Structural and optical characterization of cobalt-doped zinc oxide thin films deposited by chemical spray pyrolysis

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Abstract:

In our experimental pure and cobalt (Co) doped Zinc oxide (ZnO) thin film were prepared onto glass substrate chemical spray pyrolysis technique at 400 ^{o}C, X-ray diffraction, Atomic force microscope and optical properties were all investigated for each prepared films. Nanocrystalline films with hexagonal structure and strong (100) and (002) preferred orientation were obtained. The maximum value of average grain size is (15.7) nm with 6% Co-doping concentration. The optical transmission spectra have shown that both pure and doped ZnO films were transparent in UV-Vis wavelength region. The energy band gap of 0% Co is about 3.28 eV and decrease to 3.2 eV after 4% doping. The excellent-estimated structure, the optical results are accomplished in doped ZnO film with (4 and 6) % Co.

Keywords: Zinc oxide, cobalt, thin film, spray pyrolysis, optical properties.

الخصائص التركيبية والبصرية لأغشية أوكسيد الزنك الرقيقة المطعمة بالكوبلت والمرسبة بالرش الكيميائي الحراري

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الخلاصة:

تم في هذا البحث تحضير ودراسة الخصائص التركيبية والبصرية لا غشيه اوكسيد الزنك النقية والمشوبة بالكوبلت والتي تم تحضيرها على قواعد من الزجاج بدرجه 400 درجه سيليزية باستخدام منظومه الرش الكيميائي ، حيث تم دراسة الخصائص التركيبة باستخدام حيود الأشعة السينية ومجهر القوئ الذريه واضحت النتائج تأثير التشويب بالكوبلت علئ اغشيه اوكسيد الزنك ، حيث اظهرت نتائج الاشه السينية التركيب اسداسي للأغشية المحضرة والاتجاه السائد 100،200 والتركيب نانوني للأغشية المحضرة حيث ان اعلى حجم حببي 15،7 نانومير عند نسبه التشويب 6% كما اظهرت نتائج الخصائص البصريه انخفاض في فجوه الطاقة البصرية.

الكلمات المفتاحية: اوكسيد الزنك ، اغشيه رقيقه ,كوبلت ، خواص بصريه ، رش كيميائي.

1. Introduction

In the last few years Zinc Oxide has been studied briefly by researcher due to its interesting chemical and physical properties. It is II-vI semiconductors with (3.37 eV) direct wide band gap. [1,2].

It is showing a high refractive index [3] and highly transpareny in both regions the visible and near infrared. Thin film for ZnO is promising photonic devices use in laser diode, transparent electrodes, UV-light emitting diodes, Varistors, photovoltaic cells, hetrojunction solar cells and so on [4,5].

ZnO thin films can be prepared by many techniques like pulsed laser deposition [4], chemical vapour deposition [6], sol-gel techniques [7], , molecular beam epitxy and spray pyrolysis. [8]. In this studies Zno doped with cobalt were prepared by chemical spray pyrolysis , that is an appropriate technique for large scale production, low coast, it offers many advantage in producing nanocrystalline thin films [9], like a simple deposition on glass substrate with a large temperature, fine porous microstructure and easy control of thin film thickness. [10]

Literature data shown that ZnO nanostructure doped with various elements such as Mn, Al, Na, Mg, Ni, Ag and Cd [8,11,12], however , one of the most elements that have various applications is cobalt [13]. ZnO doped with cobalt have several applications such as ferromagnetism, transparent conduction, semiconductor and solar cells. The film was prepared to have good optical band gap energy at lower temperature and resistivity, also have high conductivity and lower cost . The films take into consideration to be an utmost essential. [14]

In this work, Co doped ZnO thin film were deposited onto glass substrate by spray porylises techniques, the solutions were sprayed on substrate and heated up to 400 ^{o}C. The effect of Co concentration on ZnO thin film was studied by XRD, AFM and Uv-Vis spectrophotometer.

