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Synthesis and Characterization of Zn_{1-X} Cr_xo Thin Films Deposited by Chemical Spray Pyrolysis Technique

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Abstract

In this study, chemical spray pyrolysis system were using to prepared the Zn1-xCrxO films where x (0, 1, 3, 5 and 7) %. Structural and optical properties is studies by XRD and UV\VIS\NIR spectroscopy. Were the average crystial size estimated by Scherers method and the Dave value decreases as CrO increasing and the value about (35.6- 10.7) nm. The energy gap for thin films increases as the CrO increasing starting (0 to 7) % to reach it is maximum value of (3.38eV). The transmittance value of undoped ZnO equal 90% and the The transmittance value decresing when ratio of doped by CrO inecresed.

Keywords: Zinc Oxide, Chromium Oxide, Thin Films, Structural Properties.

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تصنيع وتوصيف أغشية Zn1-XCrxO الرقيقة المحضرة بطريقة التحلل الكيميائي الحراري

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الخلاصة

في هذه الدراسة، تم استخدام طريقة التحلل الكيميائي الحراري في تحضير اغشية $Zn_{1-x}Cr_xO$ بنسب مختلفة (0.00, 0.01, 0.03, 0.05, 0.07). تم دراسة الخصائص التركيبية من خلال حيود الاشعة السينية XRD وتم دراسة الخصائص البصرية باستخدام المجهر UV\VIS\NIR للأغشية الرقيقة المحضرة، حيث تم حساب متوسط الحجم البلوري بطريقة شيرر ووجد ان متوسط الحجم البلوري للأغشية الرقيقة يقل مع زيادة نسبة اوكسيد الكروم بقيم تتراوح بين (10.7 -35.6) nm. وأظهرت نتائج الفحوصات البصرية ان فجوة الطاقة البصرية تزداد مع زيادة نسبة التطعيم بأوكسيد الكروم واعلى قيمة تم الحصول عليها هي (3.38) eV وان قيم النفاذية تقل مع زيادة نسبة التطعيم بأوكسيد الكروم.

الكلمات المفتاحية: اوكسيد الخارصين، اوكسيد الكروم، اغشية رقيقة، الخصائص التركيبية.

Introduction

Transitional oxide ZnO material attracted attention since of magnetic properties base on sp d exchanges interactions. They are deeply examined for spin base electronic application. ZnO have a more scientific application such as gratia transparent electrode and device of piezoelectric. Besides, ZnO is favored than III – V kind material as GaAs and GaN as it is ecofriendly and compatible with technologies of the magnetic storage [1- 3]. ZnO reemerged as an active optical components due to it is energy as a replacements of the GaN for UV light device, such as lights emitting diode, nano lasers [4, 5], photodetectors [6], and nano sensors [7]. The benefits of a ZnO relies on it is excitonics of the required energy at $60*10^6$ eV, permitting for additional efficient excitonics emission, and its vastly extra abundant in natural resource [8]. The objective of the present study the effect of Cr doping ratio of ZnO films prepeard by chemical spray pyrolysis technique then study the optical and structural properties of this films.

Experimental Details

Chemical spray pyrolysis technique were employed to prepared of Zn1-x CrxO thin films at deffrent value of x = (0,1,3,5 and 7) % by using high purity of materials, Zinc Nitrate $Zn(NO_3)_2.6H_2O$((99.0%) and Chromium(III) nitrate $Cr(NO_3).9H_2O$(99%). The solutions are prepared by dissolving the amount of Zinc Nitrate $Zn(NO_3)_2.6H_2O$((99.0%) powder with molecular weight 2.974g and amounts of hromium(III) nitrate $Cr(NO_3).9H_2O$((99%) powder withmolecular weight 4.01 g in 100 mL of the distille water at the room temperatures by using magnetic stirrer for (20 min) and resultant of solutions are spraying on glass substrates at 350 ^oC temperature. Additional conditions for example, distance of spray (28±2 cm), rate of spraying (60 sec), time of spraying (10 sec) and the pressure is (1.6 bar) and saved constant for all samplws. The thickness of all samples were measured by gravimetric technique (300 nm). The X-ray diffractions of the synthesis films are investigete by (Shimadzu/XRD/6000) copper target/CuKα/1.5418˚A) and the optical properties investigate by using UV/VIS/NIR spectroscopy (Shimadzu UV1800)

