Structural and Optical Properties of ZnS Thin Films Prepared by Spray Pyrolysis Technique

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Abstract

Zinc Sulfide (ZnS) is important II-VI semiconductors material for the development of various modern technologies and photovoltaic applications. ZnS thin film was prepared by using chemical spray pyrolysis technique. The spray solutions contains $ZnCl_2$ and $SC(NH_2)_2$ with molar concentration 0.1M/L. ZnS thin films was growth onto hot glass substrates at substrates temperature $400^{o}C$.

The Structure of the prepared film was studied from X-ray diffraction pattern, the results shows that the film was polycrystalline with hexagonal structure, the grain size of ZnS film was calculated, it was 139 Å at the high peak.

The optical properties of the film were studied using measurement from UV–VIS spectrophotometer; the results appear that a good optical transparency of about 65 % was observed in the visible region. The optical constants were studied as a function of the photon energy within the wavelength in the range (300-900) nm. The refractive index was calculated in the visible region, it was 2.45 at 500 nm. The optical band gaps for the direct and indirect transition were estimate too and it was 3.2 – 3.1 eV respectively.

Keywords: Semiconductor thin film material, polycrystalline ZnS.

Introduction

II – VI semiconductors, such as Zinc Sulphide (ZnS) have attracted growing interest owing to their possible application in optoelectronics, it is important semiconductor material for the development of various modern technologies of solid – state devices (laser diodes, solar cells). Zinc Sulphide have wide direct band gap of about 3.50 eV in the UV region; it is used as a key material for blue light emitting diodes and other optoelectronic devices such as electroluminescent displays, cathodluminescent displays and multilayer dielectric filters [1, 2].

There have been various studies on the bulk and thin film characteristics of ZnS including optical and electrical properties.

Zinc sulfide has two types of crystal structures; hexagonal wurtzite and cubic zinc blende, it has a cubic crystal structure in its most stable state. For cubic structure, the lattice constant (a) is determined from the relation [3]:

$$d = \frac{a}{(h^2 + k^2 + \mathbf{l}^2)^{1/2}} \quad \text{.........................} (1)$$

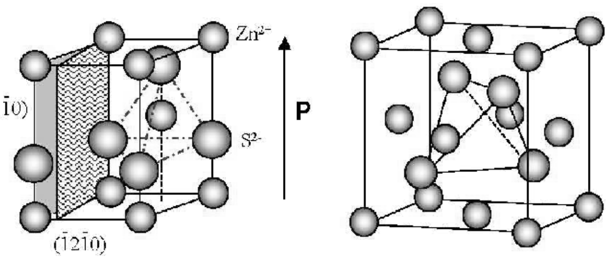
Where (hkl) are Miller indices.

For hexagonal structures, the lattice constant can be determined from the relation:

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

The crystal structure is polycrystalline having direct transition and it depending on the experimental conditions.

The nanostructures developing of II-VI based semiconductor nanostructures is of great interest, nanoscience and technology is a new and dominant player in the scientific arena [4].



(a) (b)

(a) The wurtzite ZnS structure.
(b) The zinc blend structure for the II-VI semiconductors [4].

The absorption of radiation that leads to electronic transitions between the valence and conduction bands is split into direct and indirect transitions; these transitions are described by the equation [5]:

$$(\alpha h\upsilon) = A^{*}(h\upsilon - E_g)^{r} \quad ....(3)$$

where A^{*} is constant which is proportion inversely with amorphousity, α is the absorption coefficient, $h\upsilon$ is the incident photon energy, and r takes the values (1/2, 3/2, 2, and 3) depending on the material and the type of the optical transition whether it is direct or indirect.

Thin films of ZnS were prepared using many deposition techniques such as chemical bath deposition (CBD), sol-gel technique, metal organic vapor deposition (MOVD), pulsed laser ablation molecular beam epitaxy, vacuum evaporation technique, magnetron sputtering technique and spray pyrolysis technique. ZnS thin films can be chemically deposited from aqueous solutions [6].

