Effect of Zinc Ion Concentration on Structure, Electrical and Optical Properties of ZnO Prepared by CBD

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Abstract

Effect of zinc ion concentration of ZnO thin films, prepared by using chemical bath deposition technique, is discussed. ZnO films were characterized using different techniques such as X-ray diffraction (XRD), electrical resistivity measurement, and optical absorption and transmission. The XRD analysis showed that all the films had a preferred (002) orientation. The ZnO films showed, on average 20% reflectance, the transmittance range between 35% and 45% for different morality before annealing. Optical band gap decreases with increasing zinc ion concentration. Linear increase in resistivity with increasing in molarities was shown. The films were annealed at 473 K and showed decreases in the reflectance of the films, but transmitting increase to 75% - 80%. Therefore by annealing process the hydroxide phase converted to the oxide phase. The annealed samples show a relative decrease in band gap with annealing.

Key wards: chemical bath deposition, ZnO films, zinc ion concentration effect, annealing effect, structure properties, electrical properties, and optical properties.

1. Introduction

Zinc oxide is a versatile semiconductor which has attracted considerable attention because of its catalytic, electrical and optical properties. These properties find wide technological applications. For instance, ZnO-based materials have been used in solar cells, transparent conducting films, ultraviolet-protection films, chemical sensors, varistors, light emitting diodes, laser diodes , etc.[1] .Several methods are applied to prepare ZnO films, both physical and chemical deposition technologies including sputtering[2], pulsed laser deposition[3], chemical vapor deposition (CVD)[4], molecular beam epitaxy [5], and sol–gel process [6] etc. However, most of the methods were not well suited for large area coating, low-temperature processing, and low process cost. So far, the abovementioned methods could not be used for ZnO crystal fabrication below 150 ºC. Again, the equipment is expensive for large area process. Therefore, chemical bath deposition (CBD) has been an attractive technology which is simple and low cost for thin-film fabrication. There are many previous articles discussing the ZnO films using electroless deposition in solution bath and indicating the feasibility of low temperature[7–11]. Preparation of oxide film in a chemical solution bath presents several advantages: (i) films can be obtained on substrates at low temperature, below 100 ºC, (ii) the thickness and morphology of film can be controlled by deposition parameters, (iii) the equipment is relatively cheap, and (iv) the technique is more environmentally friendly. These supply the technique compatibility for the low-cost process and good quality.

2. Experimental details

2.1. Film preparation

Aqueous zinc–ammonia complex was chosen as the cation precursor, in which analytical reagents of $ZnSO_4$ (99.7%) and concentrated ammonia (32%) were used. CBD ZnO thin films were chemically grown on glasses using $ZnSO_4$ (0.025-0.1M), ammonia 1M aqueous solution. Substrates used for deposition ZnO films are microscope glass slides washed in distilled water to remove the impurities and residuals from substrate, followed by rinsing in chromic acid (1mg of CrO_3 in 20ml of distilled water) for one day to introduce functional group called nucleation or epitaxal centers, which formed the basis for the thin films growth and finally washed again with distilled water. Glass substrates were immersed vertically into the above beaker for (10-20 min) at room temperature (80-85) ºC

3. Measurements

X-ray diffraction system (Lab X –XRD-6000 / Shimadzu) has the following characteristics: Source: radiation of CuKα with 1.54Å wavelength, Scanning speed: (5degree/min). Incidence angle: 10-60 degree. For optical measurements the deposited film from one slide was removed carefully using HCL solution. Optical measurements included transmittance and absorption spectra using phoenix-2000UV-VIS spectrophotometer in the range of 300-1100.

Thickness measurement was made by optical method using He-Ne laser with incident angle 45°. The film thickness (d) is calculated using the following formula [12]:-

$$d = \frac{\Delta x}{x} \cdot \frac{\lambda}{2} \qquad (1)$$

Where x is the fringe width, Δx is the distance between two fringes and λ is the wavelength of laser light.

The value of absorption coefficient (α) has been calculated by using the following relation [13, 14]:-

$$\alpha = 2.303 \frac{A}{d} \qquad (2)$$

Where :A is absorptance and d is the thickness of the thin film.