Results and Discussions

Results of XRD

XRD results of Zn $_{1-x}$ Cr_xO where x= (0,1,3,5 And 7) %as showed on Fig 1. The locations of the peak and the occurrence of sevral diffractions peaks lead to the conclusion that the film have a polycrystalline with hexagonal structure, it can be observed that the lattice constants (a_o and c_o) decrease as the ratio of CrO increases. From the analysis of the positions of the peaks, 2θ have values of 30.7^o ,34.5^o and 35.5 ^{o} which refers to the (100), (002) and (101) preferred planes, and agreement with (JCPDS) card number 00-36-1451. The strong peak happens at 2θ~34.5^o which is refer to (002) plane which is in agreement with report [9]. The intensity of peaks decreases when ratios of CrO incresied.

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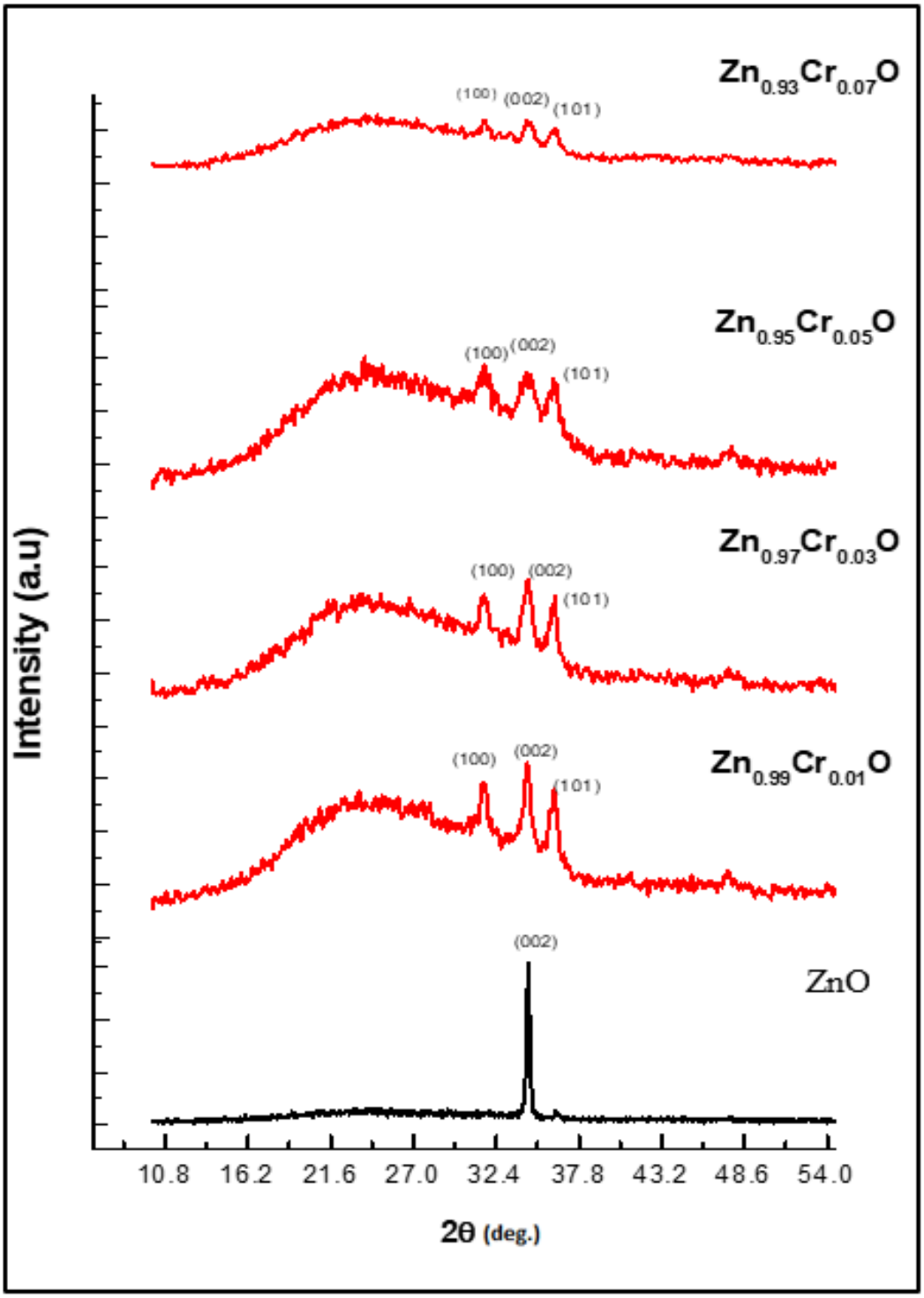

