A Study the Aluminum Doped Zinc Oxide Thin Films

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We investigated the optical properties of pure and Aluminum doped zinc oxide thin films as the n-type semiconductor. In this paper, we have studied the deposition of Al doped ZnO thin films on glass substrate at 350 °C, when the films were deposited with 0, 2 and 3 wt using spray pyrolysis technique. % of Al / Zn, the substrates were heated using the solar cells method. The substrate was R217102 glass in a size of $30 \times 17.5 \times 1$ mm. All films exhibit an average optical transparency about 85 %, in the visible region. The shift of optical transmittance towards higher wavelength can be showed by the increase of band gap energy from 3.245 to 3.281 eV with increasing of Al doping from 0 to 3 wt. %. The Urbach energy E_u increase and decrease reaching to optimal value was obtained after doping at 3 wt. %.

Keywords: ZnO, Thin film, Semiconductor doping, Spray pyrolysis technique.

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1. INTRODUCTION

ZnO is a very most important semiconductor material due to its applications [1]. It has a direct and wide band gap of 3.3 eV in the near-UV spectral region [2], and a large exciton binding energy (60 meV) at room temperature [3] Its consider that the ZnO is an n type semiconducting with high density and good crystalline quality [4], but the use of ZnO as a semiconductor in electronic devices due to the high transmittance and good electrical conductivity [5]. Therefore, ZnO thin films are promising candidates for applications in short-wavelength light-emitting devices, lasers, field emission devices, solar cells and sensors [1-7].

Semiconducting transition metal oxide (such as ZnO) based glasses have gained much interest in science and technology due to their interesting applications such as transparent conductive, ferromagnetism, semiconductors, piezoelectric and solar cells, as the doped thin films have low resistivity and good optical gap energy at low deposition, and transparent in the visible region such as in Al and doped ZnO thin films discussed by [8].

ZnO thin films can be produced by several techniques such as reactive evaporation and thermal annealing [9], molecular beam epitaxy (MBE) [10], magnetron sputtered technique [11], pulsed laser deposition (PLD) [12], the low-temperature solution method [13], potentiostatic electrodeposition [14], the sol-gel technique [15], chemical vapor deposition, electrochemical deposition [16] and spray pyrolysis [17], have been reported to prepare thin films of ZnO.

In this paper, we have studied the deposition of Al Doped ZnO thin films on glass substrate at 350 °C, when the films were deposited with 0, 2 and 3 wt. % of Al / Zn.

2. EXPERIMENTAL

In this study, the organic solar cells were fabricated thought this process. We fabricated the organic solar cells which were consisted of mirror layer inside (ITO

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glass) and substrate holder; we established the latter from opposite to maintain the substrate temperature using the mirror layer, organic solar cells use solar energy to heat a substrate glass with deposition of ZnO solution on substrate (see Figure 1). The reflective layer is designed to reflect the maximum amount of solar energy incident upon it, back through the glass substrate. The structure of the spray deposition system and fabricated organic solar cells are shown in Figure 1. The substrate was heated by absorber plate and maintained temperature of 350 °C, when the active solution sprayed on substrate glass.



Fig. 1 – The photograph of experimental setup

ZnO solution were prepared by dissolving 0.1M (Zn(CH₃COO)₂, 2H₂O) in the solvent containing equal

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volume absolute methanol solution (CH₃OH) (99.995 %) purity. ZnO : Al solutions were prepared by adding to the precedent solution *a* Aluminum chloride with ratio of Al / Zn varying between 0 and 3 wt. %. Then we have added a few drops of concentrated HCl solution as a stabilizer, the mixture solution was stirred at 60 °C for 120 min to yield a clear and transparent solution. The reaction can be represented as:

$$\operatorname{Zn}(\operatorname{CH}_{3}\operatorname{COO})_{2} \cdot 2\operatorname{H}_{2}\operatorname{O} + 2\operatorname{R} - \operatorname{OH} \rightarrow$$

$$\operatorname{Zn}(\operatorname{CH}_{3}\operatorname{COO})_{2} + 2\operatorname{R} - \operatorname{OH} + 2\operatorname{H}_{2}\operatorname{O}$$
(1)

The possible chemical reaction takes place on the heated substrate to produce ZnO thin film maybe as follows. When the droplet of solution reach the heated substrate, chemical reaction of the Zinc Acetate with water solution takes place under stimulated temperature and provides the formation of ZnO thin films [2].

