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Characteristics of Nanocrystalline ZnS thin films grown on glass with different Zn ion concentrations by CBD technique.

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Abstract: *Thin films of zinc sulfide (ZnS) with various values of Zn ions concentrations (0.2,0.3,0.4)M have been prepared by Chemical Bath Deposition Technique on glass slides substrate at 80 ºC bath temperature. The prepared films were annealed in air at constant temperature 400 ºC and constant time (180) min .*

Structural and optical properties of ZnS thin films were investigated and analyzed extensively before and after annealing . The structure properties of the prepared films were studied by using x-ray diffraction technique , it has been found that all prepared films at different Zn ions concentrations were amorphous structure, while the annealed films showed polycrystalline structure type (Hexagonal) , The lattice constants (a , c) of ZnS films were calculated and its values found about (3.86,31.6) Å , the crystallite size (Grain size) of ZnS thin films also calculated and found to vary from (20.8 to 83.7) nm ,which indicate that annealed ZnS thin films has Nanocrystalline structure .

The optical properties of ZnS thin films contained study of transmittance spectrum in the range of wave length (190-1100)nm by using UV- ViS. Spectrophotometer was carried out. Transmittance decreased with increasing the Zn ions concentrations of ZnS films , also the transmittance decreased after annealing . The fundamental absorption edge of ZnS thin films shifted toward the highest photon energies (blue shift) with increasing the Zn ions concentration and shifted toward the lowest photon energies (red shift) after annealing. The absorption coefficient values which calculated from the absorbance spectrum was larger than $10^4 cm^{-1}$ gives an indicate that ZnS films were direct semiconductors and the electronic transitions was a direct transitions.

The optical energy gap values for allowed direct transition found in the range of , (1.594-3.060) eV for (ZnS) thin films with (0.2 - 0.4 M) Zn ions concentration and in the range of (3.215-3.099) eV for the same concentrations after annealing.

Keyword: *ZnS , thin film ,CBD, structural and optical properties.*

I. Introduction

Zinc sulfide (ZnS), belongs to the group II-VI compound semiconductor materials. Nanocrystalline ZnS thin films with a wide direct band gap(3.73 eV) has a high index of reflection and a high transmittance in the visible range, and having great interest for its practical applications in optoelectronics and photonics [1]. Particularly it is suitable for host material for a large variety of dopants [2], and is used as phosphor in electroluminescence, opto-luminescence devices, photovoltaic cells [2,3], display devices, materials for LEDs and lasers and thin film solar cells [4,5]. Moreover, the content elements ZnS are nontoxic to the human body and are very cheap and abundant [4].

Previously, ZnS thin film have been deposited by many different techniques, thermal evaporation [5], self-assembly technique [6], spray pyrplysis [7] ,electron beam evaporation [8], Photochemical deposition (PCD) [9], close-space sublimation [10] , pulsed laser deposition [11], molecular beam epitaxy [12] and chemical bath deposition [13]which was used in the present study to prepare ZnS thin films.

II. Experimental

ZnS thin films were deposited using chemical bath deposition technique CBD. The total volume of the deposition bath was 100ml made from the chemical bath compositions as shown in Table 1. The films were deposited on glass substrate by mixing solutions of Zinc Sulfate $ZnSO_4$ with (0.2,0.3 and 0.4)M concentrations as the source of zinc ions (Zn^{2+})**,** Ammonia NH_3 25%, Thiourea $SC(NH_2)_2$ with 2M concentration as the source of sulfur ions (S^{2-}) and distilled water with continues stirrer , The bath temperature was maintained at 80˚C during deposition . The substrate used for deposition ZnS thin films is microscope glass slides (25.4 mm x 76.2mm x 1mm), washed in distilled water to remove the impurities and residuals from substrate surfaces, followed by rinsing in HCL acid (50 ml of HCL in 150 distilled water) for 24 hour to introduce functional group called nucleation/or epitaxe centers, which formed the basis for the thin films growth and finally washed again with distilled water.

The substrate was immersed vertically in beaker containing, the reaction mixture and solution as shown in the figure (3.3). The pH (10) was monitoring with pH meter type (HANNA Company). Deposition time was

one hours in each experiment. The substrates were taken out, washed with distilled water and dry in air, then the deposited film from one slide was removed carefully using HCL solution.

