Structure and Optical Properties of ZnCdO Thin Films Prepared by Spray Pyrolysis

Jabbar H. Khlaief
Department of Applied Science, University of Technology, Baghdad-Iraq.
E-mail: jabbaralhassen@yahoo.com.

Abstract

ZnCdO films were compounded by spray pyrolysis on glass substrates at temperature of 250C^o, using solution of zinc acetate and cadmium acetate salts with various additions concentrations of Zn (25, 50, 75)%. Structure and optical properties have been analyzed using XRD and UV-Vis spectroscopy. XRD analysis premiered that thin films were of polycrystalline nature with face centered cubic structure. The crystallinity increases when the Zn additions increases. Film additions with 75% Zn has minimum value of dislocation density and strain which confirm the improved crystallinity of the film. The optical results featured the transparency of the ZnCdO films is greater than 80% in the visible region, and we found when the concentration of Zn additions increase the optical band gap increasing from (2.49 to 2.9eV).

Keywords : ZnCdO, thin film, spray pyrolysis, optical and structural properties.

Introduction

Transparent conducting oxide (TCO) have been discerned and employed technologically for time worn(1). ZnO has prestigiously transparency in electromagnetic spectrum of visible region with an extra energy gap about (3.37eV)(2), stellar c-axis orientation, piezo electronic comportment and high excitation binding energy (60meV) which is much higher than the other semiconductors materials, all these properties makes it a good materials for optoelectronic device(3). As a result of alloying within magnisum oxide or cadmium oxide the band gap of the substance can increase up to 4eV or decrease down to 2.8eV(4) hence, CdO when combined with wide band gap materials and when the carrier density increased the band gap different between 2.2 to 2.9 eV(5). ZnO(6) and CdO(5) are well known, particularly asemulsion powders(7) these two materials which belong to transparent conducting oxide of group II-VI of the semiconductor components with n-type(8).

Then, it is anticipate that the homogenous composition of the two substance to form a new materials may change in the electrical and optical properties of both cadmium oxide and zinc oxide which is useful for various applications such as buffer layer in solar cells(9,10), photocatalysis(3) and transparent electrods(8). There are also a number of methodes used to deposit ZnCdO thin films such as sol-gel spin coating(11), spray pyrolysis(12), DC reactive magnetron sputtering(4), pulse laser deposition(13) and molecular beam epitaxy(14). Between all these techniques, spray method it is benafet and alternative for acquires thin films(15). It has advantage compared with other method because of simplicity, inexpensive, flexible and minmal waste produced also it has not need to vaccum apparatus became high(16). Then, spray pyrolysis parameters like spray nozzle distance, substrate temperature, solution concentration, spray rate, and pressure carrier gas can tune the film properties well(17).

In this literature, thin films of ZnCdO have been prepared by a technique of spray pyrolysis and investigated their structural and optical properties by used the X-ray diffraction also UV-Vis spectroscopy. In X-ray the value of full width at half maximum (FWHM) acquired from prioritized directives of two pure admixture by using the formula of Debye – Sherrer to conjecture the grain size (D)(17):-

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \quad \text{.........} (1)$$

Where λ is the X-ray wavelength which is 0.15418nm, β is full width in a half maximum of the peak that has a maximum intensity and θ is Bragg angle.

Where the dislocation density (δ) which predefined as the length of dislocation lines perunit volume, and it has been reckonsed by using the equation(18):-

$$\delta = \frac{1}{D^2} \quad \text{.....} (2)$$

Its defined as the measure of the defects value in the crystal and the amount of dislodging bushiness obtained. The strain has been speculated by using the relation(17):-

$$\varepsilon = \frac{\beta cos\theta}{4} \quad \text{.....} (3)$$

The optical properties such as absorption coefficient (α) was found to follow the equation [19]:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \quad \text{.....} (4)$$

Where (d) represent thin film thickness, (T) is transmittance.

The extinction coefficient (k_o) could be calculated by using the equation(2):-

$$k_o = \frac{\alpha\lambda}{4\pi} \quad \text{.....} (5)$$

Where (α) is the absorption coefficient and (λ) is the wave length of the incident photon.

The value of band gap for ZnCdO films deposited using spray technique calculated by using the relation [17,20]:

$$\alpha h\nu = A\ (h\nu - E_g)^m \quad \text{.....} (6)$$

Where *(A)* as a constant, E_g is energy band gap of ZnCdO film, $h\nu$ is the incident photon energy, and (m=1/2) for direct allowed transitions and (m=2) for the indirect allowed transition.

Experimental work

ZnCdO thin films were deposit onto glass substrate by using spray pyrolysis methode. The spray solution consists of cadmium acetate dehydrate dissolved in distelled water to investigate the doping effect of Zinc on CdO films, we have used zinc acetate dehydrate as a source of matrial for zinc which was added in different weight percentage such as 25, 50, 75%. The temperature of substrates were $250C^0$, the carries gas used was comperesed air and the space between the nozzle and substrates were 25cm. The studying of structure determined by x-ray diffractometer (PW/1710, Philips model) with CuKα radiation (35mA and λ=0.15418nm at 40kV) the optical measurements were studied by using UV-visible spectrophotometer (UV-1650 UV-visible recording spectrophotometer) to measure optical transmittance films in the range (300-900) nm.