Figure 1: XRD patterns of the of Zn1-xCrxO where x= (0, 1, 3, 5 and 7) %

The average of crystallite size (D_{ave}) for the main plane (002) was calculated by using the Scherrer method: [10, 11]

$$Dave = \frac{K\lambda}{\beta \cos\theta} \quad \text{..... (1)}$$

Where λ is wave length of Xray (1.5406 Å), K is factor and equivalent 0.9, θ the Bragg angle and β is the full width of half maximum. The average of crystallite size value decreases as CrO increasing and the value about (35.3- 10.7) nm for [0-7] % respectively, which is agreement wih reports [2, 5]. The Dave effected by ionic radius, the radius of chromium ions is equal to and the radius of zinc ions is the radius chromium (Cr^{+3} = 0.63 Å) is less than the ionic radius of zinc (Zn^{+2} = 0.74 Å), which allows the chromium atoms to enter as substituent atoms within the crystal structure of zinc [13].

The dislocation density (δ) was valued by used eq. [11].

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

There is a reverse relation between the crystalline size and dislocation density due to that the value of dislocation density increasing when the crystallite size decreases and increasing the ratio of CrO

The number of the crystallite (N_o) was estimated by [12- 16]:

$$No = \frac{t}{D_{av}^3} \quad \text{..... (3)}$$

Where t: Thickness of films (350 nm). It's observed that the numbers of the crystallite for film are increasing when ratio of CrO increased.

The texture coefficient (Tc) estimated by [10, 11]:

$$T_{C(hkl)} = \frac{I_{(hkl)} / I_{\circ(hkl)}}{N_r^{-1} \sum I_{(hkl)} / I_{\circ(hkl)}} \quad \text{..... (4)}$$

Where N the number of reflections, ($I_{o\ (hkl)}$) taked from JCPDS data, ($I_{(hkl)}$) is the measured intensity and hkl is the Miller indice. The texture coefficient are using for define the favored directions (hkl) for growing of crystal in a poly crystalline film as showed of the table 1, It was found that the values of the texture coefficient (Tc) is bigger than one for the undoped ZnO films, which indicates that they have one predominant direction which is (002). As for the doped thin films, the Tc is less than one, which means that it has more than one predominant direction (101), (002), (100)

