ENHANCEMENT THE OPTICAL PROPERTIES OF ZINC SULFIDE THIN FILMS FOR SOLAR CELL APPLICATIONS

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Abstract

In this work, semi-conducting ZnS compound was prepared as thin films onto glass substrates at two different substrates temperature (673, 723) K using chemical spray pyrolysis technique. X-ray diffraction was studied for the prepared films, the results shows that the films was polycrystalline with a wurtzite (hexagonal) structure. The optical properties of the films were studied by using VIS-UV spectrophotometer, the absorbance and transmittance spectrum have been recorded at wavelength within the range (300-900) nm. The optical characteristics were studied as a function of the photon energy at the mentioned wavelength. The results appear that the transparency of the films at visible region is rise from 70% to 90% at high substrates temperature. The refractive index was estimated within the visible wavelength at 500 nm, it was 2.45 at substrate temperature 673 K and its value will decrease at the highest substrate temperature. The direct optical band gap of the allow transitions for the deposits films prepared at both substrate temperatures (673, 723) K were varied from 3.2-3.4 eV respectively.

Key words: semiconductor thin film material, polycrystalline ZnS.

تحسين الخواص البصرية لأغشية كبريتيد الزنك الرقيقة لتطبيقات الخلايا الشمسية

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الخلاصة

في هذا البحث، تم تحضير مجموعة من الأغشية الرقيقة لمركب كبريتيد الزنك باستخدام تقنية الرش الكيميائي الحراري على شرائح زجاجية بدرجتي حرارة أساس مختلفة K(673-723). تم فحص الأغشية المحضرة بواسطة حيود الأشعة السينية، ومن دراسة النتائج تبين أن جميع الأغشية المحضرة هي نوع متعددة التبلور (Polycrystalline).

تم دراسة الخواص البصرية لأغشية ZnS باستعمال مطياف يعمل ضمن الأطوال الموجية المرئية وفوق البنفسجية VIS-UV. اشتملت دراسة الخواص البصرية على تسجيل طيفي الامتصاصية والنفاذية للأغشية المحضرة لمدى الأطوال الموجية 300-900 nm، تم دراسة الخواص البصرية كدالة لطاقة الفوتون عند مدى الأطوال الموجية المذكورة أظهرت النتائج بان معدل النفاذية يرتفع من 70% الى 90% في المدى المرئي عند ارتفاع درجة حرارة الأساس.

تم حساب معامل الانكسار ضمن المدى nm 500 من الطول ألموجي وكانت قيمته 2.45.عند درجة 673 K وتكون قيمته أقل عند زيادة درجة حرارة الأساس. هذا وتتغير قيم فجوة الطاقة للانتقالات الالكترونية المباشرة عند درجتي حرارة القاعدة الزجاجية K (673 و723) من 3.2 eV إلى 3.4 eV على التوالي.

1. Introduction

Semiconducting thin films of the type II–VI have received considerable attention for their optical, electrical and photo induced properties. This class of thin films recently has been extensively studied due to potential applications in optoelectronic devices, solar cells. [1]. II–VI semiconductors, such as Zinc Sulphide (ZnS) are well known for application in a wide range of optoelectronic devices, 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 3.50-3.70 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, cathodoluminescent displays and multilayer dielectric filters [2].

ZnS is highly suitable as a window layer in heterojunction photovoltaic solar cells; because the wide band decreases the window absorption loses. In the area of optics, 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 range. Also Zinc sulfide has been successfully used in electro-luminescence devices and in blue light emitting laser diode [3-5].

Before optical properties of any thin film were extracted, the refractive index of their substrate can be calculated from the relation [6]:

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

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

There have been various studies on the bulk and thin film characteristics of ZnS including optical and electrical properties. Thin films of ZnS were prepared using many deposition techniques such as chemical bath deposition, sol-gel technique, metal organic vapor deposition, pulsed laser ablation, molecular beam epitaxy, vacuum evaporation technique, magnetron sputtering technique, and spray pyrolysis technique [7]. ZnS thin films can be chemically deposited from aqueous solutions, the spray pyrolysis technique is widely used for the large-scale production of films owing to its low production cost and simplicity of operation.

The optical constants were measure by examining the transmission through a thin film of the material deposited on transparent substrate. 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 [8]:

$$(\alpha h\upsilon) = A^*(h\upsilon - E_g)^r \text{ --------------------(2)}$$

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. The theory of the optical absorption gives the relationship between the absorption coefficient and the photon energy.

Zinc sulfide has two types of crystal structures; hexagonal wurtzite and cubic zinc blende, the structure of such thin films was obtained using X - ray diffraction technique, the structure depending on the experimental conditions [9].

In this work, ZnS was prepared as thin film using the spray technique to be insure that the films have good optical prepared as it was prepared in another technique with changing the substrate temperature and if the properties of the prepared films are suitable for photovoltaic cell as window layer.

