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Structural and Optical Properties of ZnO-NiO Nanocomposite Thin Films Deposited by Spray Pyrolysis

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***Abstract*:- In this paper, ZnO, NiO, ZnO-NiO nanocomposite thin films were prepared by spray pyrolysis method at a temperature of 450°C on glass substrates of the normal type and starting solutions of zinc acetate $Zn(CH_3COO)_2.2H_2O$ and nickel acetate $Ni(CH_3COO)_2.4H_2O$. The structural properties of the films prepared using an X-ray diffraction device (XRD) were studied. The constants of the crystal lattice and the granular size were calculated. It was observed that with increasing zinc concentration, the crystal size increased and the crystal structure of the prepared films improved. The results also showed that the prepared films are multi-crystallized and that films prepared at equal ratio have two crystalline phases, one of which is a cube belonging to the vacuum group (Fm3m) and the other hexagonal belonging to the vacuum group $(P6_3mc)$. Transmittance spectra recorded using the spectrophotometer in the range of (330-2200 nm). It was observed that the transmittance increased with increasing zinc concentration. The absorption coefficient and the optical band gab energy were calculated and was observed that the band energy gap values of the pure thin films were larger.**

Keywords: Nickel oxide, Zinc oxide, Optical band gab, Spray pyrolysis, XRD

1-INTRODUCTION

Nanocomposites are a mixture of at least two phases which one of them or both is in the nanometer scale. They were extensively researched because of the nanocomposite thin films enhancements when compared to the study of the separate phases. As an example, we can cite higher electrical conductivity, better interactions at phase's interfaces, lower density, better chemical and mechanical stability and better wear resistance. The nanocomposite materials are used for many applications such as photovoltaic devices, gas sensors, and UV-Detectors [1]. The study of transparent conductive oxides (TCOs) is of great interest due to their distinctive properties as they are used in many technological applications [2]. Zinc oxide, ZnO, is a semiconductor chemical compound of the family of transparent conductive oxides with an n-type conductivity. It has a wide band gab of 3.37eV at room temperature, and has an excitonic bonding energy of 60 MeV, and is chemically and thermally stable [3][4]. These properties make zinc oxide an attractive material for a large number of applications such as blue and UV light-emitting diodes, gas sensors, ultrasound devices, etc. [5][6]. While NiO is a semiconductor of the family of transparent conductive oxides with p-type conductivity [7], nickel oxide films have a large forbidden range ranging from(3.15ev to 4ev) [8]. Nickel oxide is characterized as a reversible magnetic material [9], and it has a very high melting point of about 2000Cº, so it has durability and chemical stability [10]. The most important applications of NiO is solar cells, gas sensors, anti-reflection layers, laser mirrors, monochromatic filters, optoelectronics, and others [11] . In this research we prepared the thin films by thermal spray method (SP) because it is one of the most important physical methods that depend on interaction with the surface of the substrate. And it is the simplest and low cost method for the production of thin films used in industrial applications [12].

2-EXPERIMENTAL

Pure thin films of zinc and nickel oxides and thin films of a mixture of zinc and nickel oxides with different weight ratios and with a molar concentration of 1M were prepared using $Ni(CH_3COO)_2.4H_2O$ nickel acetate solution, which is a green solid, its molar mass (248.87 g/mol) and zinc acetate solution $Zn(CH_3COO)_2.2H_2O$, which is a white powdery substance with a molar mass of (219.5 g/mol) and a purity of (99%), where an appropriate weight of nickel acetate salt was dissolved in a mixture of distilled water and ethanol (24ml), then a weight solution Suitable zinc acetate salt in a mixture of distilled water and ethanol (24ml), then the two solutions were mixed in specific weight ratios as shown in Table (1), and a few drops of acetic acid were added to increase the transparency of the solution, then the resulting solution was placed (30ml) on a mixer magnetic and at a temperature of 85Cº until the solution is homogeneous. Ordinary glass substrates were used and cleaned using ultrasound technology (Transsonic T700/H), then these substrates were immersed in several stages with ethanol and hydrochloric acid, cleaned with distilled water and dried well to get rid of sediments and impurities until reaching a continuous drop on the surface of the substrate. These glass substrates were then placed in the spray chamber at a distance of 30 cm from the spray nozzle and