Table1: Result of XRD of of Zn1-xCrxO where x= (0, 1, 3, 5 and 7) %

Sample	Un doped-ZnO	$Zn_{0.99}$-$Cr_{0.01}O$	$Zn_{0.97}$-$Cr_{0.03}O$	$Zn_{0.95}$-$Cr_{0.05}O$	$Zn_{0.93}$-$Cr_{0.07}O$
hkl	002	002	002	002	002
2θ (deg)	34.51	34.43	34.42	34.53	34.55
β (rad)	0.0040	0.0064	0.0104	0.0136	0.0122
D_{ave} (nm)	36.3	22.7	14	10.7	11.9
δ(line nm^{-2})	0.0007	0.0019	0.0051	0.0087	0.007
No (nm^{-2})	0.0073	0.0299	0.1287	0.287	0.207
T_C(hkl)	2.676	0.787	0.746	0.730	0.793
(a_0) Å	3.249	3.242	3.235	3.232	3.218
(c_0) Å	5.206	5.231	5.206	5.234	5.202

Optical properties of thin film

Figure 2 illustrations the transmittance spectrum as a function of wavelength, within the range (350-600) nm. The transmittance value of undoped ZnO equal 90% and the The transmittance value decreased when ratio of doped by CrO increased, this indicates the increase in the energy gap. The observed result in increasing the energy gap can be attributed to the effect of (Burstein-moss) [17]

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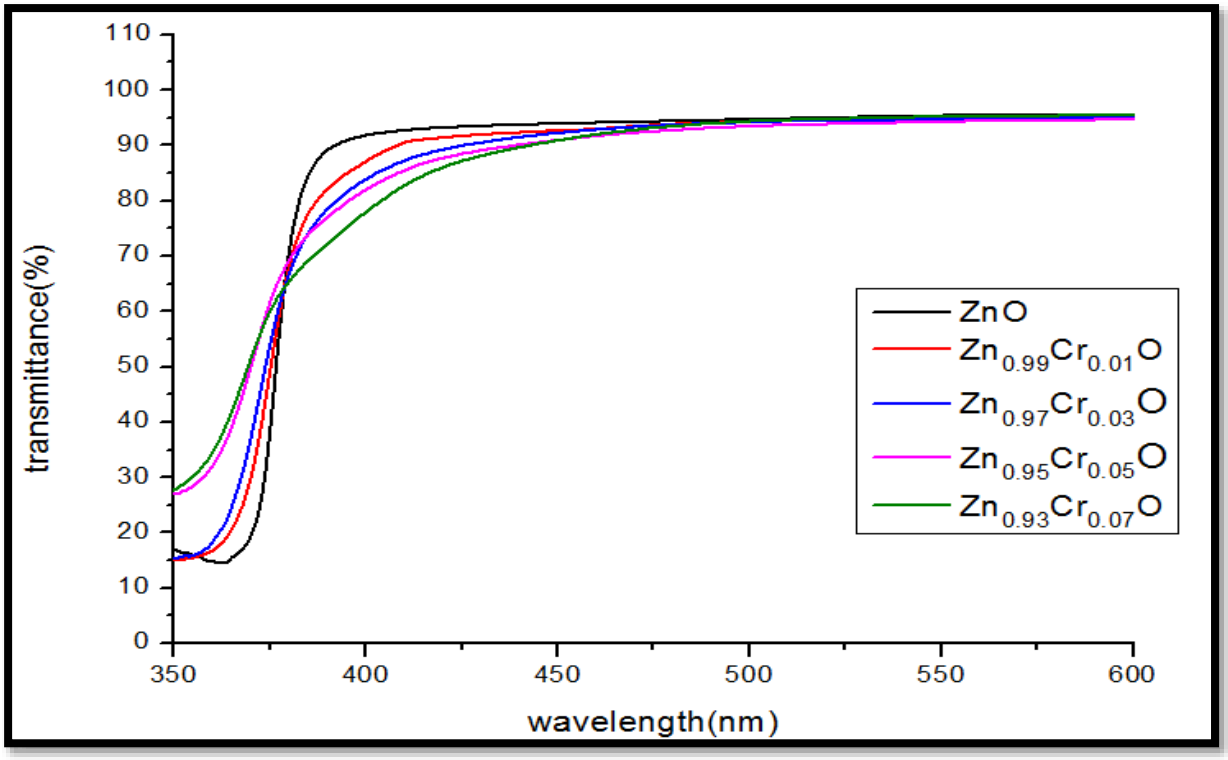