The absorption coefficient (α) and optical band gap (Eg) are related by [15]:-

$$\alpha h\nu = A(h\nu - Eg)^n \qquad (3)$$

Where : A is constant depending on transition, h is plank's constant, υ is the frequency of the incident photon, Eg is the optical bandgap of the material and n has different values depending on the nature of the absorption process, and equal 1/2 , 3/2 , 2 , and 3 for allowed, forbidden of direct and indirect transition respectively. The plot of $(\alpha h\nu)^2$ versus (hν) gives the best result. By extrapolating the liner part down to (αhν = 0) the value of E_g could be determined.

For the electrical measurements aluminum electrodes in a coplanar configuration, were evaporated in vacuum on the surface of the Cu_xS films. The electrical resistivity of the deposited films was determined using the equation [16]:-

$$R = \rho \frac{L}{A} \qquad (4)$$

Where ρ, is the electrical resistivity of the films, L the distance between electrodes and A the area of the ohmic contacts.

4. Results and discussion

The results of our structural studies of the ZnO films were done with x – ray diffraction (XRD) and show (100), (002), and (101) distinct diffraction peaks for the films grown in this study, as shown in figure (1). The intensity of the peaks increased after annealing.

Transmittance and reflectance as function of wavelength are shown in figure (2) for different molarities Film transmission decreases with increasing zinc ion concentration because of zinc ion concentration increasing causes an increase of grain size as a result of increasing the film thickness and consequence transmission decreases. The films annealed at 473 K showed decrease in the reflectance of the films as shown in figure (3), but transmitting increase after annealing. The increasing of transmission after annealing and the conversion of the $Zn(OH)_2$ film to the ZnO film by the removal of all H_2O vapor. Therefore by annealing process the hydroxide phase converted to the oxide phase. These results are consistent with other published results such as results of D.D.O. Eya et al. [17].

The ZnO films for different molarities or the film annealed at 473 K show exponential decay of absorbance with increasing wavelength as shown in figure (4), this result agrees well with literature [17]. Variation of the extinction coefficient with wavelength shown in figure (5) for different molarities or for the film annealed at 473 K, shows a steep relationship indicating sharp increase in the absorption with increasing wavelength. This conform the relation ($K = \frac{\alpha h}{4\pi}$) Where K, is the extinction coefficient, α the absorption coefficient, and λ the wavelength.

The absorption coefficient with wavelength for different morality and for the film annealed shown in figure (6). In the high photon energy region, the energy dependence of the absorption coefficient, $\alpha > 0.5 * 10^5 \text{ cm}^{-1}$ suggests the occurrence of direct optical transition. The energy gap (Eg) value is calculated by extrapolation of the straight line of the plot of $(\alpha h\upsilon)^2$ versus photon energy for different molarities as shown in Figure (7). The band gap decreases with the increase in zinc ion concentration and values were tabulated (Table 1). More probably this is related to the decrease in grain size with increasing deposition rate[18]. The annealed samples show a relative decrease in band gap with annealing. These results are consistent with other published results such as results of P.J.George et al. [19] who attribute this decrease in the band gap in the annealed samples to the grain size growth.

Figure (8) shows the variation of refraction index of ZnO with wavelength. The films at different molarities, especially those at 0.05 M , show that the refractive index remained, on average at 2.6 in both visible and NIR region.

Electrical resistivity measurement was done on the samples and was found to be increasing with increase zinc ion concentration. Figure (9) depicts the variation of resistivity with zinc ion concentration, it is clear that resistivity increases with zinc ion concentration is noticed. More probably the increasing in resistivity is due to change in average grain size which we have already studied.

Conclusion

In this investigation, the ZnOthin films were grown on the glass substrate by CBD, and the effects of zinc ion concentrations and annealing process on structure, optical and electrical properties were studied. Major findings as following

1-Transmission decreases with increasing zinc ion concentration, the transmitting increase after annealing.

2-The band gap decreases with the increase in zinc the ion concentration, while the band gap decrease after the annealing.