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the precipitation process began at 450°Cº A layer of the nickel-zinc oxide mixture was formed on the surface of the substrate according to the following two chemical equations:

$$Ni(CH_3COO)_2.4H_2O \rightarrow NiO+(4H_2O)+CH_4\uparrow+CO_2\uparrow+H_2\uparrow \quad (1)$$
$$Zn(CH_3COO)_2.2H_2O \rightarrow ZnO+(2H_2O)+2CH_3COOH \quad (2)$$

Table(1): Mixing percentages and weight ratios of the ZnO-NiO nanocomposites thin films.

samples	ZnO(%)	NiO(%)	$Zn(CH_3COO)_2.2H_2O$	$Ni(CH_3COO)_2.4H_2O$
NiO pure (S_1)	0	100	0 ml	30 ml
ZnO 0,3-0,7 NiO (S_2)	30	70	9 ml	21 ml
ZnO 0,5-0,5 NiO (S_3)	50	50	15 ml	15 ml
ZnO 0,7-0,3 NiO (S_4)	70	30	21 ml	9 ml
ZnO pure (S_5)	100	0	30 ml	0 ml

3-RESULTS AND DISCUSSION

3-1-Structural Studies

Figure (1) displays the XRD spectra of pure thin films and films prepared by weight ratios different at substrate temperature (450°C)