Results and Discussion

1- Structural properties

Fig.(1) represent the diffraction pattern of x-ray for films deposited at various concentrations of aqueous solution. The prepared films exhibit polycrystalline nature with cubic structure. In patterns whole diffraction peaks refers to wurtzite-structured ZnO reflection of planes also the samples Cd (O), Zn0.25Cd0.75 (O), Zn0.5Cd0.5 (O) and Zn0.75Cd0.25 (O) have a strong (111) and (200) phase of peak with respect to standard data (ICDD)(11, 16). It is observed that the peak corresponding to (002) plane and (201) of ZnO increases with the increase in Zn addition concentration. We can observed another important peak represent by 102, 110, 103 and 112 peak intensities increased with increasing Zn concentration corresponding to cubic CdO in addition to hexagonal peaks of ZnO. This propounds with all the compounded thin films of ZnCdO have a structure of the hexagonal wurtzite which are preferentially oriented along the c-axis perpendicular to the surface of substrate. All peaks of diffraction have been indexed according to the hexagonal phase of ZnO. In the films there are characteristic peaks of impurity phases could not be found except ZnO where take place that revealed to a good crystalline in the samples nature. The peaks sharpness clarifies that the nature of films are polycrystalline and monoclinic, these result were good agreement with references(9, 13, 14). By applied the formula (1) we can estimate the grain size which portrayed in Fig.(2). It is shows that the grain size increased with increasing the Zn addition also it could be attributed to improvement in the crystallinity at higher value of Zn addition. This improvement in the order of structure could also be attributed to the increase in the density of ZnCdO film, these predilections propounds that Zn dopant creats engender nucleation center, with the increase in Zn addition concentration, the diffraction lines become more sharp, thus illustrates an increase in the size of crystallites our results agreement with references[9, 10]. In the present work Fig.(3) show the value of δ which calculated from equation (2) when 25% Zn addition we can see that the dislocation has a maximum value because of the interaction between Zn and defcets very weak and the expanded lattice caused by Zn incorporation into CdO is the factor that affects the defect formation energies, thus the interaction between Zn and Cd for high of Zn addition assures that the good crystallinity of the films at 75% Zn addition and low defects produced which prepared by utilization this simplified spray pyrolysis method. The strain as afunction to additions concentration depicted in Fig.(4) And we found that the film has an addition with 75% Zn has the minimum value of strain resulting in a variation in lattice constant when the lattice constant decrease indicates that the large Cd ions are substituted by the smaller Zn ions in the hexagonal wurtzite ZnO structure and hence there is decrease in lattice parameter which favors for improved the crystallinity of this film[10,11].

2- Optical properties

The optical transmittance spectra of ZnCdO films processed on glass substrate with different additions of Zn concentration in the range of wavelength about 300 – 900 nm are illustrated in Fig.(5). It is observed that the optical transmission increases slightly with increasing the Zn addition concentration. Assuming that the diffusion of surface for the atoms deposited have been enhanced with increasing the Zn concentration and should be also improved. Hence, when the CdO concentration decrease, result from widening the bandgap energy of the films and transmittance of films increased up to 80%, which shows a persuaded optical window of optoelectronic applications[21]. All films appears an abrupt change in transmission attributed to the concentration of free carrier have been increased which might be to decrease in thickness of films these results indicates good crystanillity and direct transition[9,11,15]. The dependences of absorption coefficients α on wavelength have been determined from equation (4) are represented in Fig.(6) for films doped with different Zn concentration. At low wavelengths decrease occurs in the absorption coefficient around the absorption edge this decrease in (α) as the Cd concentration increase could be correlated to the decrease in the absorption due to the increased the transparency[12] and leads to increase in smoothess which might be due to the enhansment of crystallinity and the concentration of carriers have been increased that leads to fill the bottom of the conduction band also that filling prevents the photogenerated carriers from transition of into the levels that filled according to the rules of quantum and that leads to far transitions with larger photon energy.

The extinction coefficient could be calculated from relation (5). Fig.(7) show that the extinction coefficient has the same behavior but increase with increasing of Zn addition concentration. The increasing in the extinction coefficient values with increasing the addition concentration is due to increases in the absorption. Is directly return to the absorbtion of light which become large with increasing the concentration of zinc addition[2].