3-Increasing the electrical resistivity leads to increases with zinc ion concentration

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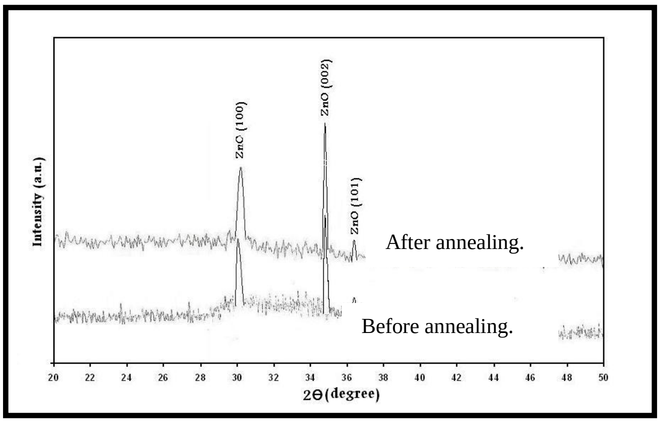
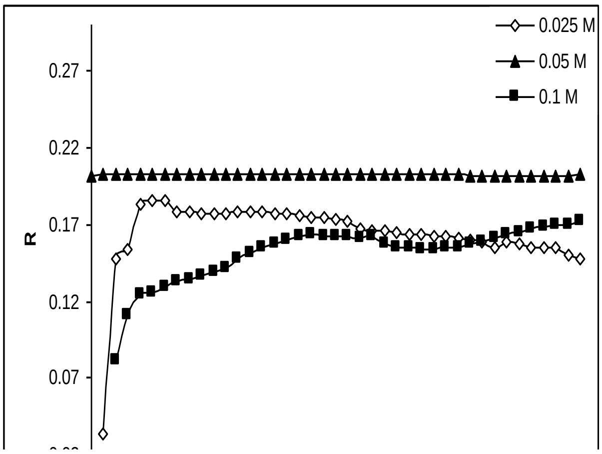


Figure (1) X –Ray diffraction spectra for ZnO films before and after annealed.



(A)

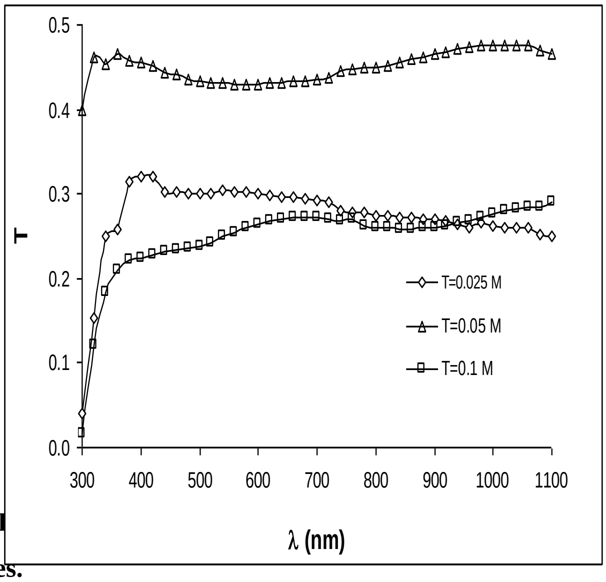
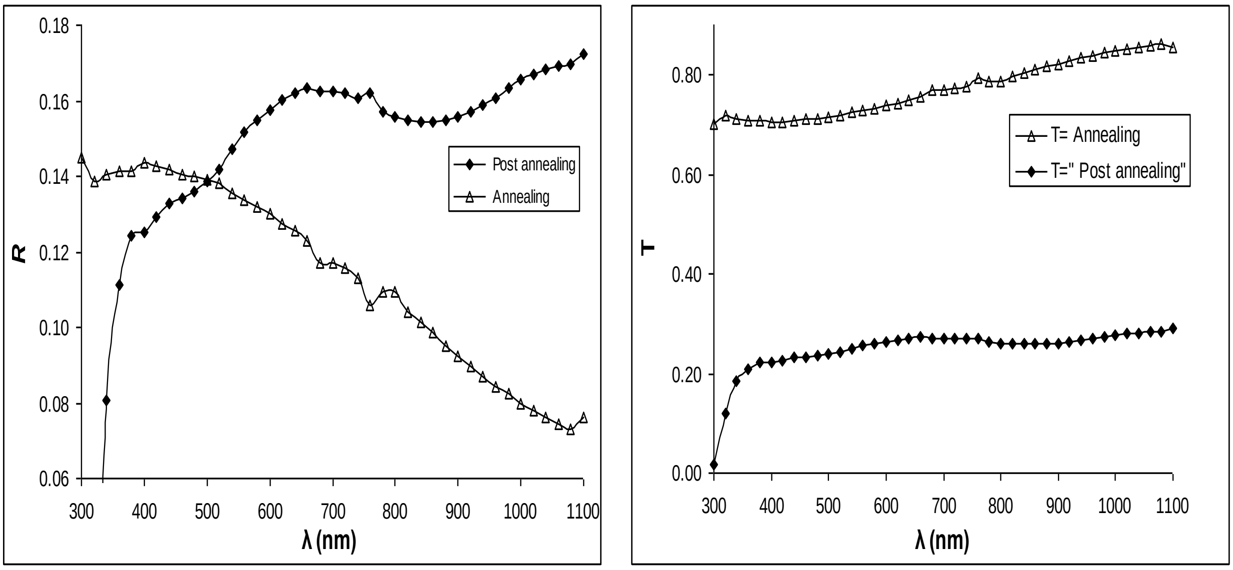