The optical properties of the prepared film depend strongly on the manufacturing technique. Two of the most important optical properties; refractive index and the extinction coefficient are generally called optical constants. The amount of light that transmitted through thin film material depends on the amount of the reflection and absorption that takes place along the light path [7].

The optical constants such as the refractive index n, the real and the imaginary parts of dielectric constant (ε_r, ε_I respectively) and the optical conductivity σ were calculated by using the equations [7]:

$$n = [(4R/(R-1)^2) - k^2]^{1/2} - [(R+1)/(R-1)] \quad .... (4)$$

where R is the reflectance and k is the extinction coefficient.

$$\varepsilon_r = n^2 - k^2 \quad ....(5\text{-}a)$$

$$\varepsilon_i = 2\,n\,k \quad .... (5\text{-}b)$$

$$\sigma = \varepsilon_i\, \omega\, \varepsilon_o \quad ....(6)$$

Where: ω; is the angular frequency, ε_o; the permittivity of the air, ε_i; the imaginary part of dielectric constant.

In many instances researches, the optical constants were measure by examining the transmission through a thin film of the material deposited on transparent substrate. The amount of light that transmitted through thin film material depends on the amount of the reflection and absorption that takes place along the light path. The absorption of radiation that leads to electronic transitions between the valence and conduction bands is split into direct and indirect transitions [8].

ZnS is highly suitable as a window layer in hetrojunction photovoltaic solar cells; because the wide band decreases the window absorption loses, ZnS can be used as a reflector because of its high refractive index (2.35), and as a transparent dielectric material (dielectric filter) because of its high transmittance in the visible region [9, 10].

Experimental Work

Zinc sulfide thin films were prepared on glass substrates (2.5x2.5) cm^2 using spray pyrolysis technique, this technique is widely used for the large-scale production of films owing to its low production cost and simplicity of operation. The glass substrates were cleaned by distils water and alcohol respectively. Solution containing Zinc Chloride ($ZnCl_2$) and Thiourea ($SC(NH_2)_2$).of molar concentration 0.1 M/L were used to prepare ZnS thin films;(all samples of thickness within the range (290±10) nm. The deposition time for one layer being about 3-4 sec, the substrate temperature was fixed around 400±10 ^{o}C.

Two experimental methods were used for thickness measurements; the "Weighting method" and the "Optical Interference Fringes method" A digital balance with accuracy of ($\pm 0.1 \times 10^{-3}$ gm) was used for weighting the needed materials and for measured the thickness of the prepared films. He-Ne laser of wavelength 632.8 nm was used for measured the thickness of the films by optical interference fringes method, the thickness of all the prepared films were varied between 380-400 nm.

The structures of the prepared thin films were obtained using the XRD techniques using radiation from CuK_α radiation target in the range of 2θ between 20^o–50^o. The optical transmission spectra of the deposited thin films were measured by UV-VIS spectrophotometer, the optical properties was calculated as a function of the photon energy at the wave length in the range 300-900 nm.

Results and Discussion

1: X-ray diffraction pattern of ZnS thin film

Zinc sulfide films have been found to grow in cubic (Zinc blend) and hexagonal forms depending upon the deposition process. In the present work, the reported hexagonal structure of ZnS is dominated.

The structure of ZnS thin films were analyzed by X-ray diffraction pattern. The d-values were calculated by calculating θ values from the peaks of the X-ray spectrum using Bragg's relation: 2dsinθ = n λ (n=1 in present study, λ= 1.54045 nm for Cu target).

The d values were compared with the standard ASTM data to confirm the structure of ZnS as listed in Table (1).

XRD pattern of the deposited Zinc sulfide thin films prepared by spray technique are shown in figure (1), the XRD patterns show the presence of (008), (102), (104), (105), and (110) planes of the ZnS material. The values of the lattice constant and the grain size of the prepared film are listed in Table (2), this study reveals that the films is polycrystalline with hexagonal structure.

Table (1)
The comparison of lattice constants value from X-Ray pattern and ASTM for all peaks of ZnS film.