2. Experimental work

Zinc sulfide thin films were prepared on glass substrates (2.5x2.5) cm^2 using the chemical spray pyrolysis technique. The Pyrex glass substrates were cleaned by distils water and alcohol respectively. Solution containing Zinc Chloride ($ZnCl_2$) and Thiourea $SC(NH_2)_2$ were used to prepare ZnS thin films. The lower part of the reaction chamber heated by electrical resistance and substrate temperature was measured with a thermocouple. The distance between the spraying nozzle and the heated glass substrate is about 28cm. The spray rate was about 10 ml/min with deposition time for one layer being about 5 sec. The substrate temperatures were fixed on 673K and 723K.

Two experimental methods were used for thickness measurements; the "Weighting method" and the "Optical Interference Fringes method", the Weighting method gives an approximate value for the thickness of the thin films with an error 30 %. A digital balance with accuracy of ($\pm$ 0.1× 10^{-3}) 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 370-390 nm. The structures of the prepared thin films were obtained using the XRD techniques in the range of 2θ between 20^o and 50^o. The optical transmission spectra of the deposited thin films were measured by UV-VIS spectrophotometer, the optical properties where calculated as a function of the wave length in the range 300-900 nm.

3. Results and discussion

3-1 X-ray analysis

X-ray diffraction technique was used to determine the crystalline structure and grain size of the thin films. 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 hexagonal structure of ZnS is dominated.

The deposited ZnS thin films were analyzed from X-ray diffraction pattern. The d-values were calculated by calculating θ values from the peaks of the X-ray spectrum by using Bragg's relation [10]:

$2d\sin\theta = n\,\lambda$ -------------------------------------(3)

Where n is the reflection order; n=1 in present study and λ= 1.54045 for CuK_α target, d is the interplanar spacing, and θ is the diffraction angle.

XRD pattern of the deposited ZnS films at the substrate temperature 673K is shown in (Figure 1), this figure shows the presence of (008), (100), (104), (105) and (110) planes is for ZnS material. This result reveals that the films are polycrystalline with hexagonal structure.

The X-ray diffraction pattern of ZnS thin film at 723K is shown in (Figure 2), at this temperature there are apparent of the sharp peaks at (008), (106), (107); the sharp peaks can be attributed to the decreasing in the crystals defects when the substrate temperatures increase [11].