The chemical deposition technique which also is referred to as the solution technique for the preparation of (ZnS) thin films is based on the slow release of (Zn^{2+}) ions and (S^{2-}) ions in solution. The slow release of the (Zn^{2+}) ions is achieved by the dissociation of a complex species of zinc $[Zn(NH_3)_4]^{+2}$which is formed from react ion of zinc salt ($ZnSO_4$) with ammonia (NH_3). The (S^{-2}) ions are supplied by the decomposition of thiourea $\left(SC\left(NH_2\right)_2\right)$ in alkaline solution (pH > 10), and react with (Zn^{2+}) ions to give zinc sulfide ZnS. Deposition occurs by an ion –by– ion process, or by colloidal particles of (ZnS) adsorbing onto the substrate . In the case where thiourea is employed in an alkaline medium, the sulfide ions are released as follows;

$$SC\left(NH_2\right)_2 \; SC(NH_2)_2 + \; OH^- = CH_2N_2 \; + H_2O \; + SH^- \text{ --------(1)}$$

$$SH^- \; + \; OH^- \; = S^{-2} \; + \; H_2O \text{ ---------- (2)}$$

When ($ZnSO_4$) is used with ammonia (NH_3) zinc complex $[Zn(NH_3)_4]^{+2}$ will be formed according to equations :

$$Zn(NH_3)_4^{+2} = 4NH_3 + Zn^{+2} \text{ ---------- (3)}$$

Then formation ZnS is according to equation :

$$Zn^{+2} \; + \; S^{-2} \; = \; ZnS \text{ ---------- (4)}$$

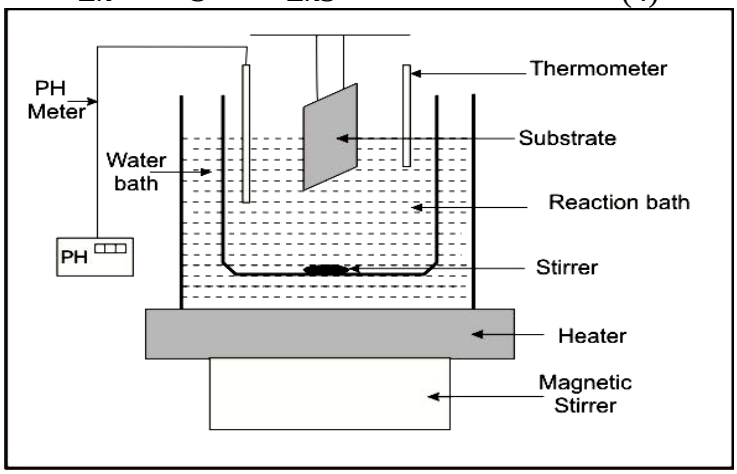

Fig. (1) Experimental arrangement for the deposition of ZnS films .

The thickness of ZnS thin films was measured using weight method, which depends on the difference between weight of substrate before and after deposition of the film. A sensitive electronic balance of type A&D company limited D0001 used . The thickness can be calculated from the relation below[14] :

$$t = \frac{m_2 - m_1}{\rho A} \text{ ----------(5)}$$

Table (1): Chemical bath compositions for the deposition of ZnS thin films.

Bath No.	$ZnSO_4$ (M) (20ml)	NH_3 (10ml)	TU (M) (20ml)	D.W (ml)	T (^oC)	t (min)	PH
Bath	0.2	25%	2	50	75-80	60	10
Bath2	0.3	25%	2	50	75-80	60	10
Bath3	0.4	25%	2	50	75-80	60	10

Where t : thickness of the film ,m_1 and m_2 : weight of the substrate before and after deposition respectively , A : area of thin film and ρ : density of element.

The crystal structure of the prepared films has been examined by X-ray diffractometer (XRD-6000 Shimadzu) with wavelength 1.5405Å Cukα radiation, the scanning angle varied in the range (20-60)^o , current 30 mA, and voltage 40 KV.