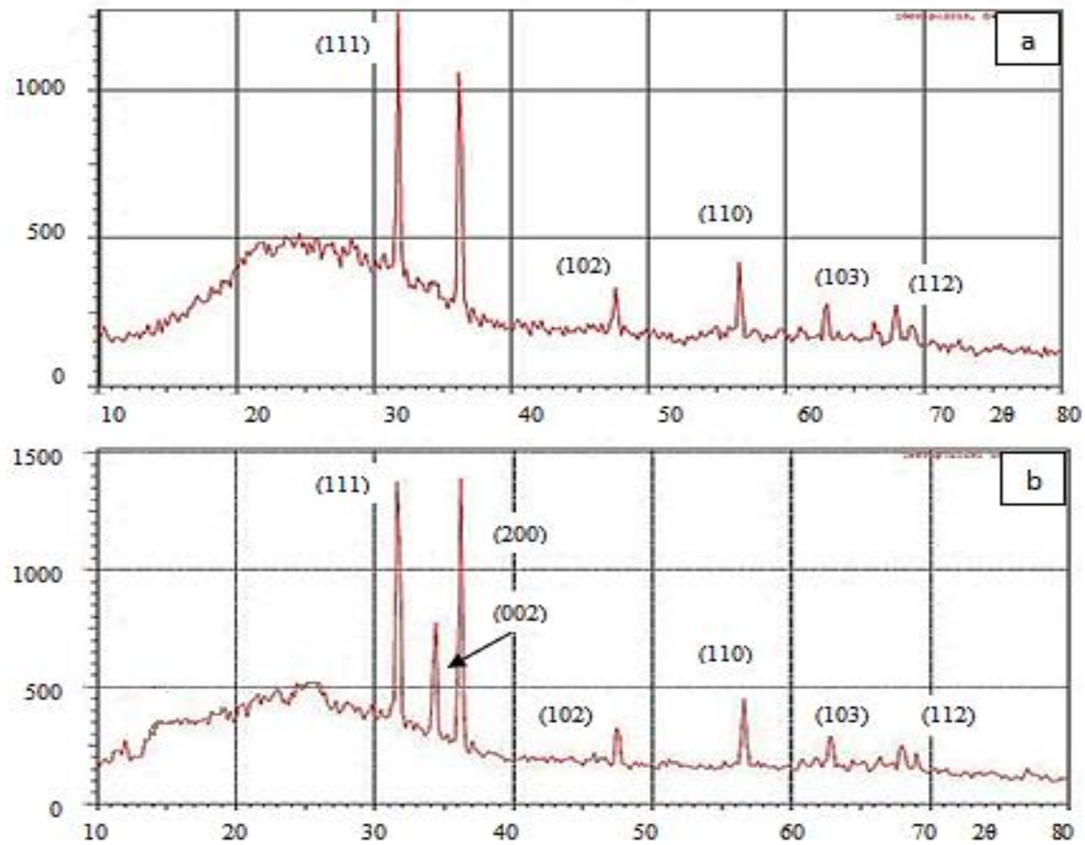
The $(\alpha h\nu)^2$ varying versus the photon energy $(h\nu)$ represents the direct band gap for different Zn additions shown in Fig.(8). The values of band gap have been estimated by using the formula (6). As the Zn additions increases the optical band gap is blue shifted from 2.49 to 2.9 eV. Thus on increase in band gap has been observed this may be due to the hexagonal phase. This band gap broadening is due Moss-Burstein effect. The effect of Moss-Burstein is related within elevation the Fermi level into the conduction band of degenerate semiconductors, which causes of broaden in band gap these results in agreements with published literatures[3,17].

Table (1)
Represent the value of different concentration.

Ratio additions ml	dislocation density δ	Strain ε	absorption coefficient $(\alpha)cm^{-1}$	extinction coefficient (k_o)	Energy gap (eV)
0	3.05E-05	0.1168	9.49E+04	1.99E-01	2.49
0.25	3.41E-05	0.1245	9.78E+04	2.03E-01	2.65
0.5	3.10E-05	0.1181	9.81E+04	2.07E-01	2.78
0.75	3.04E-05	0.116	1.09E+05	2.27E-01	2.9

Conclusions

The structural and optical properties for ZnCdO films which deposited by spray pyrolysis have been studied. The films showed a good structural properties with variousdopant concentrations of Zn (25, 50, 75)%. Structure properties reveal crystallinity increases with Zn additions increases. Film with 75% Zn addition has a minimum value of dislocation density and strain which assures to improve the crystallinity of the film. The optical transmission results showed that transparency of the ZnCdO films is greater than 80% in the visible region with optical band gap increased from (2.49 to 2.9eV) with the increasing of Zn addition concentration.



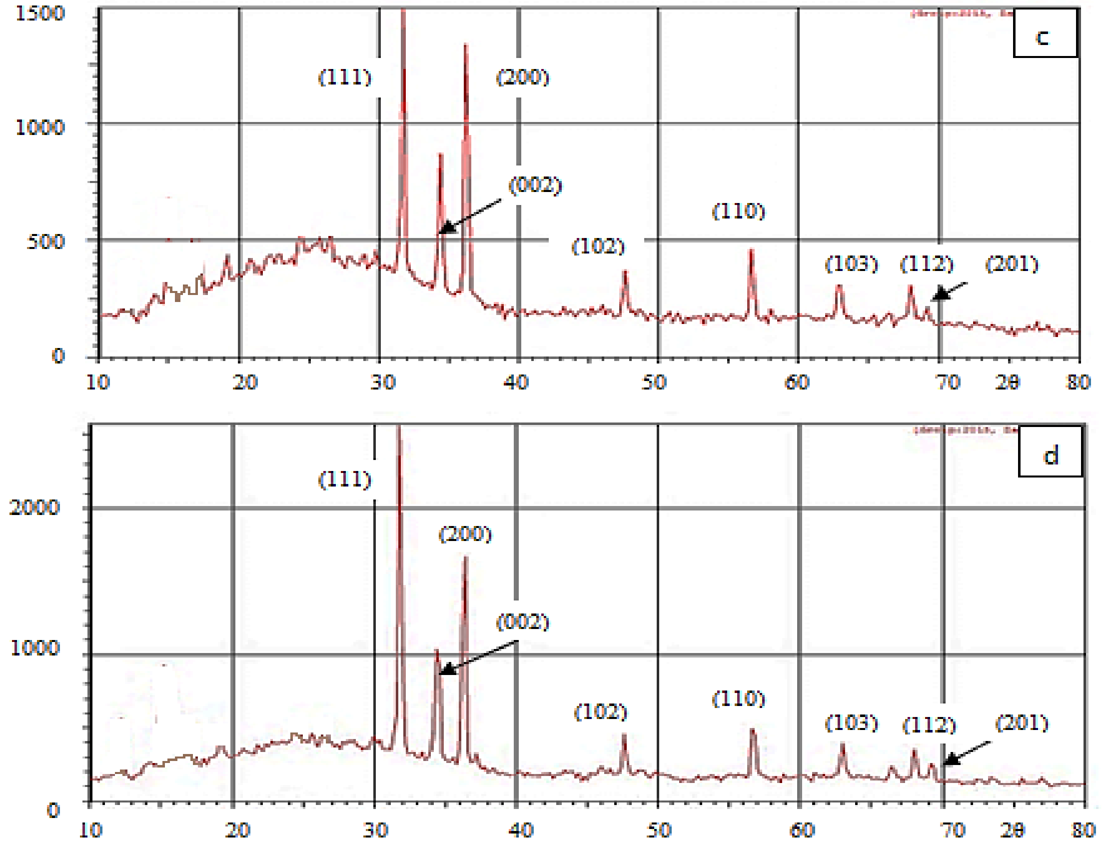


Fig.(1): X – ray diffraction for ZnCdO thin films with different Zn Additions a) 0% b) 25% c) 50% and d) 75%.