(hkl)	*ASTM (d)Å*	*XRD (d)Å*	*ASTM (a)Å*	*ASTM (c)Å*
(008)	3.16	3.158	3.8	24.96
(102)	3.20	3.210	3.8	24.96
(104)	2.93	2.960	3.8	24.96
(105)	2.66	2.643	3.8	24.96
(110)	1.904	1.916	3.8	24.96

Part of ASTM card No. 12-688(ASTM) ZnS (Zinc Sulfide) HEXAGONAL		
d	**I/I_O**	**(hkl)**
3.31	2	(100)
3.26	6	(102)
3.20	4	-
3.125	100	(008)
3.05	4	(104)
2.76	2	(105)
2.715	4	-
2.81	2	(106)
2.66	2	(107)
2.08	2	-
1.9043	50	(110)

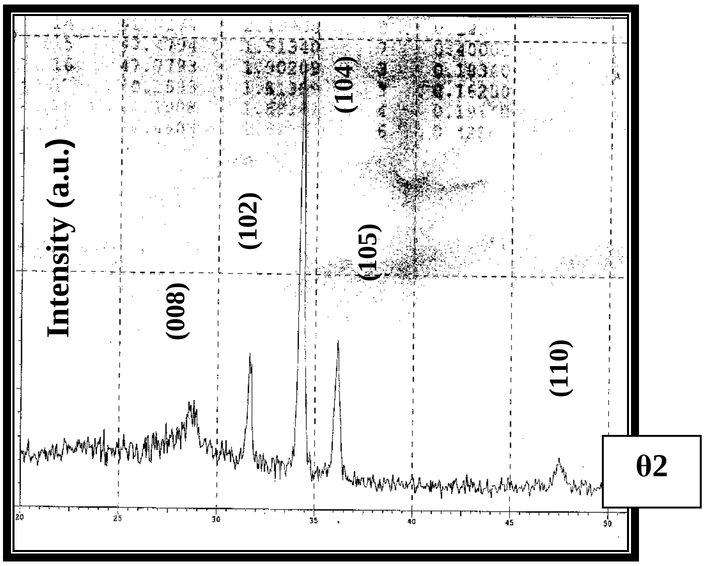


Fig. (1) X-ray diffraction pattern XRD of ZnS thin film.

The lattice constants for ZnO thin films were calculated by using equation (2). The value of the lattice constants (a, c) of ZnS thin film was 3.3 Å, 25.3 Å respectively, these value are nearly closes to a and c values at ASTM for ZnS materials.

The grain size (G) of the deposited films can be determined from half maximum intensity by using Scherer equation [7]:

$$G = \frac{k' l}{B\ Cos q} \quad \text{..................................} (7)$$

Where $k^{/}$ is approximately equal 1, λ= 1.54045 Å, θ is the diffraction angle and B is the width of diffraction line at half maximum intensity. The grain size of the films was calculated and listed in Table (2).

Table (2)
The values of the lattice constant and the grain size of ZnS film.

hkl	*(2q) Degree*	*(d) Å*	*(G.S)Å*
(008)	28.23	3.158	274
(102)	31.5	3.210	278
(104)	34.4	2.960	139
(105)	36.3	2.643	280
(110)	47.39	1.916	288

2: The Transmission Spectra

The Transmission Spectra of prepared ZnS thin films at 400°C is shown in Fig. (2), the transmittances of the films in the visible region was 65%. The moderately high transmittance of film throughout the UV-VIS regions makes it a good material for optoelectronic devices.

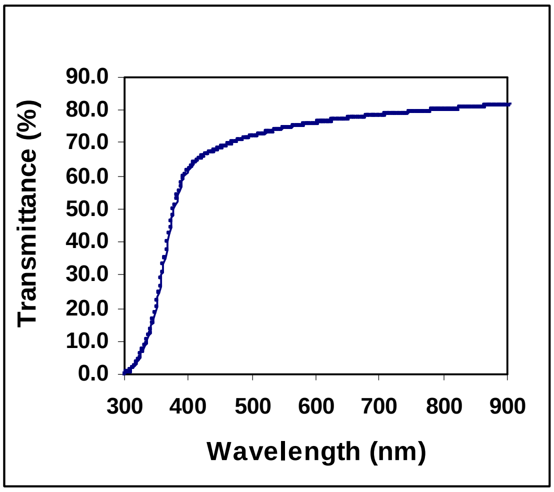


Fig. (2) The transmission spectra of ZnS film as a function to the wavelength.