The optical measurements which included transmittance and absorbance spectra in the wavelength range (190-1100) nm were carried out using UV-1650 PC UV- VIS spectrophotometer SHIMADZU. All deposited ZnS thin films of different Zn ion concentrations were furnace annealing at 400°C for 3 h in air.

III. Results and discussions

The structure of ZnS thin films were analyzed by X-ray diffraction pattern before and after annealing in air at 400^{o} C. The diffraction pattern of the as deposited films showed amorphous structure which could be attributed to many parameters among those the wide band gap, short deposition time and glass substrate[15,16]. After annealing the ZnS film with small Zn ions concentrations 0.2M shows certain small peaks, that is mean the diffraction peaks intensity is very low which indicate that the film structure has low degree of crystallinity and it was observed that ZnS film has polycrystalline hexagonal structure oriented towards (108)and (110) planes as shown in the Fig.2. Then by increasing the concentration 0.3M and 0.4M , the diffraction peaks intensity increases, that's mean the structure of the films become more crystalline by increasing the degree of crystallinity .X-ray diffraction pattern of the 0.3M ZnS thin film as in figure (3), shown the presence of (106), (107), (108) and (110) planes of ZnS material with polycrystalline wurtzite hexagonal structure, the (108) peak is the preferred orientation. Fig.(4) shows the diffraction pattern of o.4M ZnS thin film(polycrystalline wurtzite hexagonal structure) with presence of (100), (106), (107), (108) and (110) planes with the preferential orientation along the (108) plane direction. The annealing or heat treatment provides full recrystallization within a given time period, This means that the annealing leads to an improvement in the crystallinity, annihilation and rearrangement of defects of the films, and annealing treatment could increase the activation energy of crystallization. This result confirmed some earlier studies [15,17]. The d-values were calculated by using Bragg's law and compared with the standard ASTM(card no. 12-0688) data to confirm the structure of ZnS as listed in table(2). The average grain size of ZnS thin films have been determine using Scherer's formula (18):

$$D = \frac{0.9\lambda}{B\cos\theta_B} \text{---------(6)}$$

where λ, θ_B and B were the X-ray wavelength (1.54056 Å),Bragg diffraction angle and line width at half-maximum , respectively.

Table (2): Obtained results from the XRD of ZnS thin films.

Composition	Concentration (M)	d_{hkl}(Å) observed	d_{hkl}(Å) ASTM	2θ (Degree)	hkl	I/I_0 %	a (Å)	c (Å)	Grain Size (nm)
ZnS	0.2	2.489	2.52	36.047	108	73	3.76	30.8	83.79
		1s.882	1.904	48.229	110	55			62.27
ZnS	0.3	2.853	2.81	31.321	106	93	3.86	31.6	41.25
		2.628	2.66	34.07	107	89			29.71
		2.500	2.52	35.88	108	100			46.41
		1.935	1.904	46.909	110	28			54.16
ZnS	0.4	3.533	3.31	25.185	100	40	3.85	30.3	54.24
		2.830	2.81	31.58	106	85			24.09
		2.616	2.66	34.295	107	70			21.15
		2.468s	2.52	36.09	108	100			20.89
		1.93	1.904	46.79	110	35			57.91

The average grain size for all thin films of ZnS are found to vary from(20.8 to 83.7)nm which gives an indicate that the films have nanocrystalline structure. It's obvious from the results that the grain size decreases with increasing the Zn^{+2} ion concentrations of the prepared films as shown in table (2). The lattice constant a and c can be determined from the inter planar spacing of (hkl) planes equation (19):

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2} \quad \text{----------} \ (7)$$

The lattice constant a and C is obtained from d-value of the [110] peak. These are shown in table (1). In this table, it is very clear that the different concentration of ZnS films have different values of lattice constant. For the case of 0.2, 0.3 and 0.4M films, the a– lattice constant is vary from 3.76 to 3.86A^o, but for C– lattice constant is vary from 30.3 to 31.6A^o , these values are nearly closes to a and C values at ASTM for ZnS material.