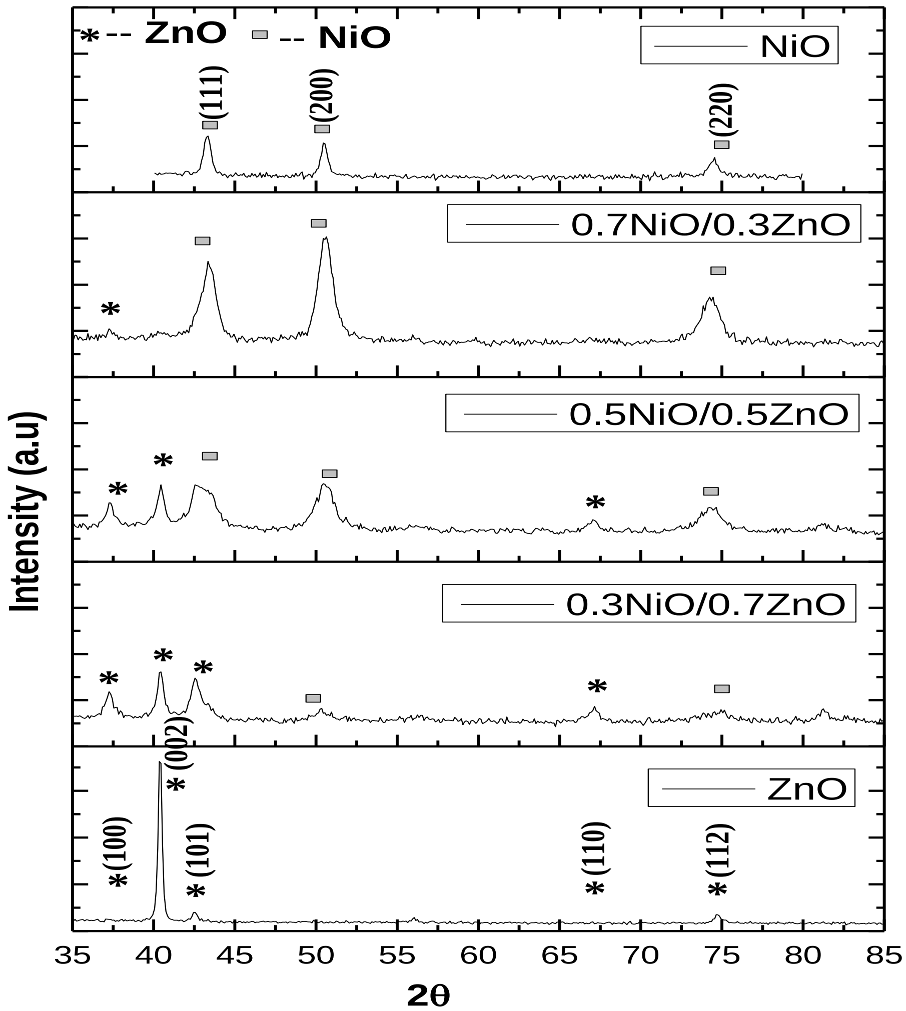

Fig. 1: XRD analysis of the thin films with different NiO -ZnO concentrations where (S_1 contains 100-0%, S_2 70-30%, S_3 50-50%, S_4 30-70% and S_5 0-100% respectively).

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Figure (1) shows clear peaks at (S_1), by comparing Miller's clues, which were as follows (111) (200) (220) with the data bank, it was found that they belong to pure nickel oxide and the preferred direction was (200) and when increasing the proportion of zinc (S_2), we note the start of The appearance of peaks related to zinc oxide and by reaching the equal ratio of oxide (S_3), we notice the appearance of clear peaks for both oxides and the formation of the two crystalline phases (cubic and hexagonal) and at the ratio (S_4) we notice a decrease in the intensity of the unit of diffraction peaks of nickel oxide while preserving the two crystal phases formed as for the sample (S_5) We note the emergence of clear peaks and by comparing Miller's clues that were as follows (112) (101) (002) with the data bank, it was found that they belong to pure zinc oxide and the preferred direction was (002).And When comparing the obtained spectra with the nickel oxide reference card No. 04-0835, it was found that the films prepared at high nickel ratios crystallize according to the cubic structure belonging to the vacuum group (Fm3m) and their crystal lattice constant a=4.176Å compared to the ZnO reference card No. 1451-36, it was found that the films prepared at high levels of zinc crystallize according to the hexagonal structure that belongs to the vacuum group ($P6_3mc$) and the crystal lattice constants have a=b=3.249 Å c=5.206 Å[13][14].

hkl are miller indices and d is the interlinear spacing given by Bragg's law:

$$\mathbf{2d\,sin\theta = n\lambda} \quad (3)$$

Where $\boldsymbol{\lambda}$ is the wavelength of the radiation $\lambda = 1.7889$ Å for CO Kα radiation, $\boldsymbol{\theta}$ is the Bragg diffraction angle of peak in degree and $\boldsymbol{n}$ is the order of diffraction taken equal unity (first order), **d** is the distance between the crystal planes.

The lattice constant (**a** and **c**) for both NiO and ZnO phases were calculated using equation (4) in the case of the hexagonal structure ,and equation (5) for the cubic structure[15][16]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + k^2 + hk}{a^2}\right) + \frac{l^2}{c^2} \quad (4)$$

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (5)$$

The values of the crystal lattice constants correspond to the reference card (36-1451) for zinc oxide and the reference card (04-0835) for nickel oxide.

The average crystallite size **D** was obtained using the Debye-Scherer formula in Equation: [17]

$$D = \frac{K.\lambda}{\beta COS\Theta} \quad (6)$$

β is full width at half maximum (FWHM) peak intensity (in Radian), **λ** is wavelength, **θ** represent Bragg's diffraction angle and **k** is 0.9 respectively.