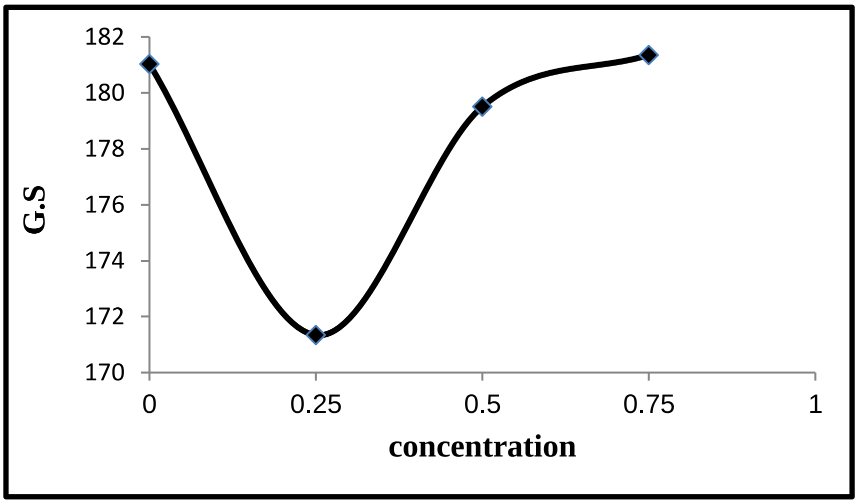


Fig.(2): Grain size of ZnCdO films with different concentration of Zn additions.

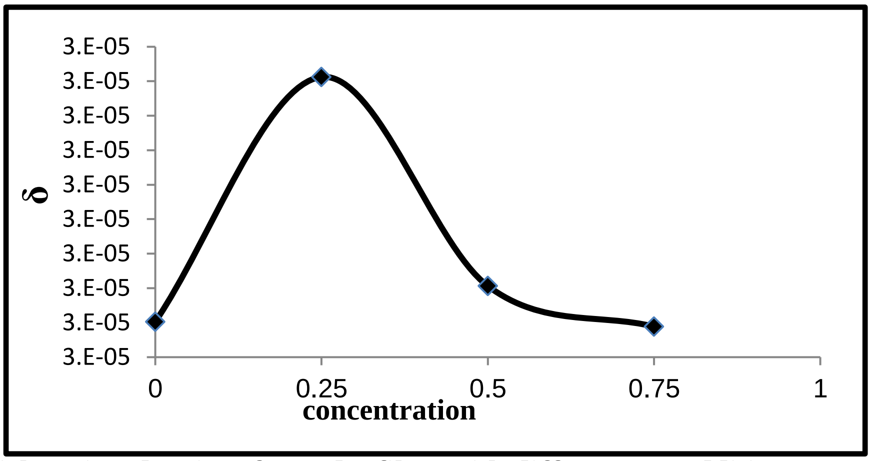


Fig.(3): Dislocation density of ZnCdO films with different Zn addition concentration.

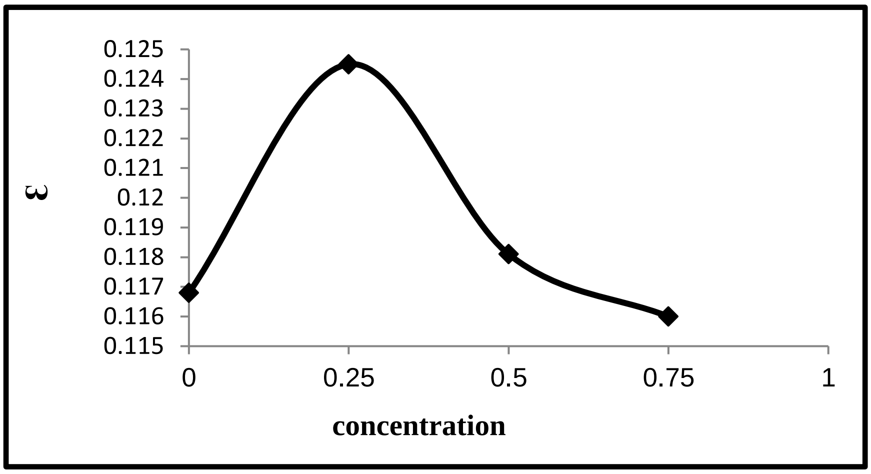


Fig.(4): Strain of ZnCdO films with different concentration of Zn addition.

