Structural and Optical Performance of The doped ZnO Nano-thin Films by (CSP)

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Abstract. In this study, were investigated structural, optical properties and morphological of ZnO and Te-doped ZnO Nano-thin films deposited by Chemical spray pyrolysis (CSP) method. The structural properties of films were studied as pure and Te dopant ZnO at concentration 2 and 4%. The films were characterized by XRD to study the structure of films. It was observed that the hexagonal wurtzite structure of ZnO for all samples. The films exhibited wurtzite (102) preferential growth in pure and the dopant ratios. Grain size values calculated from Scherrer’s formula of the films were varied in range of (79-113) nm. The band gap energy values were calculated respectively for undoped ZnO and 2% 4% Te doped ZnO samples.

Keywords: ZnO, ZnO :Te, CSP, XRD, Optical properties and AFM.

1-Introduction

ZnO is a semiconductor from II-VI group. It has a direct band gap 3.37e.V and exciton energy 60 MeV [1]. It has polycrystalline with Wurtzite hexagonal structure [2]. Due to their optical and electronic properties, they have been used at different electronic and optical applications such as solar cells[3], optical waveguide[4], Light emitting diodes (LED) [5]. Transistors (TFT) [6] and have been recognized as Spintronic material [7]. It has also application in gas, chemical and biological sensors [8]. Doping that is essential incorporation of ions of particular elements into the host material to modify its properties is a devilishly technique in semiconductor industry. Dopants for ZnO can be thought in two groups, substituted with zinc or oxygen and these different dopants cause different optical properties for ZnO owing to different treatments of zinc and oxygen. One of these appropriate dopants is (Te). Te acts as anionic dopant for ZnO and changes its optical behavior the visible region by reducing oxygen vacancies in the ZnO structure [9,10]. Further, morphology that control through doping is another main assignment as the size and shape can impact different properties of the prepared products. Doping ZnO with (Te) can tailor the luminescence properties of ZnO by passivation of oxygen defects. In the present work, we have deposited ZnO by incorporating Te in the lattices through a simple and low cost (CSP) method. Thin films products are to analyze the optical, morphological, and structural properties.
2-Materials and Methods

2-1 Materials

Zinc oxidethin films were deposited on to glass substrate. The aqueous solution containing 0.05M of Zinc acetate \((\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O})\) and 100 mL of deionized water was used to obtain the matrix solution. To prepare the doping material 0.1M of Tellurium tetrachloride to dissolve in deionized water to obtain the required percentage of dopant as a volumetric percentage 2 and 4.

2-2 Methods

Chemical spray pyrolysis method was applied. Table 1 shows the best status, which kept constant during the deposition process for ZnO and Te doped ZnO. Film thickness was obtained by Gravimetric technique and was about 350± 35 nm.

Table 1. Optimal terms of the as deposited films.

| Substrate temperature | 400°C |
|-----------------------|-------|
| Substrate to sprayer nozzle distance | 29cm |
| Sprayer rate          | 5 mL/min |
| Sprayer time          | 8 S |
| Stopping interval time| 1 min |

2-3 Measurements

Transmittance and Absorbance spectra were recorded via Shimadzu double beam spectrophotometer. Structural parameters were obtained by X-ray diffractometer (Shimadzu, model: XRD-6000). AFM (AA 3000 Scanning Probe Microscope) were utilized to study surface of the deposited thin films.

3-Result and Discussion

The crystal structure of ZnO and Te-doped ZnO films were investigated by X-ray diffraction (XRD) patterns. Figure 1 showed XRD patterns of undoped and Te-doped zinc oxide. These spectra indicated that the films had polycrystalline nature. ZnO hexagonal wurtzite structure (JCPDS card file no. 36-1451) with a peak of (100), (002), (101), (110), (200) was observed for undoped sample [11]. The peaks of (110), (200) were almost disappeared with Te doping. The most peak intensity was (002) for all samples. The highest peak intensity of (002) was also observed when Te-doping ratios were 2% and 4%, the ZnTe cubic phase peak of (200) (JCPDS card file no: 150746) emerged at low intensities[12]. Namely, ZnO binary structure changed to ZnO$_{1-x}$Te$_x$ ternary structure with the increasing Te doping ratio. ZnO$_{1-x}$Te$_x$ ternary structures with Te-doping were also observed by XRD analysis. In addition, these structures were observed by CL measurements. The reason for small intensity or no intensity of ZnTe may be very small Te atomic concentration in ZnO structures. For a peak of (002), the average crystallite size\((D)\) were estimated by using Scherrer’s formula in equation 1 [13, 14].
\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda = 1.5418 \) Å, \( \beta \) represent (FWHM) and \( \theta \) is angle of diffraction. \( D \) value of undoped sample continuously increased from 79.66 nm to 112.91 nm with increasing Te-doping content. The dislocation density (\( \delta \)), is the measure of amount of defects in crystal. (\( \delta \)) of samples was estimated using equation 2\[15,16\].

\[ \delta = \frac{1}{D^2} \]  

(2)

The calculated dislocation density values (\( \delta \)) showed increasing tendency with increasing Te content.