Materials and methods:

Pure and Co doped ZnO thin films were prepared by a chemical spray pyrolysis. Zinc acetate dehydrate (C_4H_6O. Zn. $2H_2O$) and pure (cobalt (II) chloride hexahydyrate $CoCl_2$. $6(H_2O)$) each one were dissolved in 100 ml double distilled water to prepare 0.1 M starting solution. The concentration of source materials was relativity adjusted to increase Co doping between (0,2,4,6) % vol, the prepared solution was sprayed on a 400 ^{o}C heated glass , the distance between spray nozzles and glass substrate was kept at 30 cm.

Characterizations:

Pure and Co doped ZnO phase structure and crystallographic nanostructure thin films were checked by (CuKα) XRD-6000, Shimadzu X- ray diffractometer at scanning between (25–70), the tomography of surface for prepared films were investigated by Atomic Force Microscopy (AFM) (Angstrom AA 3000). The optical properties investigated by using UV-Vis spectrophotometer in the range of wavelength (200-1100) nm.

Result and discussions:

The crystal structure of pure and Co-doped ZnO thin films.

The XRD of pure and Co-doped ZnO thin films are shown in fig. (1), as it can be seen that all the films demonstrate that the hexagonal type structure (ICCD No.4546), the diffraction peaks located at 2θ = 100, 002, 101, 102, 110, and 103 plans respectively, for pure ZnO film, whereas for all Co-doped ZnO films the diffraction peaks 2θ= (002) and (102) plans was appear.

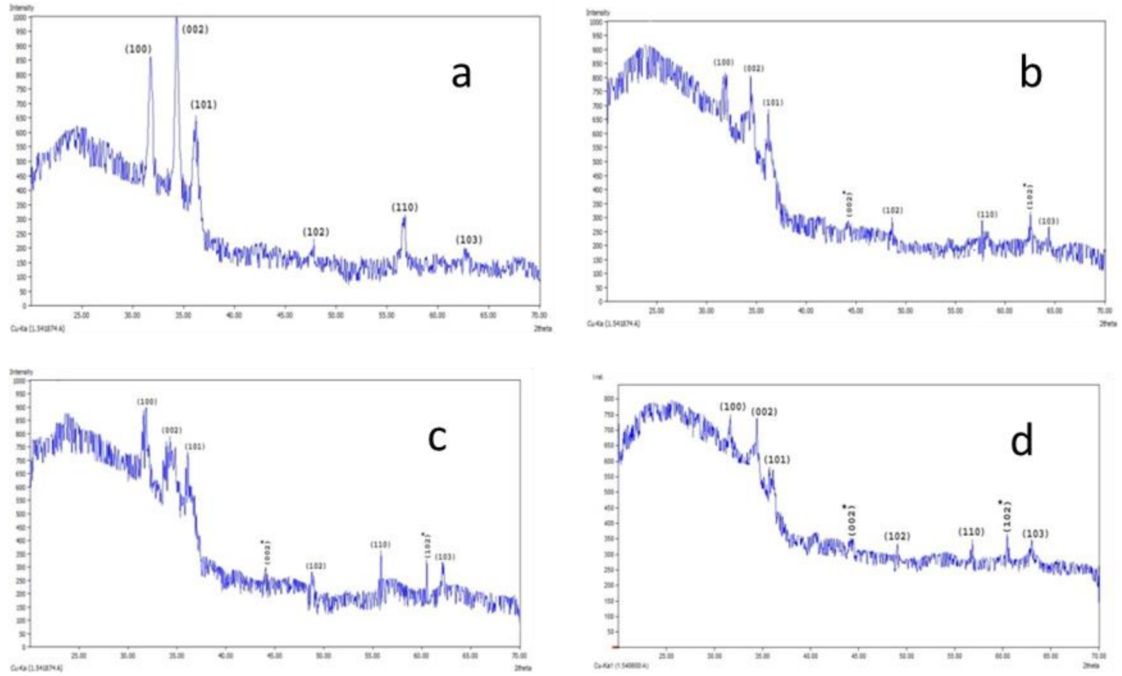

Fig (1): X-ray diffraction patterns for: [(a) 0%, (b) 2%, (c) 4% and (d) 6%] Co-doped ZnO thin films.