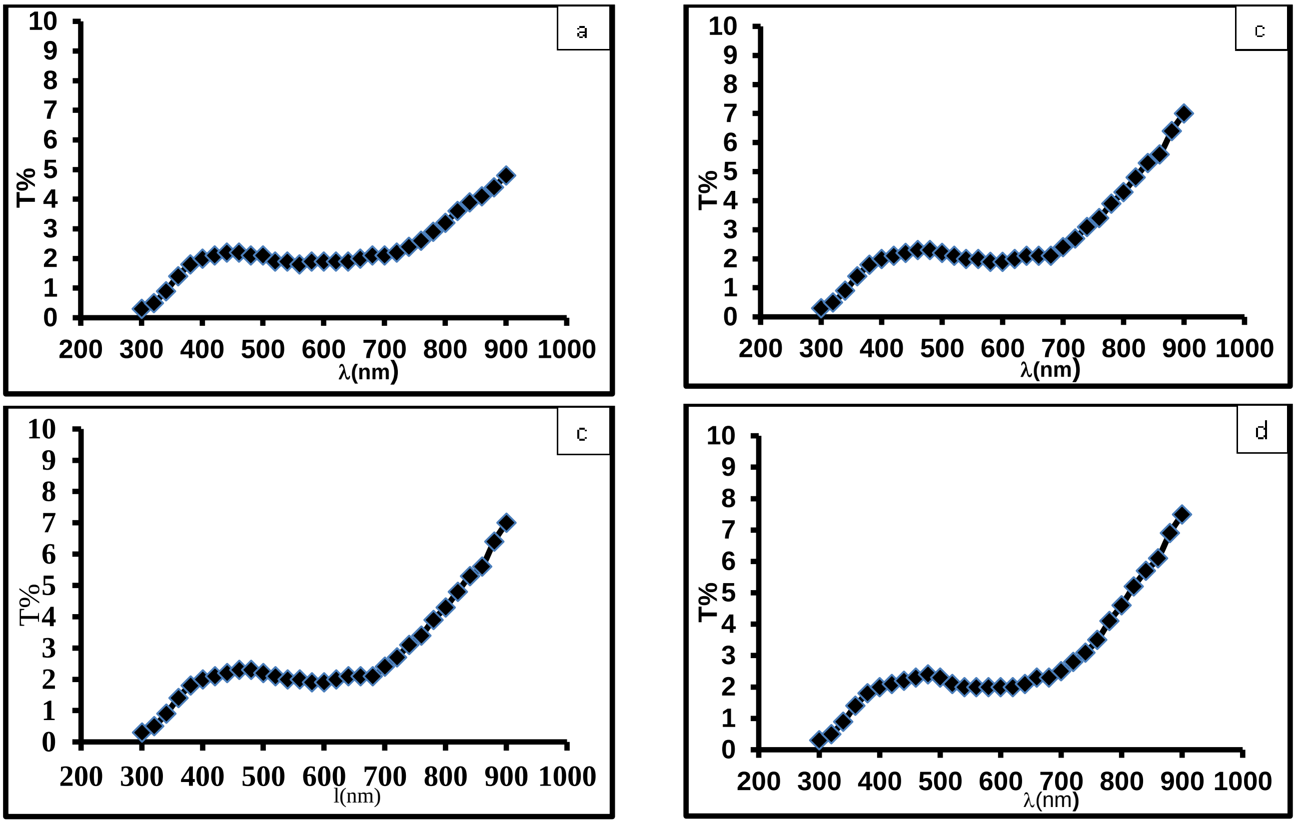


Fig.(5): Transmission spectra for ZnCdO thin films
a) without Zn addition b) 25% Zn addition c) 50% Zn addition and d) 75% Zn addition.