samples	$(2\Theta)^o$	(hkl)	$d_{hkl}(A^0)$	$\beta(rad)$	$a, c\ (A^0)$	$D\ (nm)$	متوسط D (nm)
NiO (pure)S_1	43.33	(111)	2.421	0.006	a=4.193	24.80	
	50.48	(200)	2.096	0.006	a=4.192	25.48	29.63
	74.52	(220)	1.476	0.005	a=4.174	38.62	
0.3ZnO-NiO0.7 S_2	37.33	(100)	2.794	0.006	a=3.224	24.33	
	43.43	(111)	2.417	0.010	a=4.186	16.54	
	50.61	(200)	2.092	0.010	a=4.184	17.001	18.59
	74.26	(220)	1.481	0.012	a=4.188	16.52	
0.5ZnO-NiO0.5 S_3	37.30	(100)	2.797	0.005	a=3.229	32.44	
	40.46	(002)	2.586	0.006	c=5.171	24.57	
	42.54	(101)	2.465	0.008	c=5.214	19.79	
	43.57	(111)	2.410	0.006	a=4.174	24.82	24.77
	50.45	(200)	2.094	0.006	a=4.188	25.48	
	67.17	(110)	1.617	0.006	a=3.232	27.67	
	74.33	(220)	1.480	0.008	a=4.186	23.14	
	81.24	(112)	1.373	0.010	c=5.219	20.25	
0.7ZnO-NiO0.3 S_4	37.27	(100)	2.799	0.006	a=3.231	24.32	
	40.43	(002)	2.588	0.006	c=5.175	24.56	
	42.55	(101)	2.464	0.006	c=5.204	24.74	
	50.30	(200)	2.104	0.005	a=4.208	33.96	26.43
	67.24	(110)	511.6	0.006	a=3.229	27.68	
	74.89	(220)	1.471	0.010	a=4.160	19.36	
	81.34	(112)	1.372	0.006	c=5.124	30.40	
ZnO (pure)S_5	40.40	(002)	2.589	0.005	c=5.177	32.75	
	42.54	(101)	2.464	0.005	c=5.102	32.98	34.8
	74.70	(103)	1.473	0.005	c=5.185	38.67	

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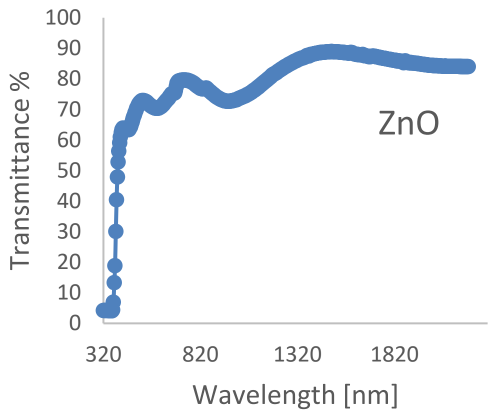
Table(2):Values of Bragg angle 2θ, hkl, d_{hkl} , full width at half maximum β lattice constants (a,c), grain size D ,average crystallite size of pure thin films and films prepared by weight ratios different at substrate temperature (450C°)

Table (2) showed that the size of crystal grains increases with increasing concentration of zinc and decreases with increasing concentration of nickel. This can be attributed to the fact that the radius of the ion Ni^{+2} ($0.69A^0$) smaller than the radius of the ion Zn^{+2} ($0.74A^0$) which gives the possibility to replace the nickel ion with the zinc ion in the crystal lattice and thus improve the structural properties of the prepared films by increasing the concentration of zinc due to the increase in the quality of crystallization of the films[18][19].

3-2-Optical Studies

The analysis of transmission spectra in range (320- 2200) nm wavelength can be shown in figures (2,3,4).

Figures (2,3,4) shows the transmission spectra of pure thin films and films prepared by weight ratios different at substrate temperature (450C°).



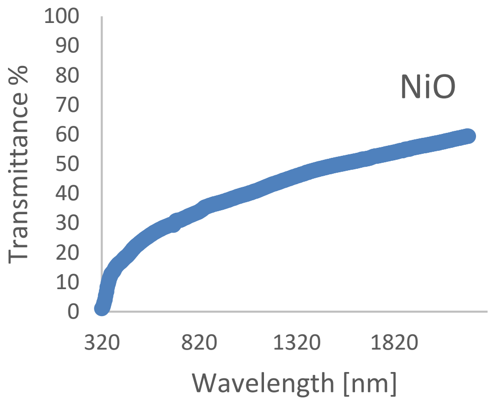


Fig 3:Transmission spectra of NiO thin film Fig 2 :Transmission spectra of ZnO thin film