The grain size of samples were determined by Sherrer formula [15]

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where: λ = 1.5406 A^0, β: full width at half Maximum (FWHM) and θ: Bragg angle.

Table (1): X-ray diffraction parameters of pure and Co doped ZnO thin films

Sample	planes	2Θ (deg)	d (nm)	FWHM (deg)	Average G.S (nm)
ZnO_{pure}	(100)	31.8	0.281	0.75	12.680
	(002)	34.9	0.256	0.5	
	(101)	36.5	0.245	1	
	(102)	47.6	0.190	0.5	
	(110)	56.5	0.162	0.75	
	(103)	62.7	0.148	1.25	
ZnO:2% CO	(100)	32.1	0.278	1	12.750
	(002)	34.9	0.256	0.55	
	(101)	36.5	0.245	0.6	
	(002)*	44	0.203	1.05	

	(102)	49	0.185	0.55	
	(110)	58	0.158	0.75	
	(102*)	63.5	0.146	0.8	
	(103)	64.3	0.144	0.75	
ZnO:4% CO	(100)	32.1	0.278	1.1	14.638
	(002)	34.9	0.2567	1.55	
	(101)	36.5	0.245	0.75	
	(002)*	44	0.20554	0.6	
	(102)	49	0.185	0.5	
	(110)	56	0.164	0.4	
	(102*)	60.5	0.1528	0.5	
	(103)	62.5	0.148	0.6	
ZnO:6% CO	(100)	31.8	0.2810	0.5	15.728
	(002)	34.9	0.256	0.5	
	(101)	36.5	0.245	0.5	
	(002)*	44	0.205	1.05	
	(102)	48.5	0.187	0.5	
	(110)	56.5	0.162	0.5	
	(102*)	60.5	0.152	0.6	
	(103)	63.1	0.147	0.8	

Table (1) presented the variation of (FWHM) and crystalline size with Co doping ratio, the variation of crystalline size was opposite to (FWHM), the crystalline size increase with Co-doping ratio, it shows that higher crystalline size when 6% Co-doping ratio, the increase of

Crystalline size was revealed the enhancement of crystallinity under c-axis orientation for ZnO thin films.