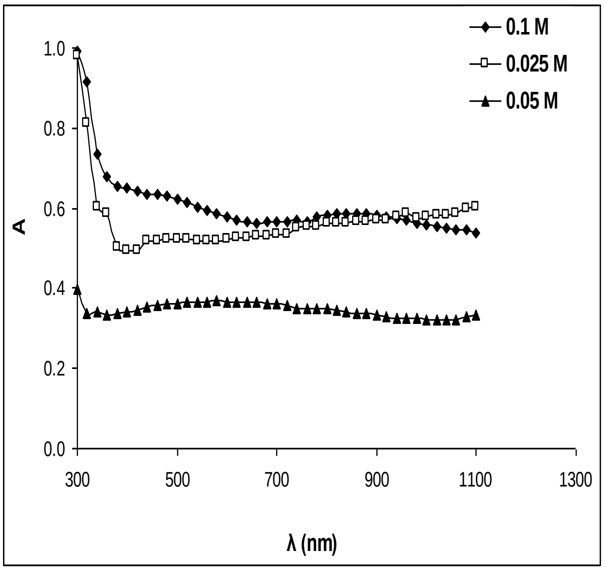
Figure (2A,B) transmittance (T) and reflectance (I

molarities.



(A) **(B)**

Figure (3A,.B) transmittance (T) and reflectance (R) as function of wavelength before and after annealing.



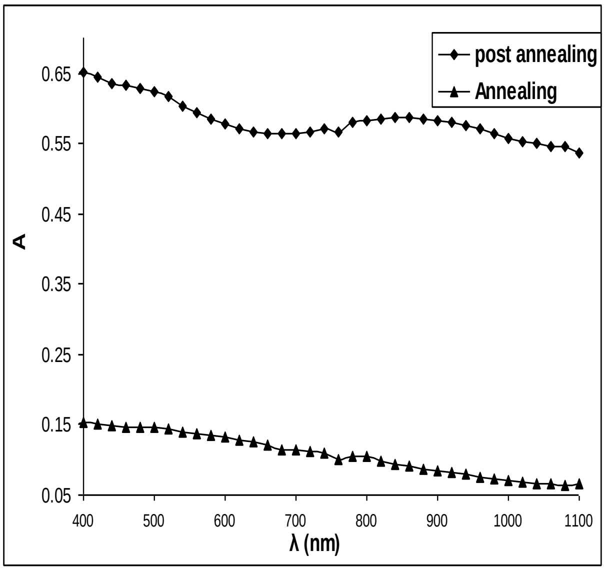


Figure (4) A. absorbance (A) as function of wavelength under various molarities.

Figure (4) B. absorbance (A) as function of wavelength before and after annealing.