Fig.(5) shows the transmittance spectra of as deposited and annealed ZnS films which deposited at 80°C, in the range of incident light wavelength from (190 to 1100) nm. The transmittance decreases with the increasing of the Zn ion concentration of the films before and after annealing for a specific wavelength. This may be refer to the different thickness and roughness of the films. It can be seen that the deposited film at low Zn ion concentration has higher transparency, because it was thinner than the others. Moreover, the film was not densely covered by particles and the space of particles was large so the light can transmit easily. So the concentration of Zn or thickness of films is very important to obtain high quality ZnS films. Fig.(5) also shows the transmittance of annealed ZnS films was lower than that of deposited ZnS film . It can be seen that the annealed films had a smooth optical absorption feature, which can be attributed that the surface of ZnS became homogenous, and defects density decreased after annealing [16,20].

All the samples of ZnS films show high transmittance in VIS and NIR region. The optical spectral of 0.4M A annealed sample of ZnS films exhibit the lowest transmittance.

The graph of optical absorption coefficient, α Vs. photon energy hν is shown in fig. (6) for ZnS thin films of different Zn ion concentrations .The data from absorption spectrum are used to calculate the absorption coefficient by using equation.:

$$\alpha = \frac{2.303A}{t} \text{ ---------- (8)}$$

Where A and t is the absorbance and the thickness of the film respectively.

It is clear that the films have a high absorption coefficient ($\alpha > 10^5$ cm^{-1}) which gives an indicate that all films have direct band gap. Maximum values of absorption coefficient are observed at shorter wavelengths. Annealing process increases the value of the absorption coefficient in the whole spectra and shifts the fundamental absorption edge towards the higher values of the photon energy which can be attribute to the enhancement of the crystallinity of the films [21]. The direct energy gap values were calculated by using Tauc relation (22) :

$$\alpha(h\upsilon) = A^*(h\upsilon - E_g^{opt})^r \text{ ----------(9)}$$

Where A* is constant and r = 1/2 for direct allowed transitions. The band gap energy was determined by extrapolating the linear region of the resulting curves shown in the Figs. (7),(8),(9),(10),(11) and (12). The nature of the plots indicates the existence of direct optical transition. From figs. (7),(8) and (9) the energy band gab increasing from 1.594 to 3.060 eV with increasing the Zn ion concentration of films from 0.2 to 0.4 M which refer to the increasing of films thickness. It may be mentioned that, in amorphous chalcogenide thin films, the number of defects are higher due to the existence of unsaturated bonds [23,24]. The increase in the thickness of the films results in a homogeneous network with low density of defects [25] thereby, increasing the optical band gap. Figs.(10),(11) and (12) shows the energy band gaps of the annealed films with different Zn ion concentrations, where the annealing process leads to increasing the band gaps of the films . Annealing process having different effect leads to increase in the energy gap values, because the annealing process decreases the secondary levels and the structure defects which lead to the contract tails region. This leads to expand in the optical energy gap and increases with increasing the time and temperature of annealing[3,26] . Table (3) show the results of the optical energy gap of ZnS thin films before and after annealing .

Table (3): The result of energy gap of ZnS thin films before and after annealing.

Concentration Of CuS thin film (M)	Direct energy band gap Eg^{opt} (eV) before annealing	Direct energy band gap Eg^{opt} (eV) after annealing
0.2	1.594	3.215
0.3	2.722	3.132
0.4	3.060	3.099

V. Conclusions

The main conclusions that can be drawn from the results of the present study are:

1. The crystal structure nature of the ZnS thin films was amorphous before annealing, while after annealing process it becomes polycrystalline structure type (Hexagonal) .

2. Results of the grain size values of annealed ZnS thin films indicate that the films have Nanocrystalline grains structure.

3. The optical transmittance ZnS thin films decreases with increasing the concentration of Zn ions in the Bath solutions, while it decreases after annealing process .

4. The optical energy gap values of ZnS thin films for allowed direct transition increased with the increases of the Zn ion concentration before annealing ,while its values decreases after annealing process, therefore films with 0.2, 0.3 and 0.4 ion concentrations can be used as a filter For the wavelengths 385.69, 395.91 and 400.12 nm respectively, and as window for the above wavelengths.

5. ZnS thin film have a wide direct band gap in the UV region, so it can be used as a key material for blue light emitting diodes and other optoelectronic devices such as electroluminescent displays.