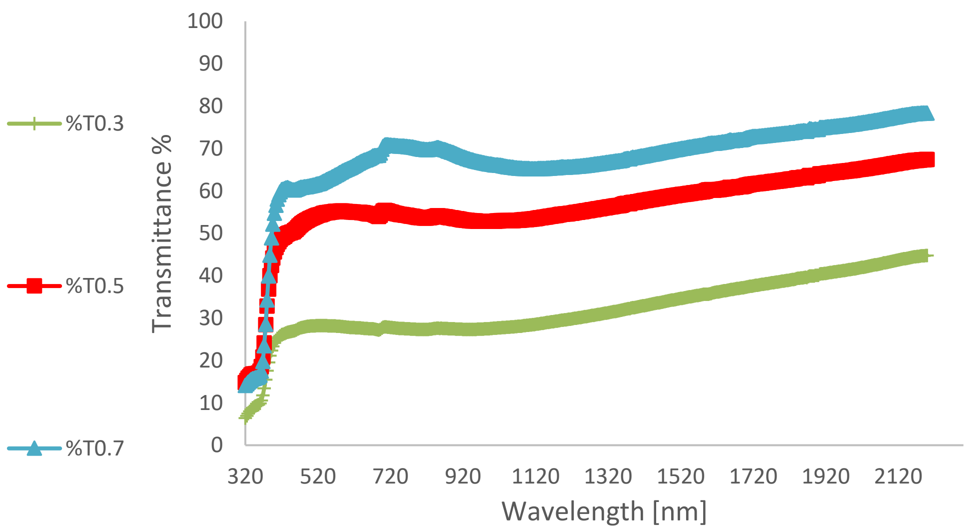


Fig 4: Transmission spectra of ZnO-NiO thin films.

The transmittance spectrum of the pure nickel oxide film shows that the transmittance increases with increasing wavelength and that the highest value (60%) was in the near-infrared field Fig. (2). The transmittance spectrum of the pure zinc oxide film also shows that the transmittance increases with increasing wavelength and that the highest value was (90%) in the same field Fig. (3). The transmittance spectra at the mixing ratios (S_2, S_3, S_4) show that the transmittance increases with increasing wavelength

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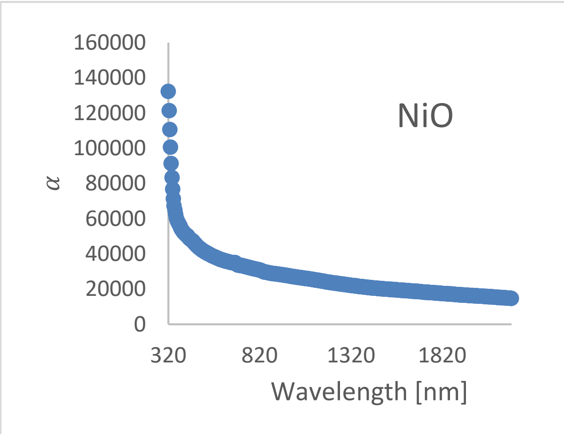
and its highest value was for sample (S_2) about (40%), for sample (S_3) about (65%) and for sample (S_4) about (75 %) in the near-infrared field, and we observe an increase in permeability with increasing concentration of zinc Fig. (4).[13][14][20].

Absorption coefficient, α was obtained using Equation:[21]

$$\alpha = 2.303\frac{A}{d} \qquad (7)$$

(**d**) is the film thickness, (**A**) is absorbance.

Figures (5,6,7) shows A plot of Absorption coefficient, **α** against wave length of pure thin films and films prepared by weight ratios different.