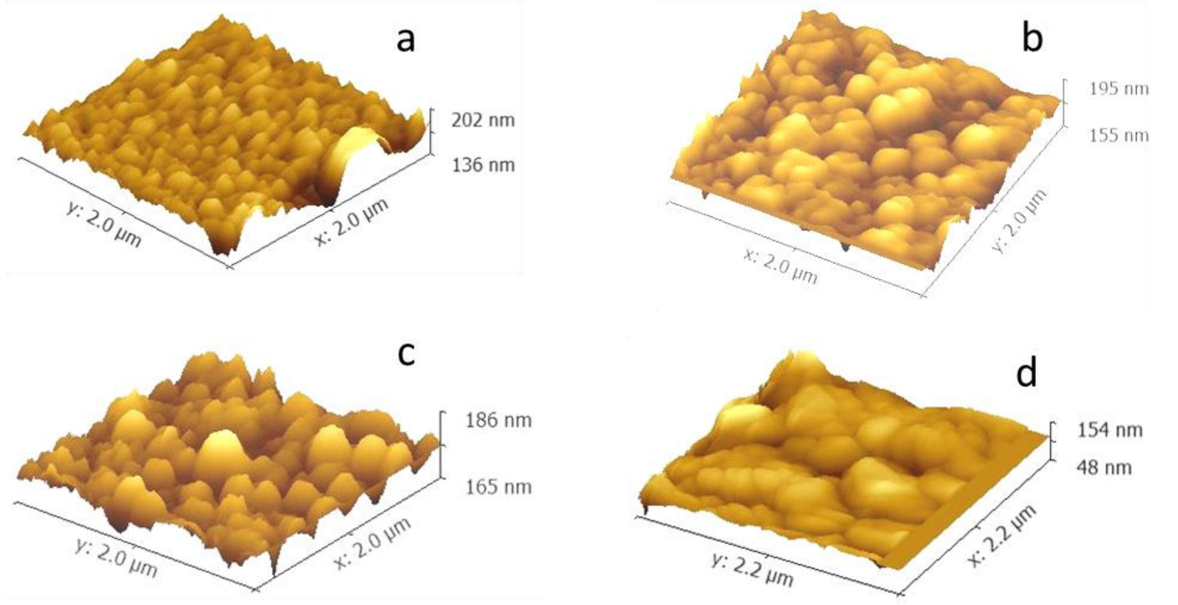

Fig: 2: 3-D images for: [(a) 0%, (b) 2%, (c) 4% and (d) 6%] Co-doped ZnO thin films.

Table (2): AFM data for pure ZnO and different Vol.% of Co thin films

Sample	RMS (nm)	Roughness (nm)	Average Diameter (nm)	Average Height (nm)	Surface Thickness (nm)
ZnO pure	2.21	4.2	30.5	202	136
ZnO:CO 2%	5.85	6.37	42.1	195	155
ZnO: CO 4%	6.66	7.1	46.4	186	165
ZnO: CO 6%	9.04	11.68	60.7	154	48

From fig. (2) the morphology of the films showed the regular and homogenoues structure. The RMS and roughness were increased with increased Co- doping concentration. The average diameter was increased with Co-concentrations, while both of average height and surface thickness were decreased with Co–concentration, the result of AFM with XRD analysis that clearly indicate crystallinity is influenced by the concentration of Co – doping.

Fig (3) shows the transmission spectra of all prepared films as a function of doping levels. As it can be seen strong transparency region is located between (400-1100) nm, the average transmission has the value about 88%, Co doping caused a decrease in the optical transmission of ZnO thin films. The increase of doping concentration between 0 to 4 %, but for 6% Co doping the optical transmittance was increased up to 90%, the decrease of transmittance may occur because of the increase in the particle size due to the progression of Co in ZnO thin films, this result is agreement with [14].

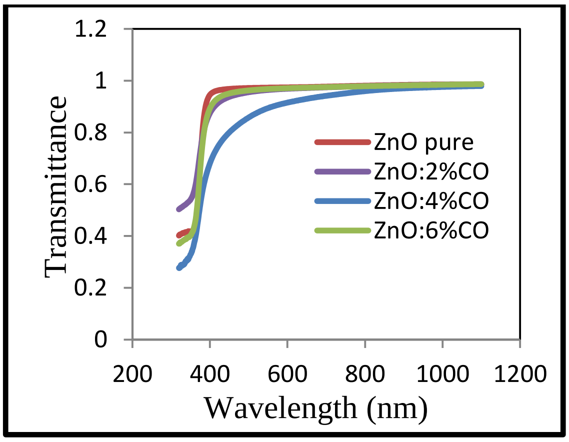

Fig. (3) Transmission spectra of pure and Co- doped ZnO thin films.

Fig. (4) shows the optical absorbance of all prepared films. In the fig.(4) it can be noticed that high absorbance at UV region, the absorbance decrease in (410-760) nm wavelength region whereas it is transpared in the UV region. The absorbance decrease in visible and near infrared region where its transparent in the uv region.

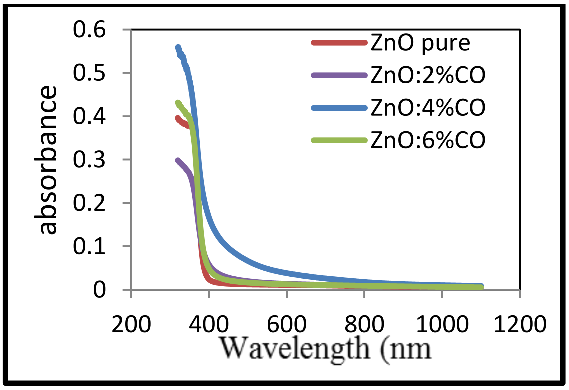

Fig. (4): Absorbance spectra for pure and doped ZnO thin films.