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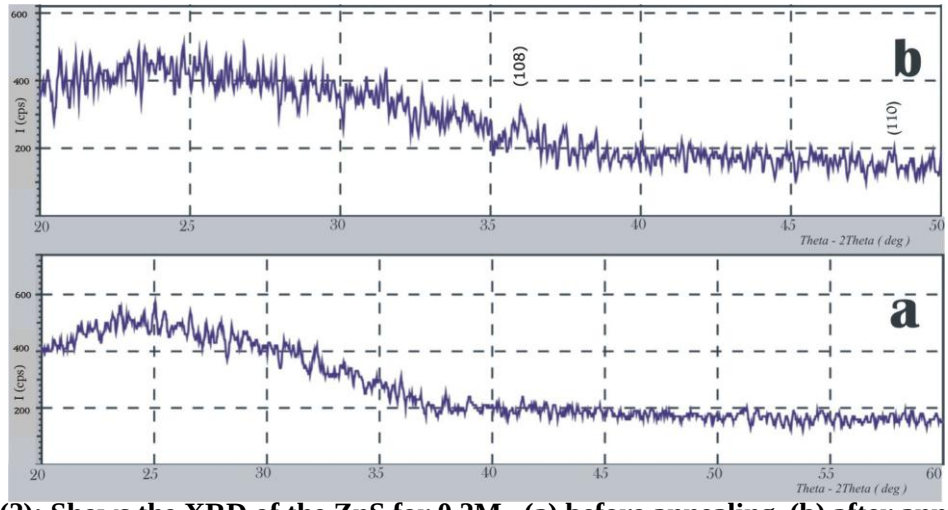

Fig. (2): Shows the XRD of the ZnS for 0.2M . (a) before annealing ,(b) after annealing .

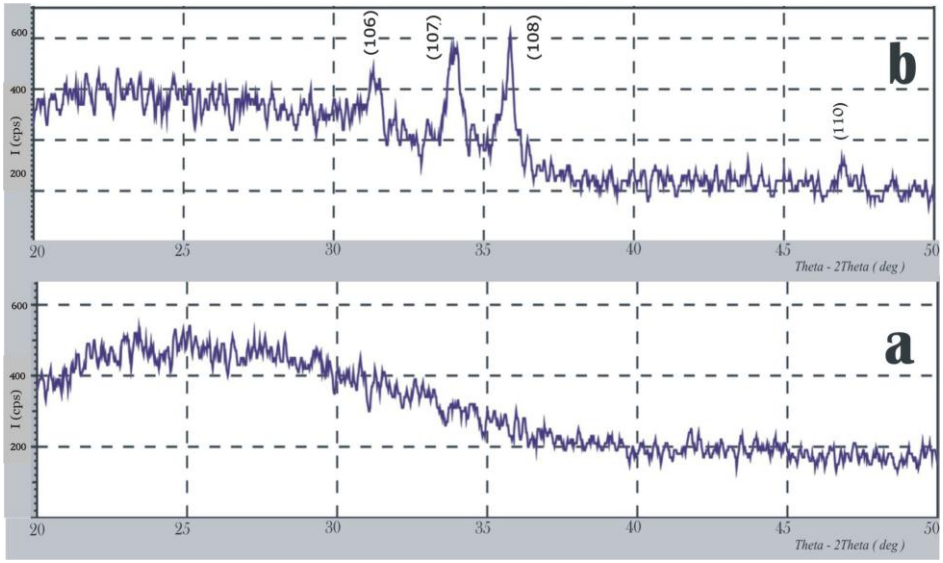

Fig. (3): Shows the XRD of the ZnS for 0.3M . (a) before annealing ,(b) after annealing.