Figure 2: Transmittance for Zn1-xCrxO where x= (0, 1, 3, 5 and 7) %

The absorption coefficient (α) were estimated by using [10, 16]:

$\alpha = 2.303\ A/t$ ..... (5)

Where A is absorbance**.** Figure (3) shows the change of the absorption coefficient as a function of the photon energy of the prepared films, its noticed that the absorption coefficient increases with increasing of the ratio of CrO doping, and then the symmetrical shift occurs in the spectrum of the absorption coefficient in the basic absorption edge due to the effect of (Burstein-Moss) [18].

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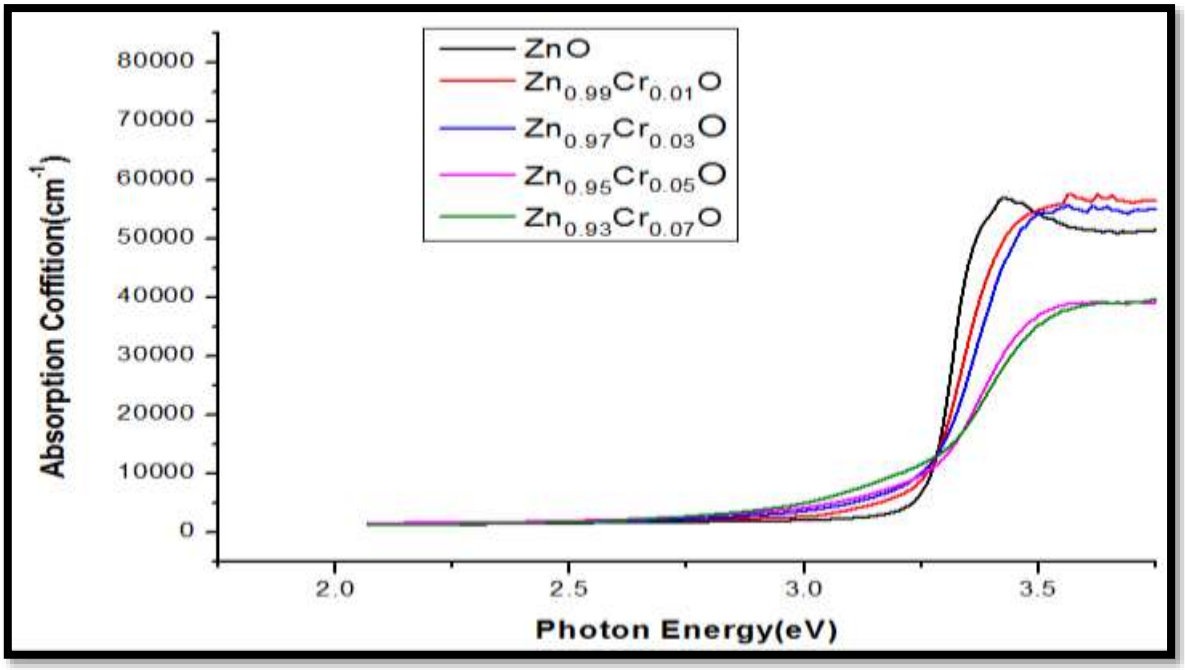

Figure 4: Absorption coefficient of Zn1-xCrxO where x= (0, 1, 3, 5 and 7) %

The energy band gap is valued by using eq. [10, 12, 16]:

$$\alpha\, hv = Z(hv - E_g)^s \quad \text{..... (6)}$$

Where hν is the photon energy, Z is the constant and independed of the photon energy. s=1/2 to directs transitions. The optical energy gap for the allowed direct electronic transitions for undoped zinc oxide and doped with chromium films was calculated by drawing the linear relationship between (αhν)2 and the photon energy. and the cut-off point represent the value of the energy band gap (Eg) for the films. It is observed that the optical energy gap for thin film increases as the CrO increasing from 0% to 0.07 to reach it is maximum value about (3.38 eV), and this increase is due to the effect of (Burstein-Moss) [18, 19], as shwon in Table 2.