![XRD pattern of ZnO Te doped ZnO.](image)

**Figure 1.** XRD pattern of ZnO Te doped ZnO.

| Structural parameters of ZnO and Te doped ZnO. |
|-----------------------------------------------|
| [100] 31.76° | [002] 33.02° | [102] 38.26° | [200] 47.045° | [202] 55.09° |

| 0% | 2% | 4% |
|-----------------------------------------------|
| ![Graph showing XRD pattern](image) | ![Graph showing XRD pattern](image) | ![Graph showing XRD pattern](image) |
Optical transmission spectra of doped and undoped samples were drawn in Figure (2-a). From transmittance spectra, there was reduction continuously with Te doping at all wavelength ranges. The optical transmission shifted red with increasing tellurium content. The transmittance in the short wavelengths showed decreasing tendency with increasing Te concentration. The decreasing transmittance with Te dopants were observed by [17]. Absorption coefficient ($\alpha$) of films was evaluated by equation 3[18, 19]:

$$\alpha = \ln \left( \frac{1}{T} \right) \div d \quad (3)$$

Where $T$ is transmittance and $d$ is film thickness. Figure (2- b) represents the absorption coefficient. Optical band gap was estimated by following relation [20, 21]:

$$\alpha h\nu = A (h\nu - E_g)^{1/2} \quad (4)$$

Where $h\nu$ photon energy and $A$ is constant. Values of $E_g$ for pure ZnO and doping Te (2, 4) were determined by plotting in Figure (3) were found as (300-900) nm. From the results illustrate, when Te doping concentration is increased the band gap of ZnO: Te continuously decreased [22].

| Doping% | Plane (hkl) | $2\Theta$ (Deg.) | Lattice constant $a$ (Å) | Lattice constant $c$ (Å) | FWHM (Deg.) | D (nm) | $\varepsilon$ x $10^4$ | $\delta$ x $10^{-4}$ (1/nm²) |
|---------|-------------|------------------|--------------------------|--------------------------|-------------|--------|----------------|--------------------------|
| 0       | (102)       | 38.26            | 4.457                    | 5.927                    | 0.6002      | 14.01  | 26.15         | 50.94                    |
| 2       | (102)       | 38.26            | 2.665                    | 4.947                    | 0.6078      | 13.83  | 26.48         | 52.24                    |
| 4       | (102)       | 38.26            | 3.249                    | 5.206                    | 0.2455      | 34.25  | 10.7          | 8.52                     |
Figure 2. Transmittance versus Wavelength of ZnO and Te doped ZnO.

Figure 3. Illustration the energy band gap for the ZnO with different Te doping by (CSP).
Surface morphology and surface roughness of the deposited films were studied by AFM technique. Figure 4 offer AFM images of the deposited thin films. It show that pure films have a soft surface morphology and increasing with doping. The increase of surface roughness may be assigned to larger grain formation. Figure 4 shows the root-mean-square (RMS) of average surface roughness, particle or grain size, and 3D surface morphology. Moreover, in Table 2 determined rough parameters, it's obvious that (RMS) increased significantly with the increment of dopant.

![Figure 4. AFM parameters (a,b and c) AFM, 3D image of ZnO and Te doped ZnO(d, e and f).](image)

**Table 3.** Surface morphology of ZnO and Te doped ZnO.

| Te: Doping (%) | Avg. Diameter (nm) | Average roughness (nm) | R. M. S. (nm) |
|---------------|--------------------|------------------------|--------------|
| 0             | 79.66              | 0.438                  | 0.519        |
| 2             | 111.02             | 2.37                   | 3.2          |
| 4             | 112.91             | 6.69                   | 7.97         |
4-Conclusions

ZnO Nano-thin films were prepared on glass substrates by the (CPS) method. The effects of doped condition on structural, optical properties and surface morphology of films were evaluated. The XRD were showed the polycrystalline with orientation (100), (002), (101), (110), (200) of ZnO and ZnO: TeNano-thin films. Surface morphologies of this showed average roughness 6.69nm and diameter of about 112.91nm.

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