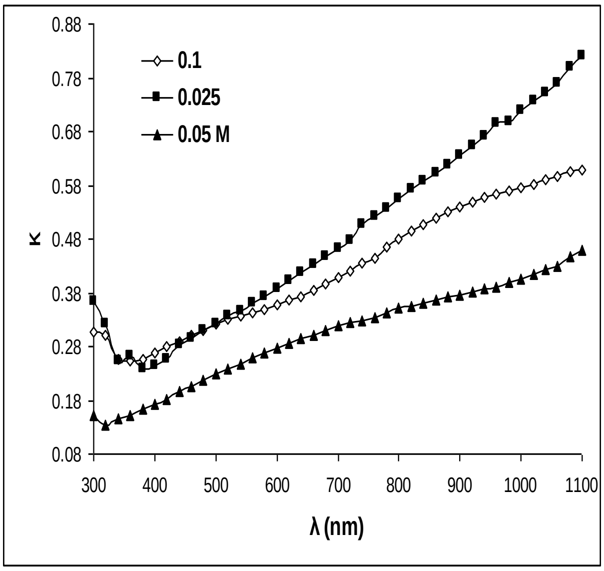


Figure (5) A. variation of extinction coefficient (K) as function of wavelength for different molarities.

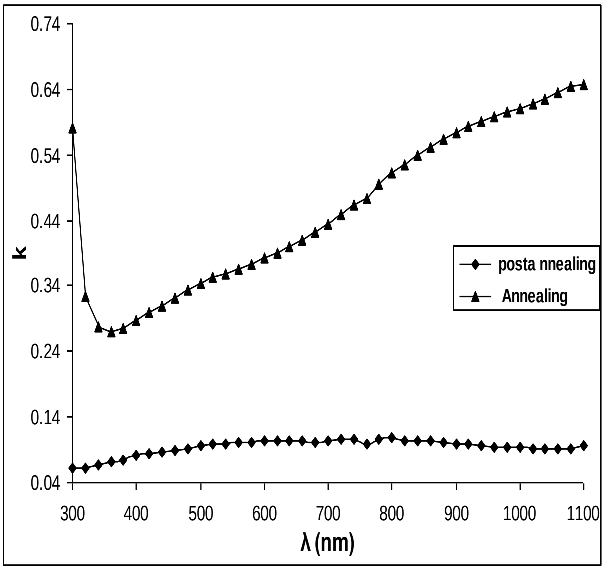


Figure (5) B. variation of extinction coefficient (K) as function of wavelength before and after annealing.

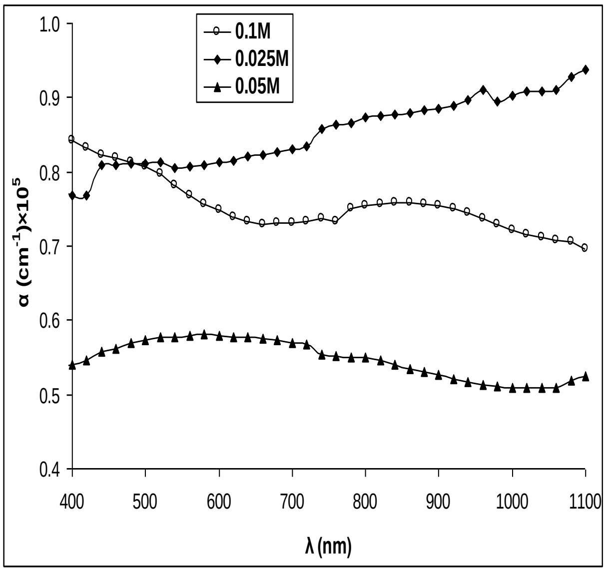


Figure (6) A. variation of absorption coefficient (α) as function of wavelength for different molarities.

