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Effect of annealing temperature on the optical properties of ZnO nanoparticles

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ABSTRACT

In this work, ZnO films were prepared by drop casting technique. The films were deposited on quartz substrates under different annealing time (15,30,45 and 60 min.) at a constant temperature (800 °C). The optical properties were achieved by measuring the absorbance and transmittance spectra in the wavelength range (200-900) nm. It was found that the absorbance decreases while transmission increases as the annealing time increases, while the reflectance decreases as the annealing time increases. The optical measurements indicate the kind of transition which was a direct allowed with an average band gap energies lie between 3.3 eV and 3.54 eV with the change of annealing time.

Keywords: nanoparticles; ZnO film; optical properties; drop casting technique

1. INTRODUCTION

Zinc oxide (ZnO), a representative of II–VI semiconductor compounds, is a very versatile and important material. ZnO has a unique properties among semiconducting oxides due to its piezoelectric and transparent conducting properties. It has a high electrical conductivity and optical transmittance in the visible region. These properties make it an ideal candidate for applications like transparent conducting electrodes in flat panel displays and window layers in solar cells [1-3].

ZnO has a wide band gap (3.37 eV) and a large exciton binding energy (60 meV) and enter many potential applications such as laser diodes, solar cells, gas sensors, optoelectronic devices. A wide band gap has many benefits like enabling high temperature and power operations [4-6]. It is well known that semiconductor nanocrystals or nanoparticles (NPs) may have superior optical properties than bulk crystals owing to quantum confinement effects. The synthesis and properties of various ZnO nanostructures have been reported, such as nanorods, nanowires, nanotubes, quantum wells and NPs [7-11]. Among these, the NP nanostructure may be of fundamental importance as a three-dimensional confined system bridging the gap between bulk materials and molecular compounds. So far, a variety of techniques have been employed for the synthesis of ZnO NPs, such as metal organic chemical vapour deposition (MOCVD), spray pyrolysis, ion beam assisted deposition, laser-ablation, sputter deposition, template assisted growth and chemical vapour deposition [12-19, 24-26]. In this paper we report the fabrication of ZnO nanoparticles thin film via drop casting technique, and annealing under 800 °C at different time and study the optical properties of the as deposited films.

2. EXPERIMENTAL

(10 g) of ZnO was grinding for (5 min) by electric grinder device (GOSONIC 500W) in order to obtain a fine powder. 60 ml of re-distlled water were mixed with 0.02 M of ZnO powder using a magnetic stirrer for 20 minutes. This solution was taken into centrifuge tube and centrifuged at 1600 rpm for 10 minutes.

Five drops of this solution were taken and drop casted on to a quartz substrate in order to obtain thin films and kept under ambient conditions for drying. These thin films were annealed for different time (15, 30, 45 and 60) minutes, kept at a constant temperature of 800 °C. UV-VIS spectra were measured with (Shimadzu UV-1650 PC) in the wavelength range (200-900) nm. Reflectance was recorded by (A SR300 Spectroscopic Reflectometer) in the wavelength range of (200-900) nm.

3. RESULTS AND DISSCUSION

Figure 1 shows the optical transmittance spectra of ZnO thin films in the wavelength range of (200-900) nm. The films are highly transparent in visible and infrared range of the electromagnetic spectrum with the maximum value of about (85 %) recorded for film with higher annealing time (60 min.), and the transmittance increased with increasing annealing time. The increase in optical transmittance with temperature can be attributed to the increase of structural homogeneity and crystallinity [20]. Figure 2 shows the absorbance of ZnO films with different annealing time. It is clear that the films have high absorption at short wavelength, the figure show that the absorption decreases with increasing of annealing time.

The change of reflectance as a function of wavelength in the range (200-900) nm is shown in Fig. 3 for different annealing time. It is clear from the figure that the reflectance decreases with increasing annealing time. The optical band gap of the films is determind by applying Tauc model [21] in high absorption region by the relation [21]

$$\alpha h\vartheta = B \ (h\vartheta - E_g)^n \tag{1}$$

where $h\vartheta$ is the photon energy, E_g is the optical energy gap, B is a constant. For direct transition $n = \frac{1}{2} or \frac{2}{3}$ and the former value was found to be more suitable for ZnO thin films.

The optical energy gap is determined by plotting $(\alpha h \gamma)^2$ as a function of photon energy as shown in Fig. 4. Red shift of the optical band gap could be obtained by decreasing the value of the optical energy gap with increasing the annealing time for all the samples. This is due to the growth of grain size and the decrease in defect states near the bands and in turn decreasing the value of E_q [22].



Fig. 1. Transmittance versus wavelength for ZnO thin films at different annealing time (15, 30, 45 and 60 min.).



Fig. 2. Absorbance versus wavelength for ZnO thin films at different annealing time (15, 30, 45 and 60 min.) at 800 °C.



Fig. 3. The reflectance versus wavelength for ZnO thin films at different annealing time (15, 30, 45 and 60 min.) at 800 °C.



Fig. 4(a). Direct allowed energy gap for ZnO thin films of different annealing time (15 min.) at 800 °C.



Fig. 4(b). Direct allowed energy gap for ZnO thin films of different annealing time (30 min.) at 800 °C.



Fig. 4(c). Direct allowed energy gap for ZnO thin films of different annealing time (45 min.) at 800 °C.



Fig. 4(d). Direct allowed energy gap for ZnO thin films of different annealing time (60 min.) at 800 °C.

Figure 5 illustrates the variation of (ε_r) as a function of photon energy. It is clear from the figure that (ε_r) increase slightly with increasing of photon energy. Also that (ε_r) decrease with increasing of annealing time.



Fig. 5. Real part of dielectric constant (ϵ_r) for ZnO thin films at different annealing time (15, 30, 45 and 60 min.) at 800 °C

Figure (6) illustrates the variation of (ε_i) as a function of photon energy. The figure shows that (ε_i) decrease with increasing of photon energy. Also that (ε_i) decrease with increasing of annealing time.



Fig. 6. Imaginary part of dielectric constant (ϵ_i) for ZnO thin films at different annealing time (15, 30, 45 and 60 min.) at 800 °C

Figure 7 show that static refractive index after applying Cauchy equation which is represented by the following equation [23].

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 + D/\lambda^6 + \cdots$$
 (2)

where *A*,*B*,*C*,*D*,... are experimentally determined constants.

It is clear from the figure that static refractive index decreased with increasing of annealing time



Fig. 7(a). Refractive index versus wavelength after applying Cauchy equation (15 min).



Fig. 7(b). Refractive index versus wavelength after applying Cauchy equation (30 min).



Fig. 7(c). Refractive index versus wavelength after applying Cauchy equation (45 min).



Fig. 7(d). Refractive index versus wavelength after applying Cauchy equation (60 min).

4. CONCLUSION

In summary, we have successfully fabricated ZnO nanoparticles using the drop casting technique. This method produced a large quantity of ZnO nanocrystals at relatively high purity and very low cost. The optical transitions in ZnO are direct and value of optical energy gap decreases with increasing annealing time. The value of the static refractive index was decreased as the annealing time Increase.

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