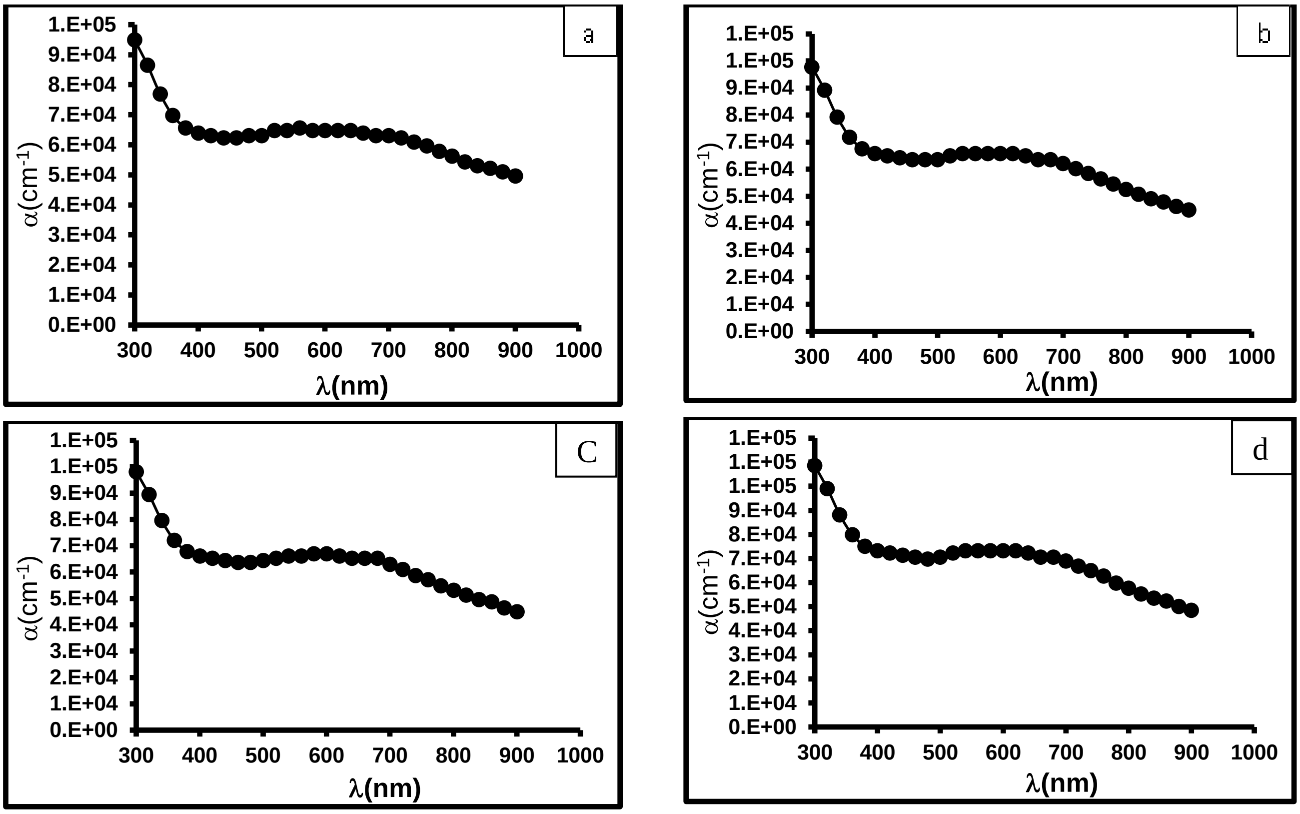
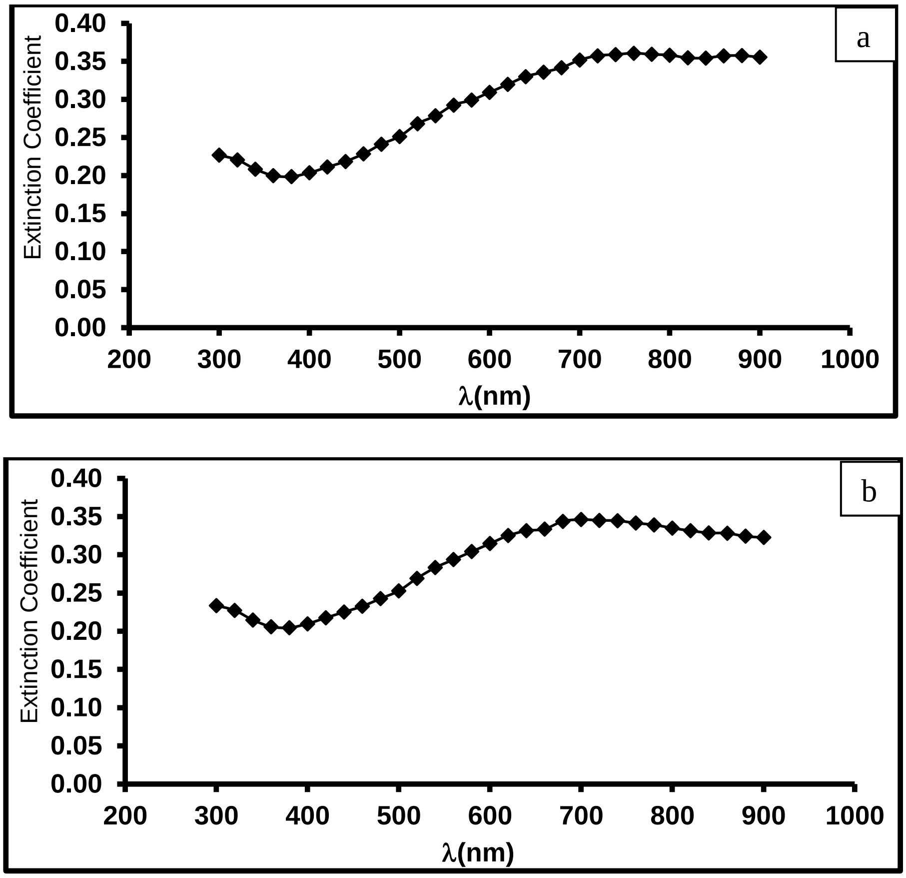


Fig.(6): Absorption coefficient of ZnCdO thin films for
a) 0% Zn addition b) 25% Zn addition c) 50% Zn addition and d) 75% Zn addition.



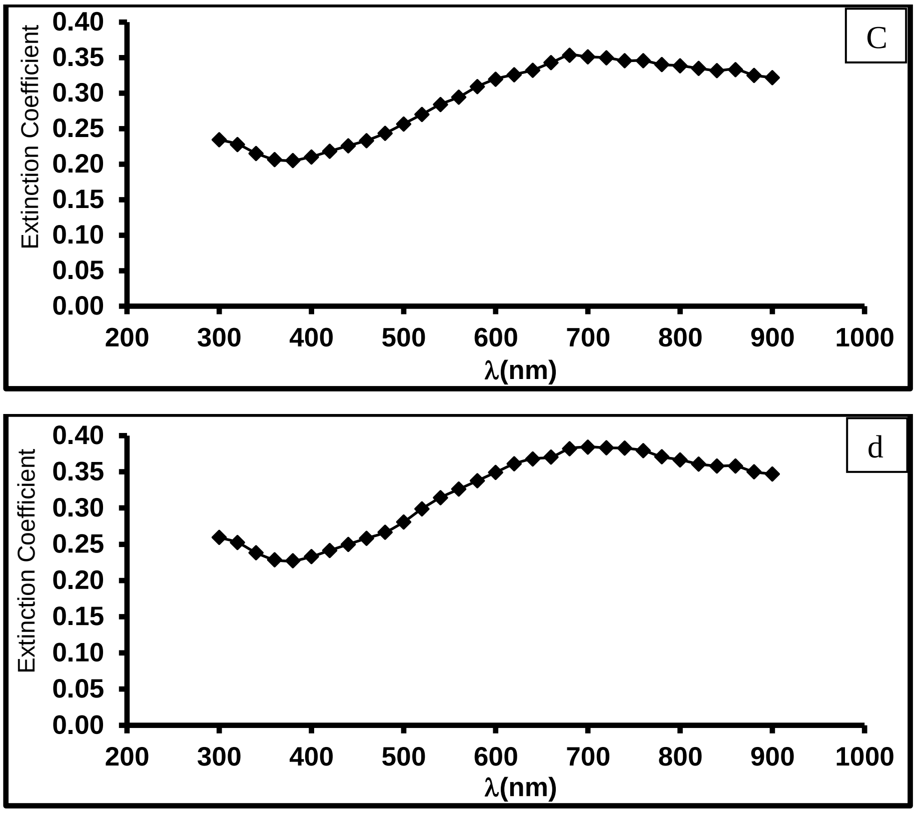


Fig.(7): Extinction coefficient of ZnCdO thin films for
a) 0% Zn addition b) 25% Zn addition c) 50% Zn addition and d) 75% Zn addition.