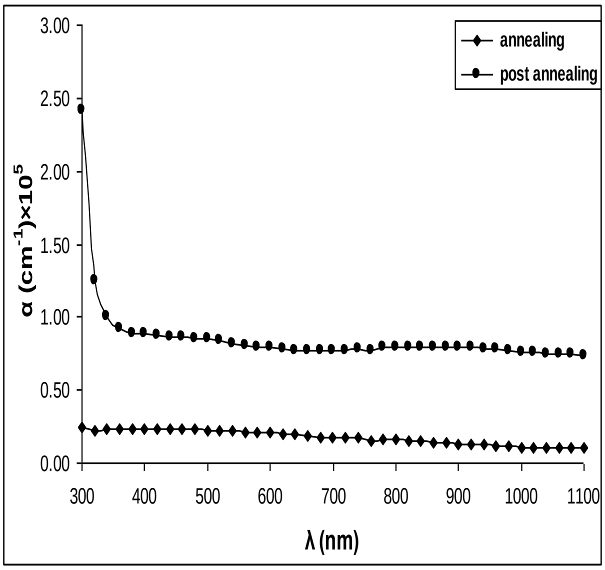
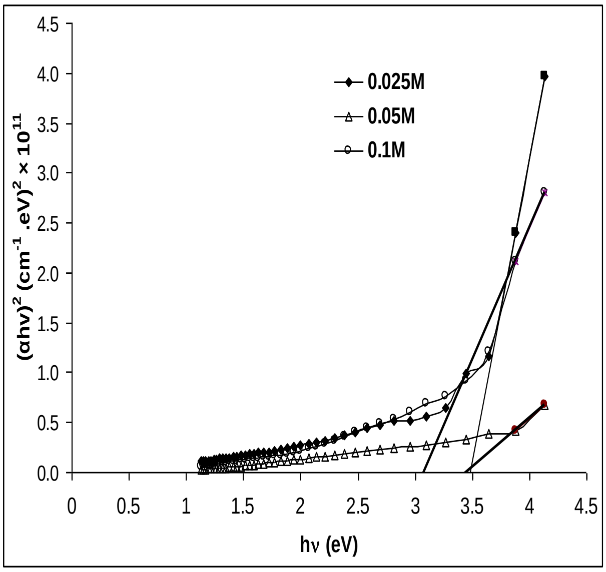


Figure (6) B. variation of absorption coefficient (α) as function of wavelength before and after annealing.



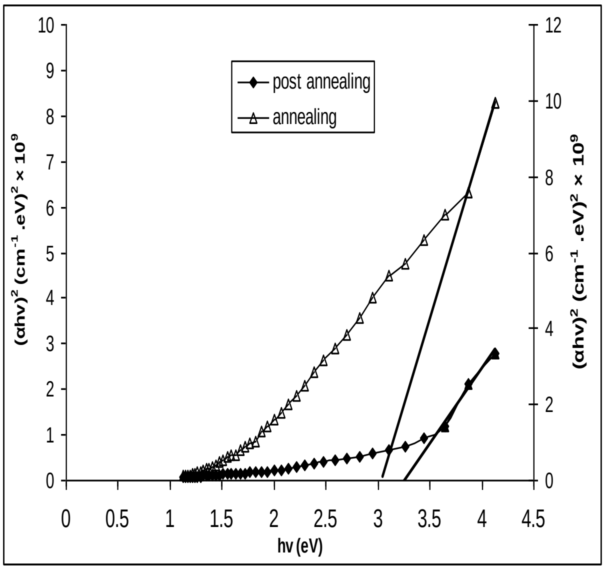
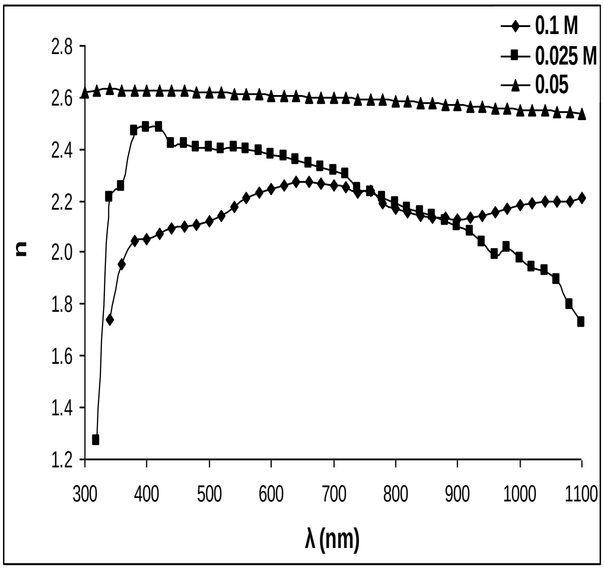


Figure (7) A. plots of $(\alpha h\upsilon)^2$ versus(hυ) for for different molarities

Figure (7) B. plots of $(\alpha h\upsilon)^2$ versus(hυ) before and after annealing.