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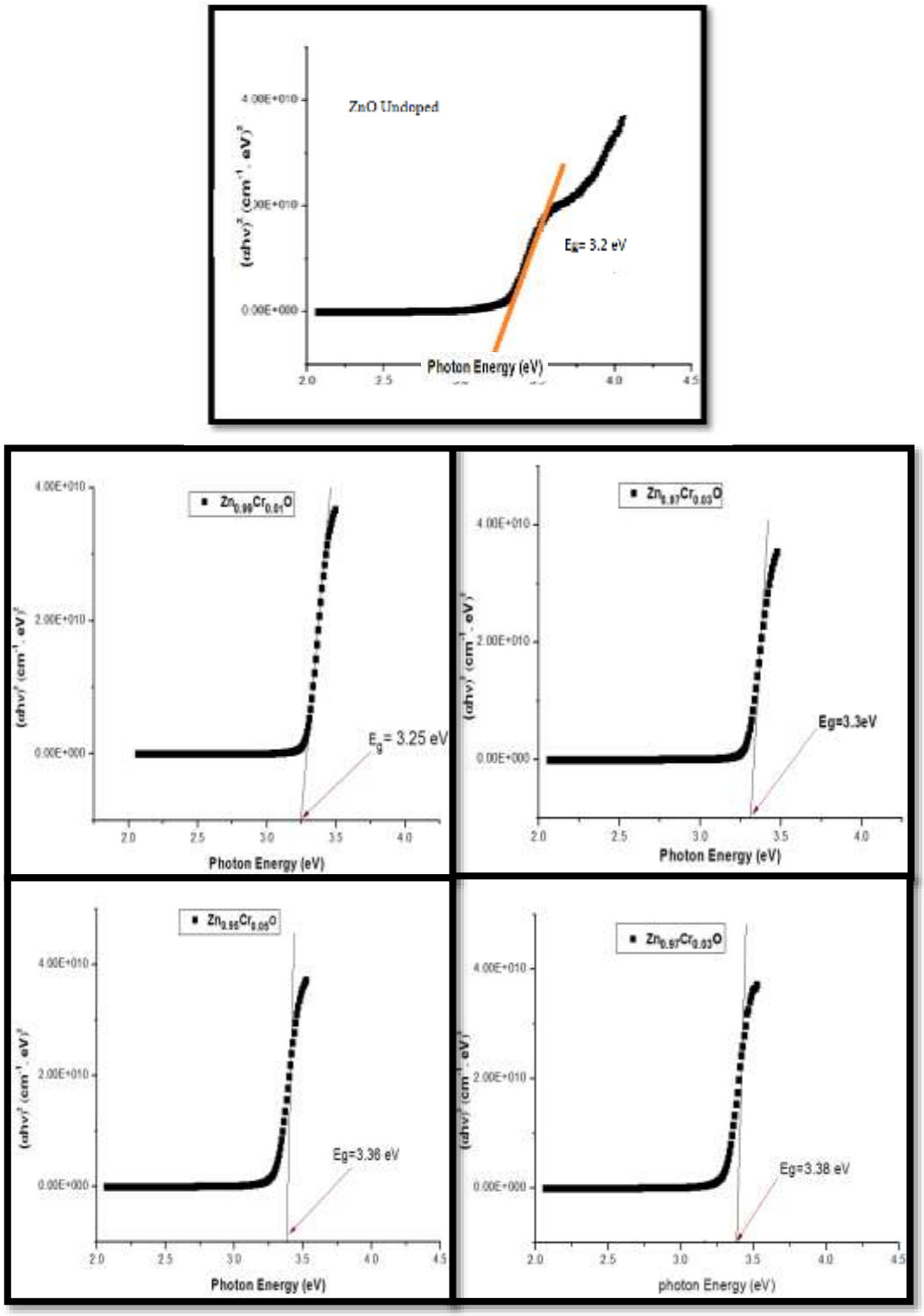