3: The Absorption Spectra

ZnS films have good absorption at short wavelength region, the absorption decreased with increasing of the wavelength, as show in Fig. (3). The increase of the absorption occur when the photon energy be equal to the value of the energy gap then the electronic transfers between the valance band and the conduction band will began.

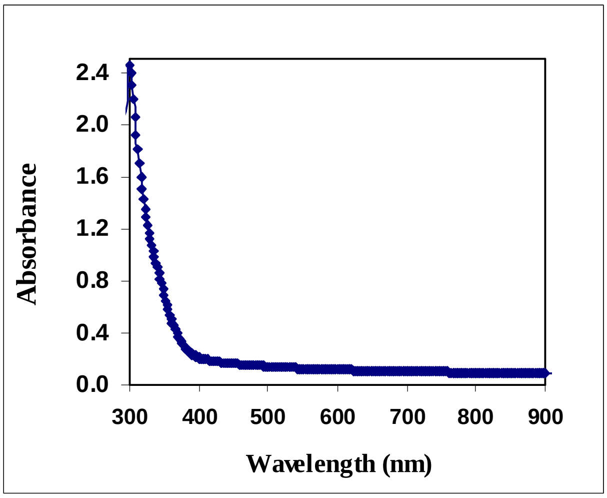


Fig. (3) The absorption spectra of ZnS thin films as a function to the wavelength.

4: The reflectance Spectra

The reflectance (R) of ZnS film can be calculated from the absorption and the transmittance spectrum using the relation; R+T+A = 1. Fig. (4) show the reflectance of ZnS film as function of the wavelength, R is almost constant in the range 600-900 nm, then rapid reduction will appear in the range 350-500 nm, that mean the absorption of the film will be very little amount at the photon energy less than the value of the energy gap; hυ< Eg.

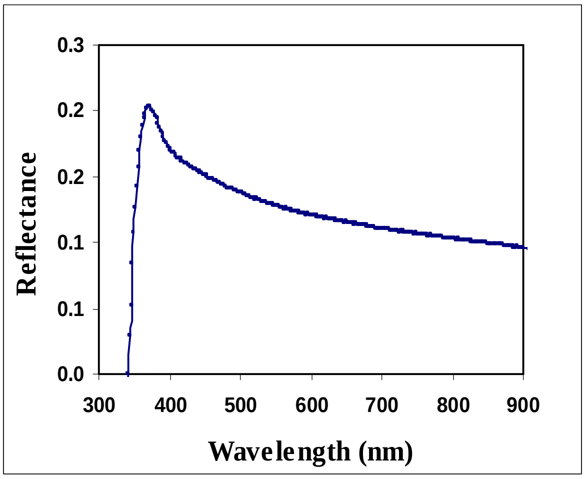


Fig. (4) The reflectance spectra of ZnS thin film as a function to the wavelength.

5: Absorption Coefficient and Extinction coefficient

The absorption coefficient (α) of ZnS film was determined from the absorbance measurements, α was calculated using the following equation:

$$\alpha = 2.303A/t \qquad (8)$$

Where A is the absorbance, t is the thickness of the film. The absorption coefficient of ZnS film was calculated to be $5.2\times10^4 cm^{-1}$ at 3.4 eV photon energy. Fig. (5) Shows the absorption coefficient as function of the photon energy; α decrease in the law photon energy because the probability of the electrical transfer between valance band and the conduction band is very rare and it will increase in the edge of the absorbance toward the high energy (hυ>3eV).