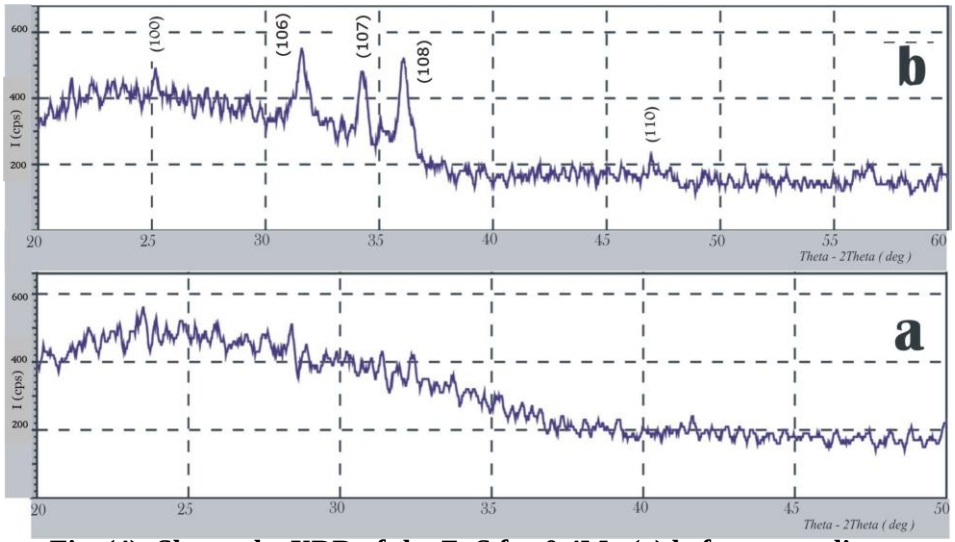

Fig. (4): Shows the XRD of the ZnS for 0.4M . (a) before annealing , (b) after annealing .

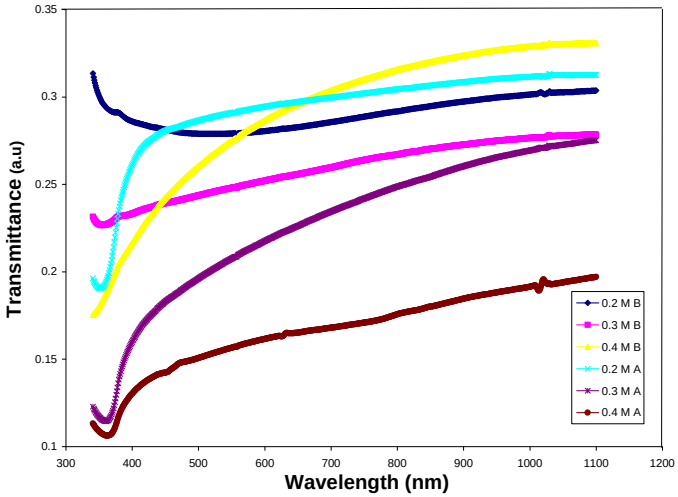

Fig. (5): Shows the transmittance of the zns for 0.2,0.3,0.4 M . before(B) and after (A) annealing .

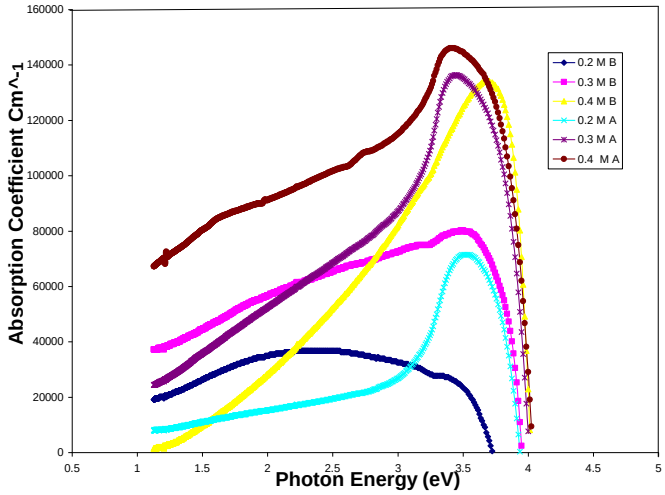

Fig. (6): Shows the absorption coefficient of the ZnS for 0.2,0.3,0.4M. before(B) and after (A) annealing.