Optical reflectance spectrum for pure and Co-doped ZnO films shown in fig (5).

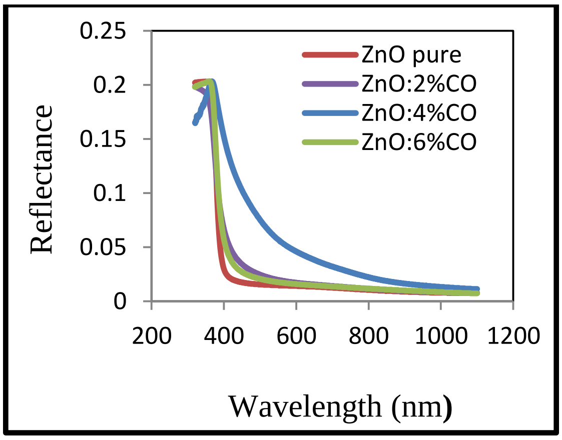

Fig. (5): Optical reflectance spectrum of pure and Co-doped ZnO films.

From fig. (5) it can be seen that there is a rapidly decreases in reflectance with wavelength and Co-doping concentration in the region (260-500) nm, this can be attributed to increase the donor state levels by doping processes.

The absorption coefficient was calculated from: [16]

$$\alpha = \frac{2.303A}{t} \ldots\ldots(2)$$

Where t is the thickness of films

In Fig (6) was shown the variation of absorption coefficient with wave length for all prepared thin films.

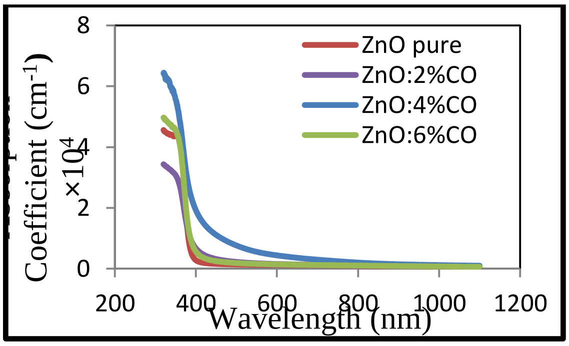

Fig. (6) the variation of absorption coefficient with wave length of pure and Co-doped ZnO films.

It can be noticed from the fig. (6) That the higher absorption coefficient in the UV-region and then flat rapidly to become almost constant in visible–near infrared region with increasing Co concentration in ZnO thin films.

The absorption coefficient is related to optical energy gap according to Tauc relations [17], the optical band gap can be estimate from the straight portion of graph between [16] V_s photon energy.

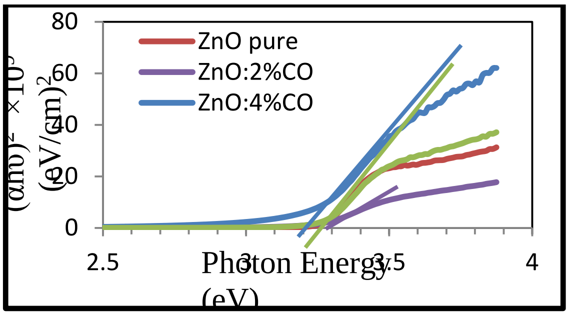

Fig. (7) variation of $(\alpha h\nu)^2$ versus photon energy of pure and Co-doped ZnO films.

The energy band gap of pure ZnO is about 3.28 eV and decrease to 3.2eV after 4% doping, while after 6% the energy gap increase to 3.26 eV and this value is roughly equal to the energy gap of the pure ZnO.

The variation of the band gap with Co concentration can be explained in terms of Moss – Burstein effect [18]

In Fig (8) was shown the extinction coefficient of pure and Co-doping ZnO films, the increase of Co concentration in ZnO thin film shows rise in excitation coefficient, this result is agreement with [14].