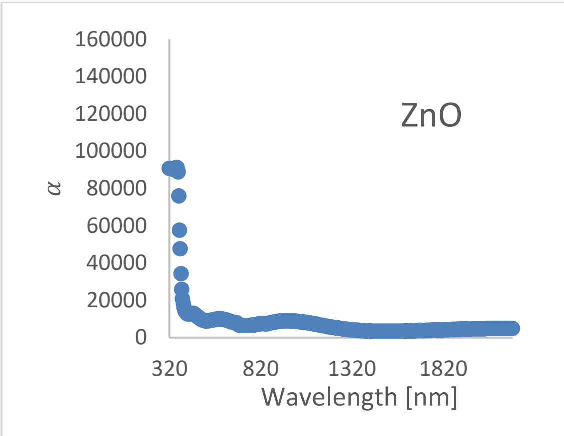


Fig 5: A plot of Absorption coefficient, α against wave length of NiO thin film

Fig 6: A plot of Absorption coefficient, α against wave length of ZnO thin film .

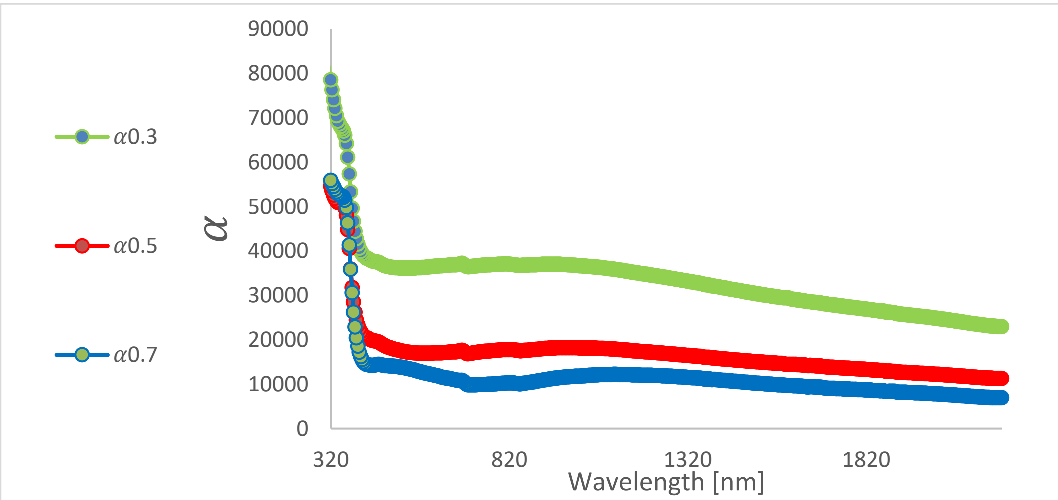


Fig 7: A Plot of Absorption coefficient against wavelength of ZnO-NiO thin films.

Figures (5,6,7) shows that absorption coefficient has decreased by increases wavelength. And the absorption coefficient has decreased by increasing concentration of zinc Fig. (7).

Recorded optical data were further analyzed to calculate the band-gap energy of the thin films using classical relation: [21]

$$\alpha = A\frac{(h\upsilon - E_g)^n}{h\upsilon} \qquad (8)$$

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(**n**) is an integer depending on the nature of electronic transitions. For the direct allowed transitions **n** has a value of 1/2 and **A** is energy dependent constant. (**h**) is plank's constant and ***hυ*** is the energy of the incident photon, υ is the frequency.

Figure (8) shows the plot of $(\alpha h\upsilon)^2$ versus hυ for pure thin films and films prepared by weight ratios different.. The optical band-gap is obtained by extrapolating the straight-line portion of the plot at α= 0.