Figure 5: Tauc's plot of Zn1-xCrxO where x = (0, 1, 3, 5 and 7) %

Table 2: Optical energy gap value of Zn1-xCrxO where x = (0, 1, 3, 5 and 7) %

Films	Undoped ZnO	$Zn_{0.99}$-$Cr_{0.01}O$	$Zn_{0.97}$-$Cr_{0.03}O$	$Zn_{0.95}$-$Cr_{0.05}O$	$Zn_{0.93}$-$Cr_{0.07}O$
Eg (eV)	3.2	3.25	3.3	3.36	3.38

The coefficient of extinction (K_o) is estimating by [10, 14, 16, 20]:

$$K_o = \frac{\alpha\lambda}{4\pi} \quad \text{..... (7)}$$

Where λ is wavelengths for incident photon. Figure 6 displayed extinction coefficient as function of wavelength for Zn1-xCrxO where x= (0, 1, 3, 5 and 7) %. Its observed that the coefficient of extinction (Ko) decreases at small wavelength (350 to 400) nm and next that the (Ko) keep on constant. The values of Ko increases when the CrO increasing and it was maximum (~ 00.25) for the film prepared at x=0.05. This increasing is due to the increased in the value of the absorption coefficient at these energies, which indicates the occurrence of direct electronic transitions [19].

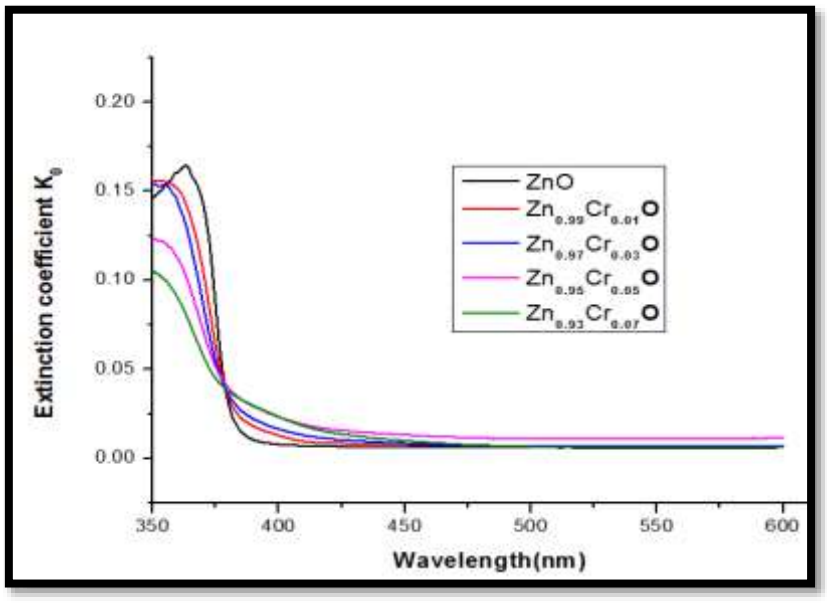

Figure 6: Extinction coefficient for Zn1-xCrxO where x= (0, 1, 3, 5 and 7) %

Conclusions

The chemical spray technique was using to prepared of Zn1-xCrxO films where x= (0, 1, 3, 5 and 7) %. Rusults of XRD indicated that the all samples are polycrystalline in nature with hexagonal structures. The energy band gap to the thin film increases as the CrO increasing and the maximum value is (3.38 eV). The transmittance value of undoped ZnO thin film equal 90% may be used as window of the solar cell.

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