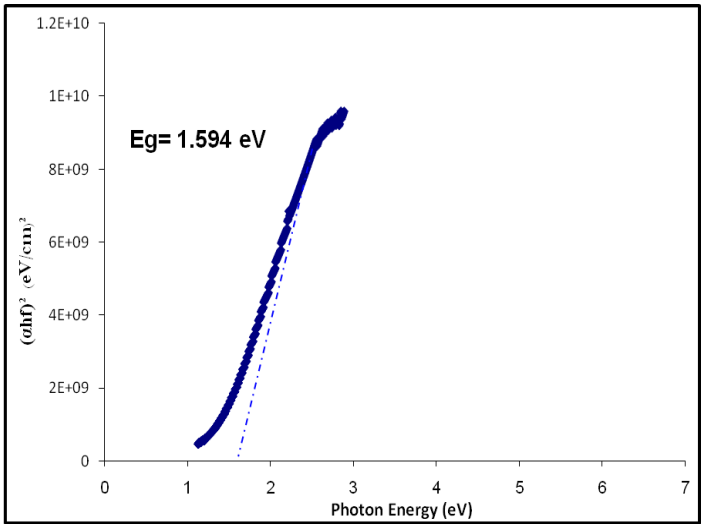

Fig. (7): The direct optical energy gap for ZnS 0.2M before annealing

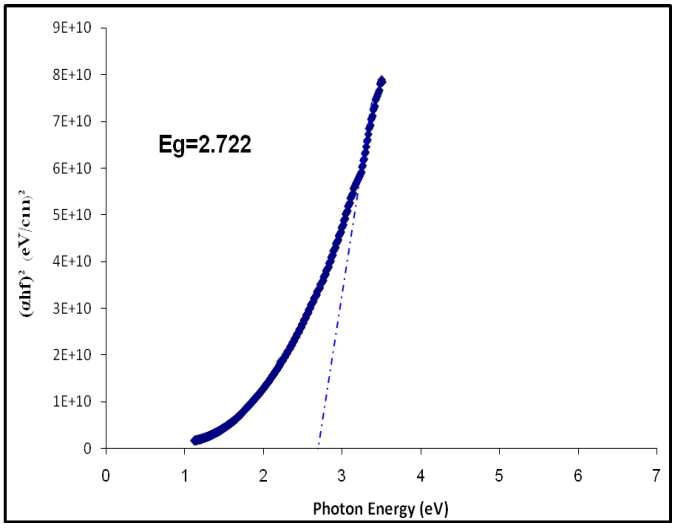

Fig. (8): The direct optical energy gap for ZnS 0.3M before annealing .

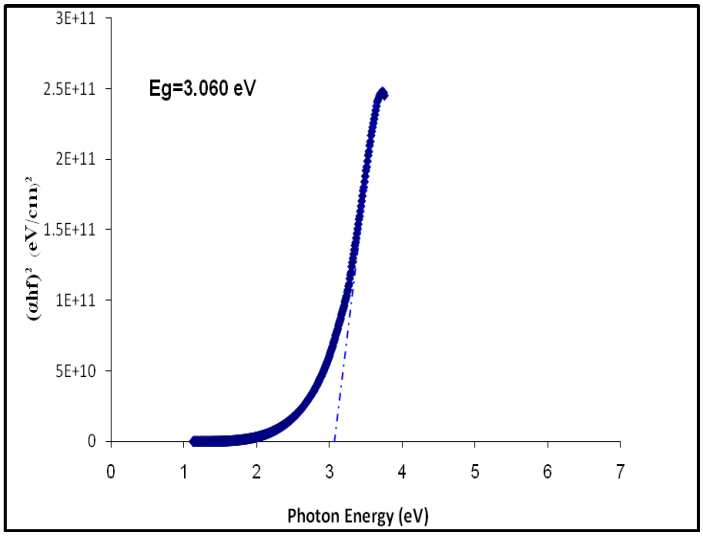

Fig. (9): The direct optical energy gap for ZnS 0.4M before annealing .