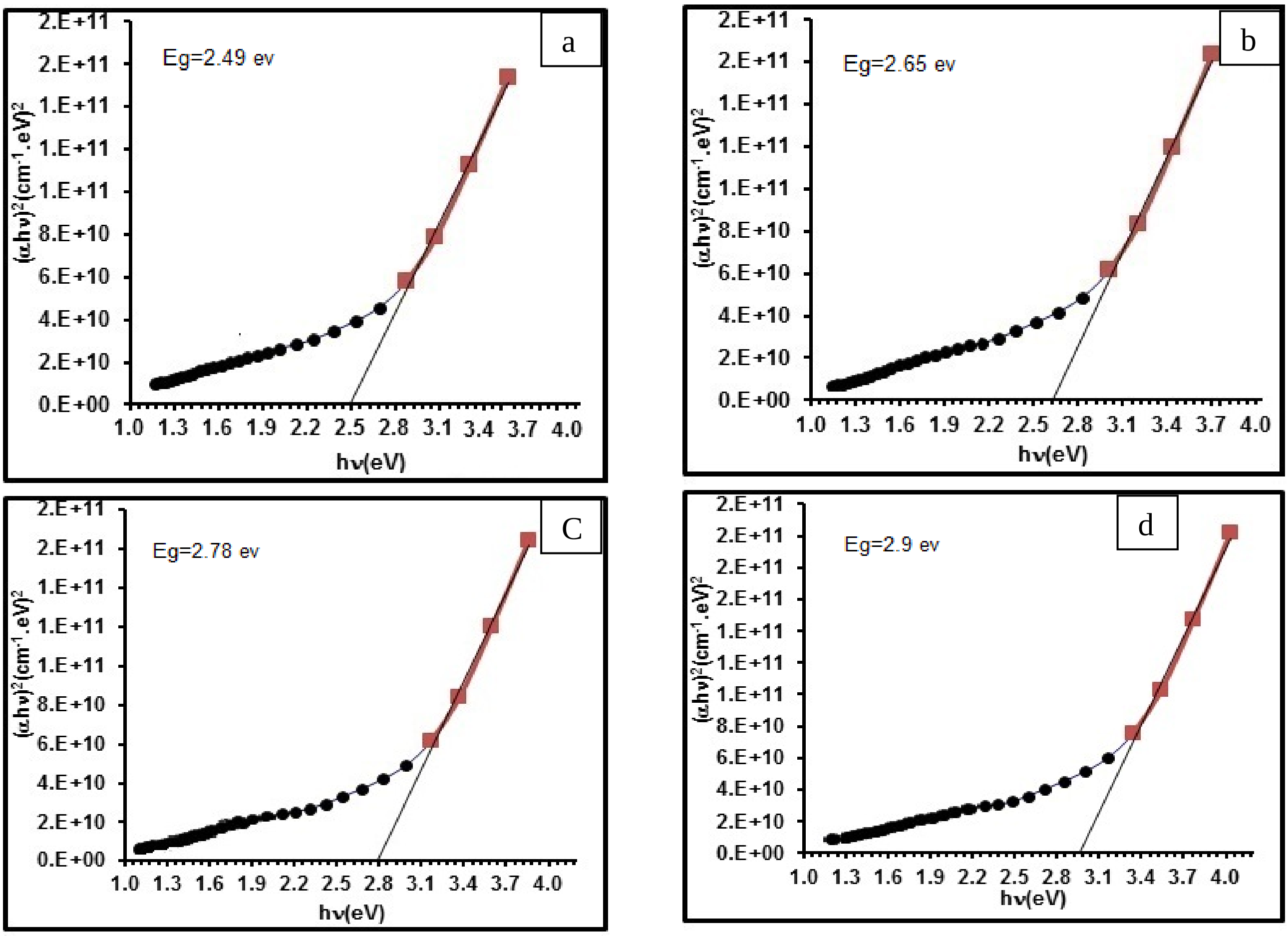


Fig.(8): Direct band gap of ZnCdO thin films for
a) 0% Zn addition b) 25% Zn addition c) 50% Zn addition and d) 75% Zn addition.

References

[1] G. A. Flores*a*, B. V´. P´erez*b*, A. P. Rodr´ıguez*a*, M. V. Garcia*a*, S. C. T´ellez*a*, J. A. Guzm´an*a*, C. Falcony*c*, and M. A. Frutis*a* "Electrical and structural characteristics of spray deposited $(ZnO)_x(CdO)_{1-x}$ thin films" Rev. Mex. Fis. 59, 403–411, (2013).

[2] W. H. Abass "Annealing Effect on the Optical Properties of (ZnO)x(CdO)1-x Films Obtained by Spray Pyrolysis" Ibn Al-Haitham Journal f or Pure and Applied Science 25(1), (2012).

[3] Umer Mushtaq and Souad. A. Mohamad "ZnxCd1-x (O) Thin Film Nanorods for PV Applications" International Journal of Nano Science and Technology 1(3), 9-16 (2013).