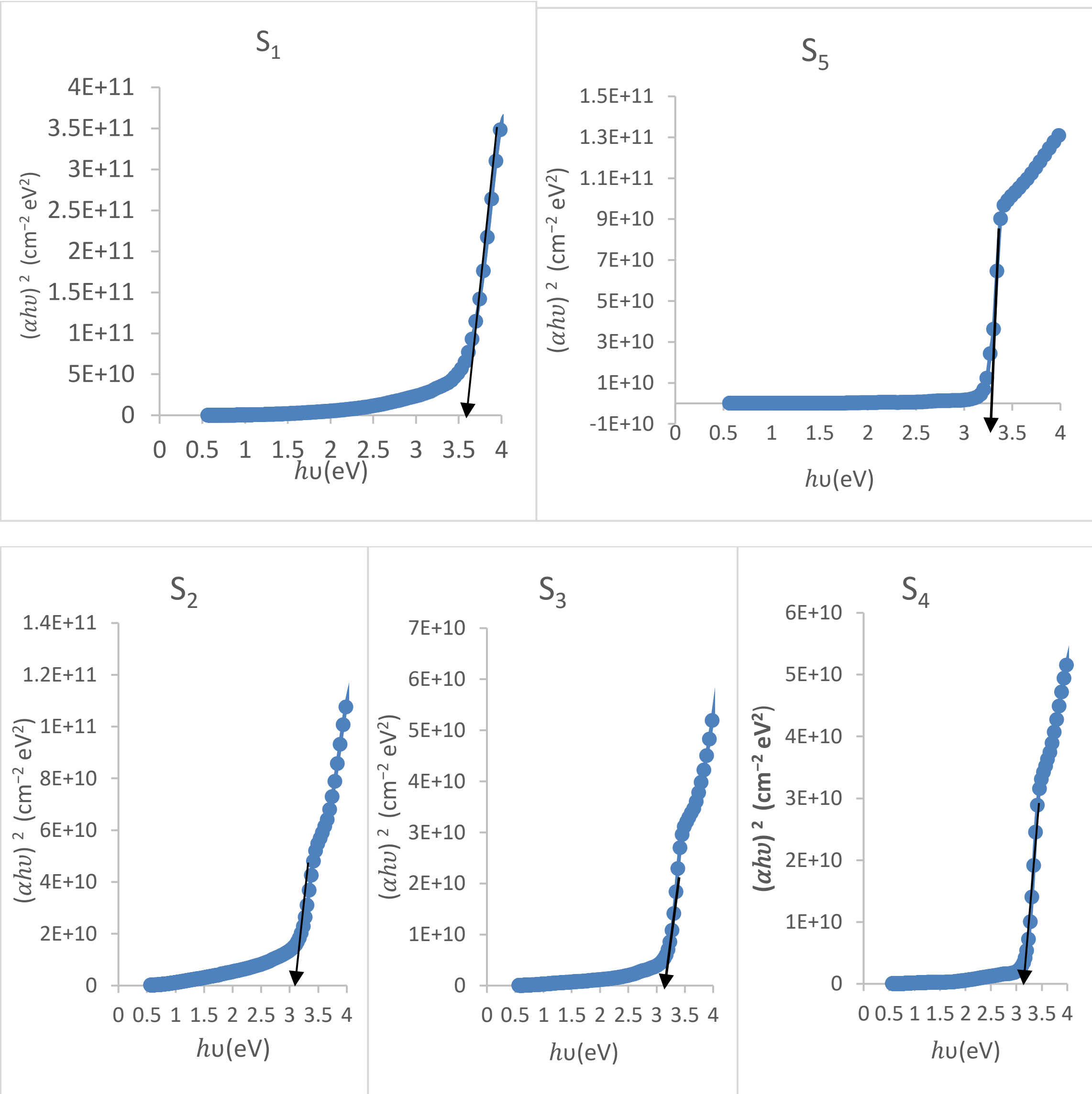

Fig 8: $(\alpha h\upsilon)^2$ versus hυ for pure thin films and films prepared by weight ratios different.

Figure (8) shows the energy gaps value of the prepared thin films where the band gap value of NiO film was (3.60 eV) and decreased in (S_2, S_3, S_4) samples to be (3.21, 3.19, 3.17 eV) respectively and then increased to (3.23 eV)) for the pure ZnO film and we observe a decrease in the energy gaps with the increase of the zinc concentration.[14].

4-CONCLUSION

ZnO, NiO and ZnO-NiO nanocomposite samples were prepared by spray pyrolysis method and their structural studies using XRD technique. The **XRD** results reveal that the prepared films are multi-crystallized. The optical measurements shows that the transmittance increased with increasing zinc concentration and energy gaps decreased with increasing concentration of zinc.

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