows in Table 1 a decrease in band gap which may be attributed to the presence of unstructured defects, that increase the density of localized states in the band gap and consequently decrease the energy gap [19-21].
Table 1: The optical parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$n(o)$</th>
<th>$\varepsilon_\infty$</th>
<th>$S_o \times 10^{13}$ m$^2$</th>
<th>$\omega$</th>
<th>$\Delta o$</th>
<th>$M_1$ eV$^{-2}$</th>
<th>$M_3$ eV$^{-2}$</th>
<th>$E_U$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>6.80</td>
<td>13.35</td>
<td>3.40</td>
<td>1.72</td>
<td>2.96</td>
<td>3.780</td>
<td>501</td>
<td>1.96</td>
<td>0.0423</td>
<td>616</td>
<td></td>
</tr>
<tr>
<td>1wt.%</td>
<td>6.32</td>
<td>15.81</td>
<td>3.16</td>
<td>1.87</td>
<td>3.50</td>
<td>5.758</td>
<td>491</td>
<td>2.50</td>
<td>0.0625</td>
<td>691</td>
<td></td>
</tr>
<tr>
<td>3wt.%</td>
<td>6.20</td>
<td>25.90</td>
<td>3.11</td>
<td>2.27</td>
<td>5.16</td>
<td>8.788</td>
<td>459</td>
<td>4.18</td>
<td>0.1076</td>
<td>844</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4: Variation in $(n^2 - 1)^{-1}$ as a function of $(h\nu)^2$ of ZnO:In films.

Fig. 5: Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^2$ of ZnO:In films.
Conclusions

Pure and In doped ZnO thin films were deposited onto preheated glass substrate by spray pyrolysis at a temperature 450 °C. Absorbance spectra were used to determine the optical constants of the films, and the effects of doping percentage on the optical constants were investigated. With increasing the doping percentage to 3wt%, the optical conductivity of the prepared films increases, also the optical constants increases. The single–oscillator parameters were determined. The change in dispersion was investigated before and after doping and its value increased from 13.35 for the undoped films to 25.90 for the doped films with 3wt% of In.

References