[4] Ma De Wei et al "Structural and optical characterization of $Zn_{1-x}Cd_xO$ thin films prepared by dc reactive magnetorian sputtering" Chin. Phys. Lett. 20(6), 942-944, (2003).

[5] Hassan H. Afify, Ninet M. Ahmed, Magdy Y. Tadros, Fatma M. Ibrahim "Temperature dependence growth of CdO thin film prepared by spraypyrolysis" Journal of Electrical Systems and Information Technology 1, 119–128, (2014).

[6] R. Ferro, J. A. Rodríguez, I. Jiménez, A. Cirera, J. Cerdà, and J. R. Morante "Gas-Sensing Properties of Sprayed Films of (CdO)x(ZnO)1-x Mixed Oxide" IEEE Sensors Journal, 5(1), 48-52, (2005).

[7] E.K. Elmaghraby, M.A. Kaid and M.F. Zaki "Optical Characterization of $(CdO)_x(ZnO)_{1-x}$ Composite by Spray Pyrolysis Technique" Acta Physica Polonica A 125(1), 82-86, (2014).

[8] Halima B., Noureddine B. and Kamel S. "Characterization by the Impedance Spectroscopy of (ZnO)(X)(CdO)(1-X) Composite Thin Films" Sensors & Transducers, 27, 67-74, (2014).

[9] Hind T. Derraz "A structural study and a Prediction of Optical Constants of the Thin Films of ZnxCd1-xO (x=1-0.6-0.4-0) using an Effective Model" Open Journal of Applied Chemistry and Biotechnology (OJACB), 1(1), 1-7, (2013).

[10] S. J. Helen, Suganthi Devadason, T.Mahalingam "Effect of Zinc Doping on Cdo Thin Films Prepared by Spray Pyrolysis Technique" International Journal of Science and Research (IJSR) ISSN (Online): 2319-7064, Impact Factor: 4.438, 61-63, (2013).

[11] Amritpal Singh and Praveen Kumar "Structural, morphological and optical properties of sol gel processed CdZnO nanostructured films: effect of precursor solvents" International Nano Letters, 3-57, (2013).

[12] Usharani K., Balu AR., Shanmugavel G., Suganya M., Nagarethinam VS. "Transparent Conducting CdO Thin Films Fabricated by Low Cost Simplified Spray Technique Using Perfume Atomizer" IJSRR 2(3), 53-68, (2013).

[13] Kumar, V, Lethy, K, Kumar, A, Krishnan, R, Pillai, NV, Pillai, V, Philip "Effect of cadmium oxide incorporation on the microstructural and optical propertiesof pulsed laser deposited nano structured zinc oxide thin films" Mater.Chem. Phys. 121, 406-410, (2010).

[14] Sadovef, S, Blumstengel, S, Cui, J, Puls, J, Rogaschewski, S, Schafer "Visible band-gap ZnCdO heterostructures grown by molecular beam epitaxy". Appl. Phys. Lett. 89, 201-207, (2006).

[15] P. Sri devi "Structural and Optical Properties of Cerium Doped Zinc Oxide Thin Films using Spray Pyrolysis" Journal of Nanoscience and Nanotechnology, 2, 34-37, (2014).

[16] Azhar I. Hassan, Khawla S. khashan and Aseel A. Hadi "Optical and Structural Properties of Cdo Thin Film" Eng. &Tech. Journal, 31(5), 613-620, (2013).

[17] G. Shanmugavel, A.R. Balu and V.S. Nagarethinam "Preparation of Cadimum Oxide Thin Films by Spray Technique Using Perfume Atmoizer and Effect of Solvent Volume onThier Physical Properties" International Journal of Chemistry and Materials Research, 2, 88-101, (2014).

[18] Han X, Liu R, Zhude Xu et al. "Annealing studies on the structural and optical properties of electrodeposited CdO thin films" Electochem. Commun. 7 (2005).

[19] J. A. Najim, J. M. Rozaiq "Effect Cd Doping on the Structural and Optical Properties of ZnO Thin Films" International

Letters of Chemistry, Physics and Astronomy 10(2), 137-150, (2013).
[20]. A. Karpinski, N. Ouldhamadouche, A. Ferrec, L. Cattin, M. Richard-Plouet, L.Brohan, M.A. Djouadi, P-Y. Jouan “Opticalcharacterization of transparent nickel oxide films deposited by DC currentreactivesputtering” Thin Solid Films 519, 5767–5770, (2011).
[21] Douaa S Jbaier “Physical Properties of Cdo Thin Films Prepared by Spray Pyrolysis Technique” Eng. &Tech. Journal, 31(2), 185-193, (2013).

الخلاصة

اغشية اوكسيد الكادميوم–الزنك تم تحضيرها بطريقة الرش الكيميائي الحراري على قواعد من الزجاج وبدرجة حرارة 250 درجة مئوية، باستخدام محاليل لاملاح الكادميوم والزنك وبنسب اضافة مختلفة لمادة الزنك (25,50,75%). الخصائص التركيبية والبصرية تم تحليلها باستخدام حيود الاشعة السينية ومطياف الاشعة المرئية – فوق البنفسجية. واظهرت نتائج حيود الاشعة السينية أن الاغشية الرقيقة ذات طبيعة متعددة التبلوروبتركيب الوجه المركزي المكعب. وبينت نتائج النفاذية البصرية بأن اغشية اوكسيد الكادميوم زنك ذات نفاذية عالية اكبر من 80% للمنطقة المرئية. وقد وجدنا عند زيادة تركيز اضافة الزنك ان فجوة الطاقة تزداد من (2.49 الى 2.9 الكترون فولت).