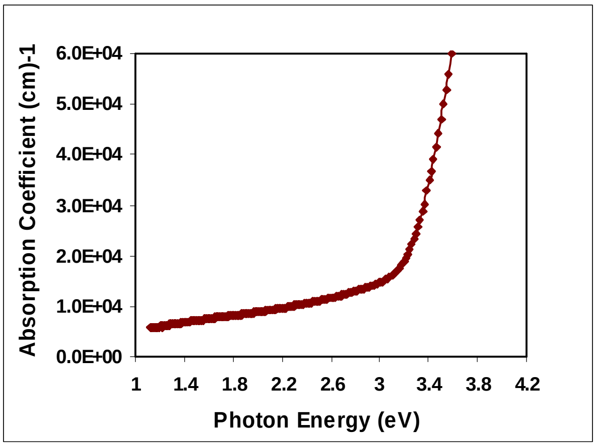


Fig. (5) The absorption coefficient of ZnS thin film as a function to wavelength.

The extinction coefficient k can be determined from a transmittance spectrum as a function of the photon energy at the wavelength within the range 300-900 nm, it can be determined from the relation:

$k = \alpha\, \lambda/4\pi$ ....(9)

Extinction coefficient k versus wavelength spectra is shown in Fig.(6), there is a little decreasing in the extinction coefficient in the visible range; (400-700) nm, then the rapid rise appeared within the range 300-400 nm, the increased extinction coefficient at the wavelengths below 400 nm is due to the high absorbance of ZnS thin films in that region.

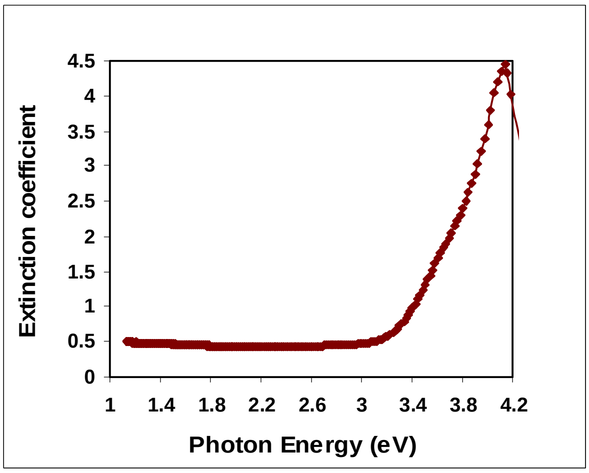


Fig. (6) The extinction coefficient of ZnS thin films as a function to the photon energy.

6: Refractive index

The refractive index ***n*** was determined from a transmittance spectrum as a function of the photon energy within the wavelength in the range 300-900 nm. The Refractive index (n) can be determined from the transmission spectrum using equation (4).

There is a decreasing in the refractive index in the visible range; it was estimated 2.45 at 500 nm, as show in Fig. (7), the refractive index changes slightly and steadily after 500 nm to 900 nm. The reported value of the refractive index in the visible region is 2.35 [9, 10].