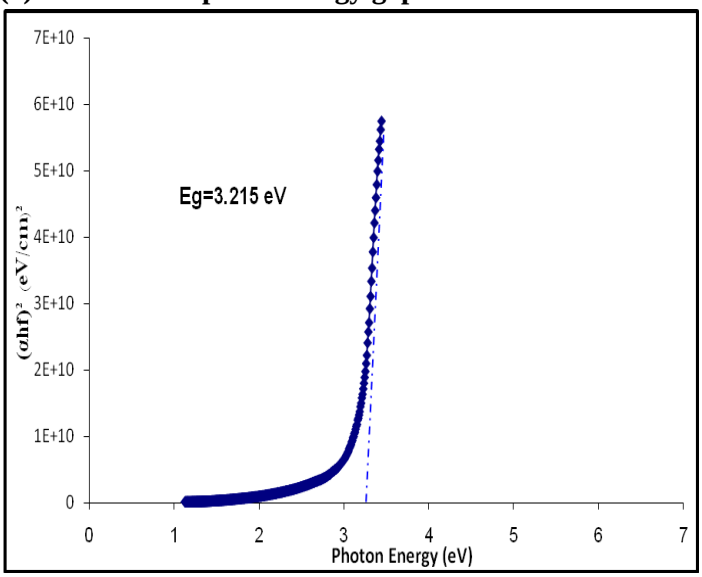

Fig. (10): The direct optical energy gap for ZnS 0.2M after annealing .

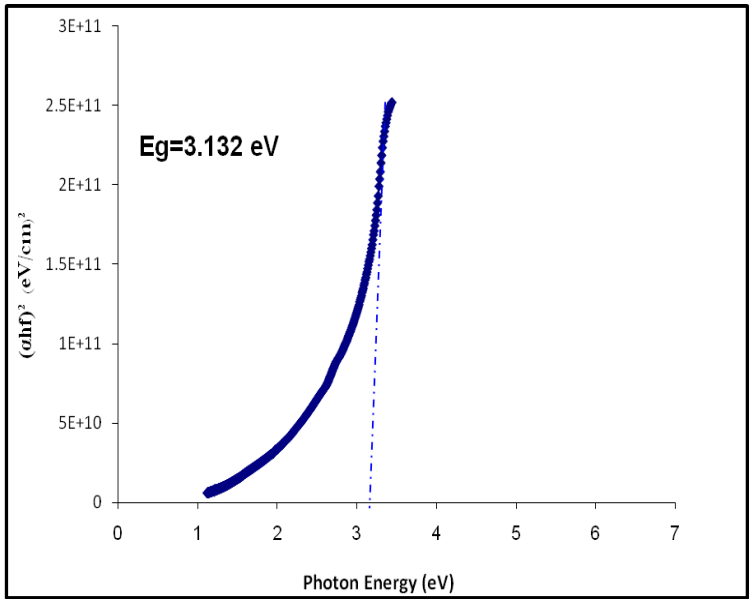

Fig. (11): The direct optical energy gap for ZnS 0.3M after annealing .

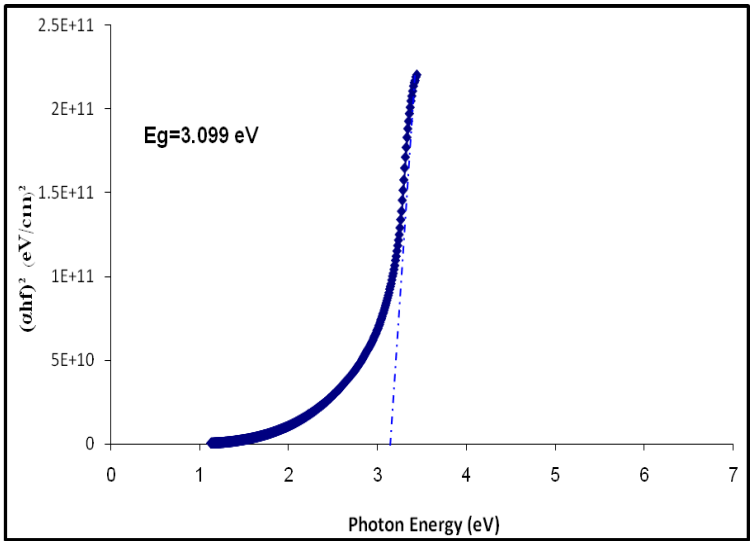

Fig. (12): The direct optical energy gap for ZnS 0.4M after annealing .