$$\operatorname{Zn}(\operatorname{CH}_{3}\operatorname{COO})_{2}$$
. $2\operatorname{H}_{2}\operatorname{O}$ $\xrightarrow{300 \, ^{\circ}\operatorname{C} \text{ or } 350 \, ^{\circ}\operatorname{C}}{\operatorname{deposited as}} \rightarrow$ (2)
ZnO+CO₂+CH₄+ steam

$$\text{ZnO} + x\text{AlCl}_{3} \rightarrow \text{Zn}^{+2}\text{Al}_{x}^{+3}\text{O}^{-2} + \frac{1}{2}\text{Cl}_{2}^{-}$$
 (3)

The resulting solutions were sprayed on the heated glass substrates by spray pyrolysis technique, the substrates were heated by using the solar cells method, and this letter was prepared in our laboratory. The thin films were deposited at a substrate temperature of 350 °C glass in the size of $30 \times 17.5 \times 1$ mm, which transforms the liquid to a stream formed with uniform and fine droplets of 35 µm average diameters.

The optical transmittance of the films was measured in the range of 300-900 nm by using an ultraviolet-visible spectrophotometer (SHUMATZU 1800).



Fig. 2 – Transmission spectra $T(\lambda)$ of undoped ZnO thin film

3. RESULTS AND DISCUSSION

Figure 2 and 3, shows the optical transmissions spectra of undoped ZnO thin films Figure 4 and Al doped ZnO thin films Figure 5, the thin films were deposited at a substrate temperature of 350 °C. As it can be seen, a height transparent spectra $T(\lambda)$ the undoped film become transparent, it is found that the optical transmission, around 85 %, in the visible region. The region of the absorption edge in the all layers due to the transition between the valence band and the con-

duction band is located between 360-390 nm, in this region the transmission decreased because of the onset fundamental absorption.

The optical band gap energy E_g was measured from the transmission spectra using the following relations [18]:

$$(Ah\nu)^2 = C(h\nu - E_{\sigma}) \tag{4}$$

where A is the absorbance, C is a constant, hv is the photon energy ($hv = 1240/\lambda(eV)$) and E_g the band gap energy of the semiconductor. As it was shown in (Fig. 4) a typical variation of $(Ahv)^2$ as a function of photon energy (hv) used for deducing optical band gap E_g , it is determined by extrapolation of the straight line portion to zero absorption (A = 0) [19] the values of E_g are listed in Table 1. Besides, we have used the Urbach tail energy (E_u), which is related to the disorder in the film network, as it is expressed follow [20]:



Fig.3 – Transmission spectra $T(\lambda)$ of Al doped ZnO thin film

$$A = A_0 \exp\left(\frac{h\nu}{E_u}\right) \tag{5}$$

where A_0 is a constant $h\nu$ is the photon energy and E_u is the Urbach energy. The Urbach tail energy E_u is calculated from the slope of $h\nu$ vs. photon energy $(h\nu)$ plot and the obtained values are shown in Table 1.



Fig. 4 – The typical variation of $(Ah\,\nu)^2$ vs. photon energy of deposited ZnO thin film at 300 and 350 °C

As clearly seen in the Figure 4, The shift of optical transmittance of Al doped ZnO thin films towards higher wavelength can be showed by the increase of band gap energy from 3.283 to 3.224, when the Al concentration increase from 0 and 3 wt. % (see Table 1).



Fig. 5 – The typical variation of LA vs. photon energy of deposited ZnO thin film at 300 and 350 °C

Table 1 - The optical properties of Al doped ZnO thin films

Al / Zn (wt %)	E_g (eV)	E_u (meV)
0	3.283	068.68
2	3.271	114.89
3	3.224	091.07

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This is indicates that the Al doped ZnO thin films is an n type semiconducting with high optical transmittance and good band gap energy. However, in Figure 5 obtained inversely for the Urbach energy, The Urbach energy E_u increase and decrease reaching to optimal value was obtained after doping at 3 wt. % (see Table 1), indicating the reduction of structural disorder and defects in the Al doped ZnO thin films.

4. CONCLUSIONS

In conclusion, highly transparent conductive ZnO thin films were deposited on glass substrate by spray pyrolysis technique. The ZnO thin films were deposited at different concentrations of Aluminum solution; the substrates were heated using the solar cells method. All films exhibit an average optical transparency about 85 %, in the visible region. The shift of optical transmittance towards higher wavelength can be showed by the increase of band gap energy from 3.245 to 3.281 eV with increasing of Al doping from 0 to 3 wt. %. The Urbach energy E_u increase and decrease reaching to optimal value was obtained after doping at 3 wt. %.

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