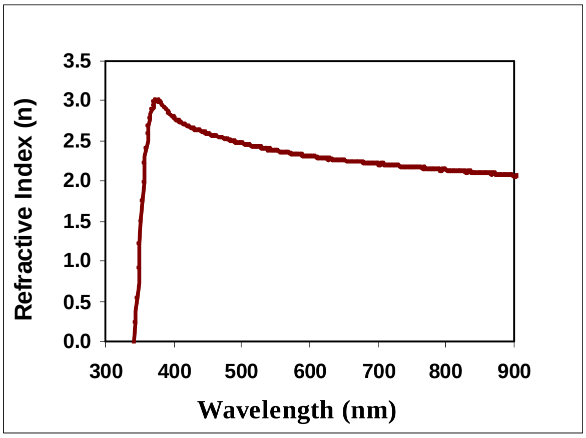


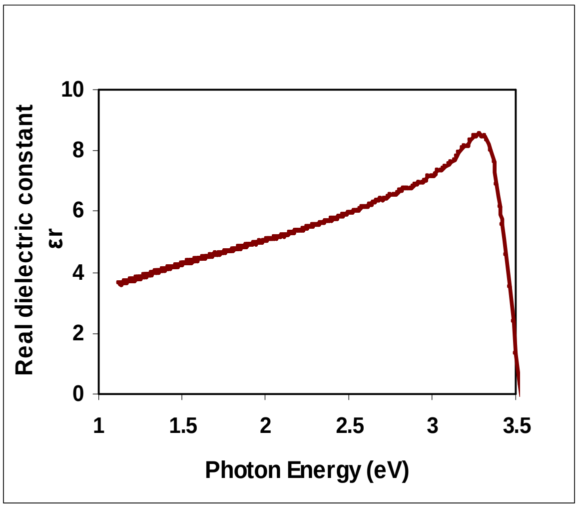
Fig. (7) The refractive index of ZnS thin films.

7:The optical conductivity and the dielectric constants ε

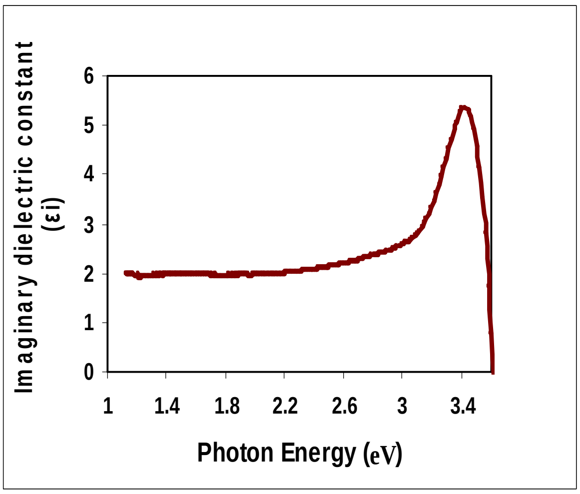
The optical conductivity was calculated by using equation (6). The real and imaginary parts of dielectric constant (ε_r, ε_i) were calculated by using equations (5-a, 5-b).

Fig. (8-a, b) shows the plots of the real and the imaginary parts of the dielectric constant against the photon energy (hν), the value of ε_r and ε_i are decreased at low incident photon energy.

Fig. (9) show the plot of the optical conductivity against the photon energy, the value of σ is also decreased at low incident photon energy.



(a)



(b)

Fig. (8) The real and the imaginary parts of dielectric constant of ZnS thin films.

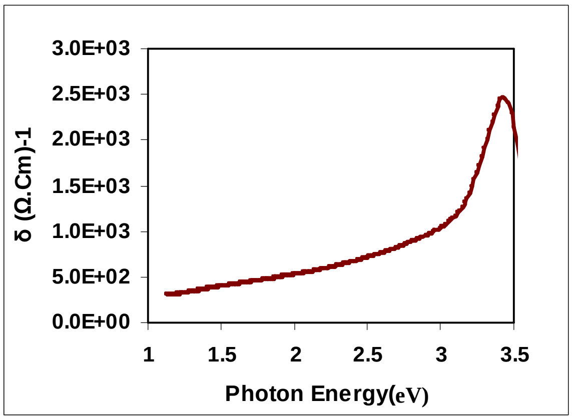


Fig. (9) The optical conductivity of ZnS thin film.

8: The Optical Energy Gap

The optical energy gap for the direct allowed transition between valence bands and conduction bands of ZnS thin films was calculated from equation (3) using r=1/2.The values of the band gap of ZnS thin film for the direct transition can be determined by extrapolating the straight line portion of the $(ahu)^2$ versus hu , as shown in Fig.(10-a).

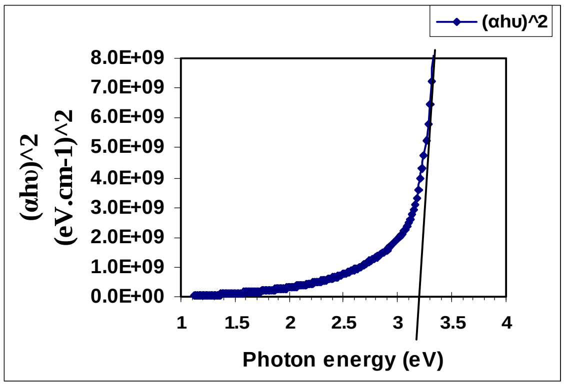


Fig. (10-a) The optical energy gap for the direct allow transition of ZnS thin film.