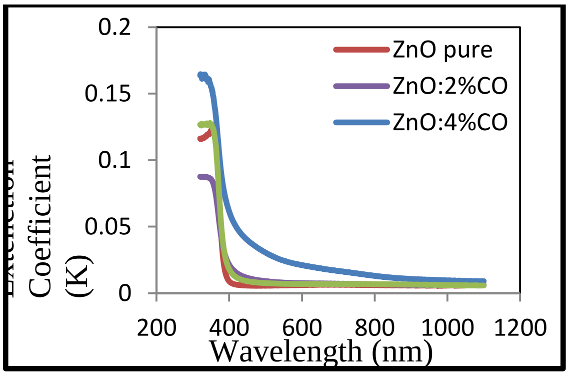

Fig. (8) the extinction coefficient of pure and Co-doping ZnO films

Fig (9) , (10) shows the real $\varepsilon_1= n^2-k^2$[16]and imaginary $\varepsilon_2=2nk$ [16] parts of the dielectric constant respectively and they indicated the same pattern curves but the value of real parts higher than those of imaginary parts.

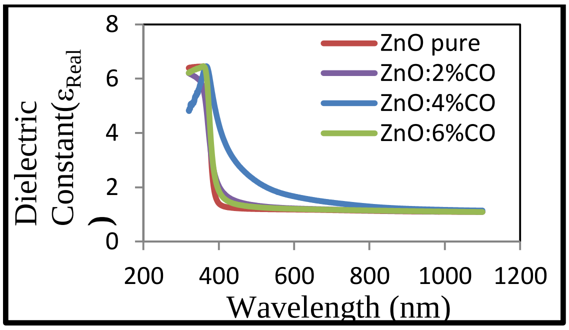

Fig. (9): variation of real part of dielectric constant with wavelength.

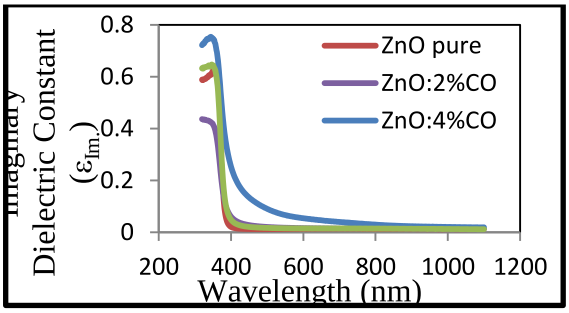

Fig: (10) variation of imaginary part of dielectric constant with wavelength.

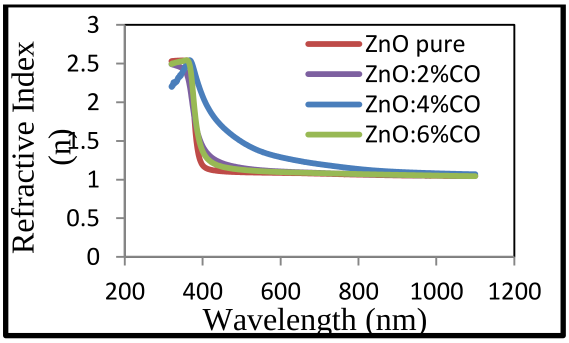

Fig (11): the plot of refractive index as a function of wavelength.

In Fig. (11), it can be noticed that the average value of refractive index decreased with the increase of Co-concentration, this may refer to Co doping has decreased the optical density of the medium.

Conclusions

The result of this work found highly transparent conductive Co-doped ZnO thin films which were deposited onto glass substrate via chemical spray pyrolysis. The substrate temperature was 400 °C. The investigation of structural and optical properties were done using many techniques. The properties of thin films were improved by increase Co-concentration. All prepared films are nanocrystalline-hexagonal structure with strong 0 0 2 peak; the maximum value of crystallite grain size G = 15.7 nm is attained with 6% Co concentration in ZnO film. The energy of band gap decreased from Eg= 3.28 eV to 3.2 eV for pure and 4% Co-doped ZnO thin films respectively.

Acknowledgments:

Thank Dr. Mohammed Ahmed Mohammed from University of Al-Qadisiyah/ College of Agriculture and Dr. Rana Galib from Babylon university/ college of medicine for the instrumental support given to this work.

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