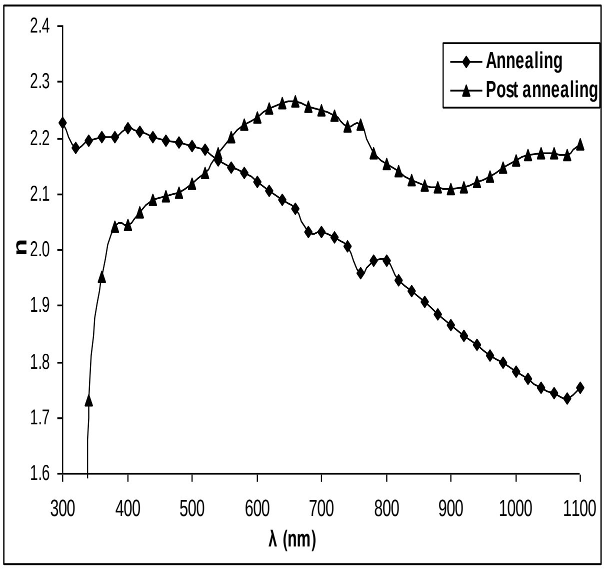


Figure (8) A. refractive index as a function of wavelength for different molarities.

Figure (8) B. refractive index as a function of wavelength before and after annealing.

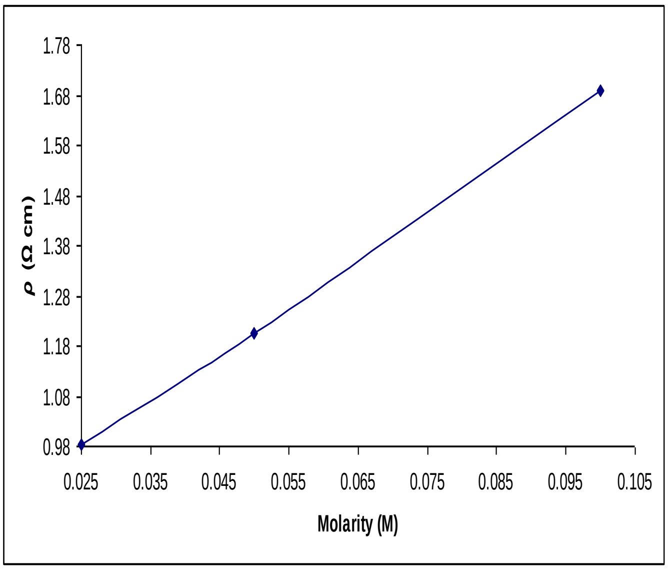


Figure (9) Variation in resistivity as function of Zninc ion concentrations.

Table (1): The result of energy gap at different concentrations of zinc ion

Concentration of Zinc ion	energy band gap Eg (eV)
0.025	3.48
0.05	3.45
0.1	3.12
0.1 annealing	3.08

تاثير تركيز ايون الزنك على الخصائص التركيبية، البصرية، والكهربائية لاغشية ZnO المحضرة بطريقة الترسيب بالحمام الكمياوي

الخلاصة

في هذا البحث تم مناقشة تاثير تركيز ايون الزنك على اغشية اوكسيد الزنك(ZnO) المحضرة بطريقة الترسيب بالحمام الكمياوي . تم دراسة خصائص اغشيةZnO باستخدام طرق مختلفة مثل حيود الاشعة السينية، قياس المقاومية الكهربائية ، الامتصاصية والنفاذية البصرية. اظهرت نتائج حيود الاشعة السينية ان جميع الاغشية المحضرة تمتلك اتجاهية(٠٠٢). اظهرت اغشية اوكسيد الزنك انعكاسية حوالي ٢٠%، معدل النفاذية (٣٥%-٤٥%) لمختلف التراكيز قبل التلدين . قيم فجوة الطاقة كانت تقل مع الزيادة في تركيز ايون الزنك. كما تم ملاحظة الزيادة الخطية في المقاومية الكهربائية مع الزيادة في المولارية. الاغشية الملدنة عند ٤٧٣K اظهرت نقصان في قيم الانعكاسية لكن النفاذية ازدات بعد التلدين وتراوحت قيمها بين (٧٥%-٨٠%) لهذا فان عملية التلدين ادت الى تحويل طور الهدروكسيد الى طور الاوكسيد. كما ان عملية التلدين سببت بقليل فجوة الطاقة البصرية.