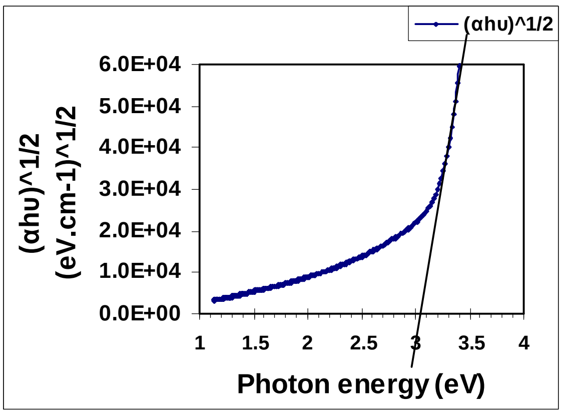


Fig. (10-b) The optical energy gap for the indirect allow transition of ZnS thin films.

Direct band gap energy of ZnS thin films was estimated to be 3.2 eV, the value of the optical energy gap for direct allowed transition of ZnS thin films prepared at substrate temperature 400 ^{O}C is in good agreement with previously reported value [2, 6]. The wide direct band gap makes these films good material for potential applications in optoelectronic devices such as multilayer dielectric filters, and solar cell due to decreases the window absorption loses and that will improves the short circuit current of the cell. The optical energy gap for the indirect allowed transition of ZnS thin films was calculated from equation (1) using r= 2, as show in Fig. (10-b), it was 3.05 eV.

Conclusions

Zinc sulfide luminescent thin films were deposited onto glass substrate by using spray pyrolysis technique, the films was successfully growth at substrates temperature of 400 ^{O}C. XRD analysis shows that the deposited ZnS films are polycrystalline with hexagonal structure.

It was observed that the prepared films have wide direct energy gap, the estimated value of the energy gap is in good agreement with the recent reported value. The wide band gap makes these films good material for optoelectronic devices.

Acknowledgment

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الخلاصة

يعتبر كبريتيد الزنك من أشباه الموصلات المهمة نوع II-VI وذلك لدخوله في العديد من التقنيات الحديثة وكذلك في تطبيقات الخلايا الفوتوفولتائية. تم تحضير مجموعة من الأغشية الرقيقة لمركب كبريتيد الزنك باستخدام تقنية الرش الكيميائي الحراري، تم تحضير محلول الرش المتكون من خلط نسب معينة من كلوريد الخارصين والثايوريا بمولارية مقدارها 0.1 M/L وقد تكونت أغشية كبريتيد الخارصين الرقيقة على شرائح زجاجية ساخنة بدرجة حرارة أساس 400^{O}C.

درست الخواص التركيبية للغشاء المحضر من خلال الفحص بواسطة حيود الأشعة السينية، وقد أظهرت النتائج أن الغشاء المحضر نوع متعددة التبلور (Polycrystalline). تم حساب الحجم الحبيبي وكانت قيمته Å 139 عند أعلى قمة.

تم دراسة الخواص البصرية لغشاء ZnS باستعمال مطياف يعمل ضمن الأطوال الموجية المرئية وفوق البنفسجية VIS-UV. أظهرت الدراسة البصرية بان معدل النفاذية تقترب من 65% عند المدى المرئي. تم حساب الثوابت البصرية كدالة لطاقة الفوتون لمدى الاطوال الموجية nm 300-900. وكانت قيمة معامل الأنكسار ضمن المدى المرئي 2.45 عند 500 nm. اما قيم فجوة الطاقة للانتقالات الالكترونية المباشرة والغير مباشرة فكانت 3.2 eV و 3.1 eV على التوالي.