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

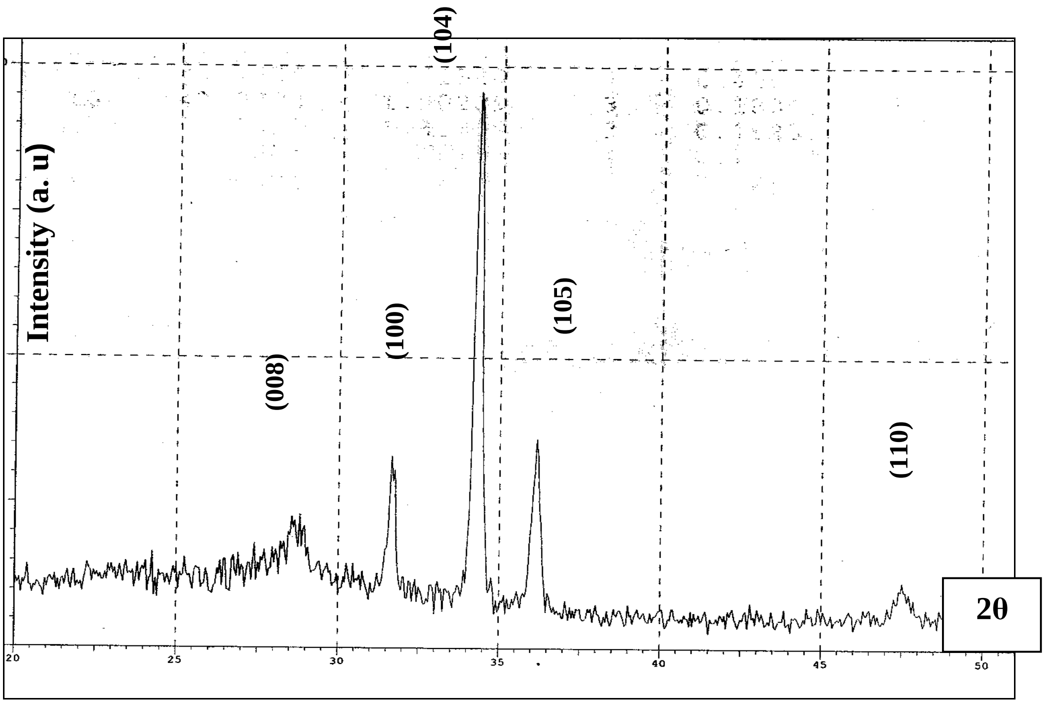

Figure 1: X-ray diffraction pattern XRD of ZnS thin film at 673K

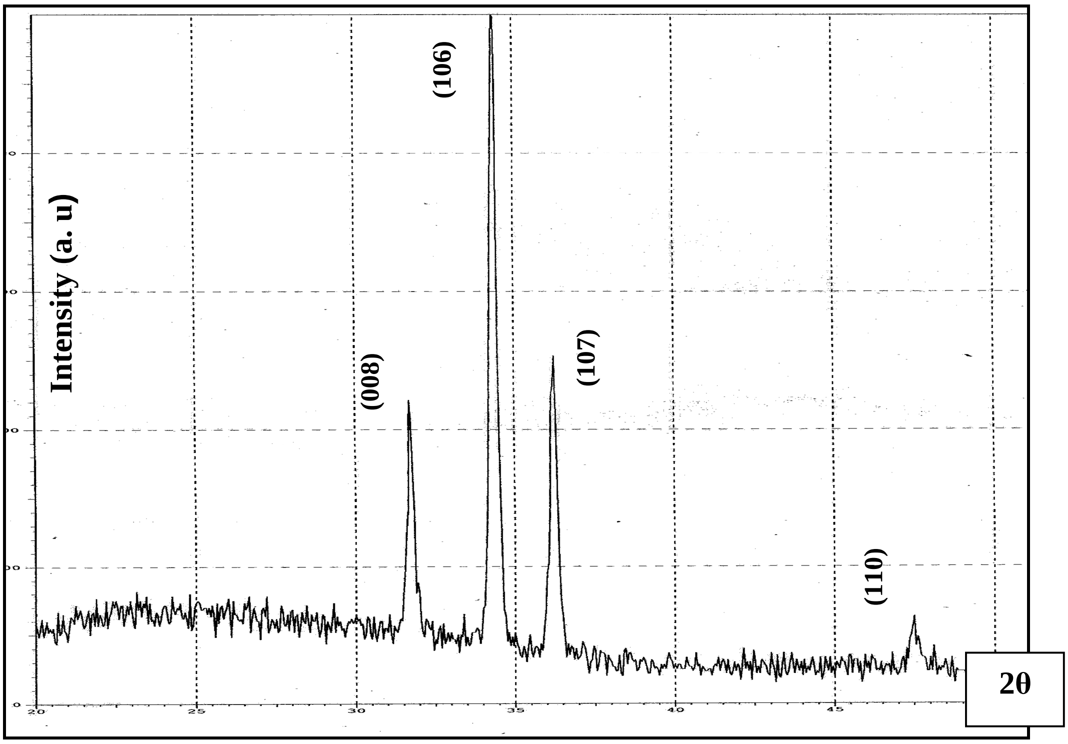

Figure 2: X-ray diffraction pattern (XRD) of ZnS thin film at 723K

Table 1: The comparison of d values from X-Ray pattern and ASTM for all peaks of ZnS films prepared at 673K and 723 K

Temp.(K)	hkl	(2θ) Degree	ASTM (d)Å	XRD (d) Å	Grain Size(Å)
673	(008)	28.23	3.125	3.12	-
	(100)	31.5	3.26	3.20	278
	(104)	34.4	2.93	2. 96	139
	(105)	36.3	2.66	2.75	280
	(110)	47.39	1.904	1.90	-
723	(008)	31.5	3.16	3.13	205
	(106)	34.5	2.61	2.56	104
	(107)	36.5	2.49	2.49	140
	(110)	47.4	1.904	1.903	-

3-2 The transmission spectra

The Transmission spectra of ZnS thin films that prepared at 637K and 723K are shown in (Figure 3), the transmittances of the deposit films at 723K in the visible region increase from 70% to 90%. The moderately high transmittance of film throughout the UV-VIS regions makes it a good material for optoelectronic devices as a window layer.

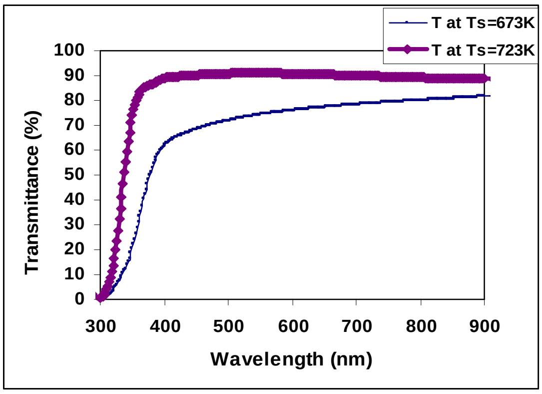

Figure 3: The transmission spectra of ZnS films as a function of wavelength at both substrate temperature of 673K and 723K

3-3 The absorption spectra

ZnS film has good absorption at short wavelength region, and then the absorption decreased at long wavelength, as show in (Figure 4), the films that prepared at T_S=723K showed lower absorption in same wavelength region.

The absorption will increase when the photon energy be equal to the energy gap (hυ=Eg) because of the electronic transfers occur between the valence and the conduction band.

The reduction in the absorption of the film at T_S=723K is due to the advantage of the structure (low defect in the crystal structure) at this temperature and that improve the optical properties of the film.

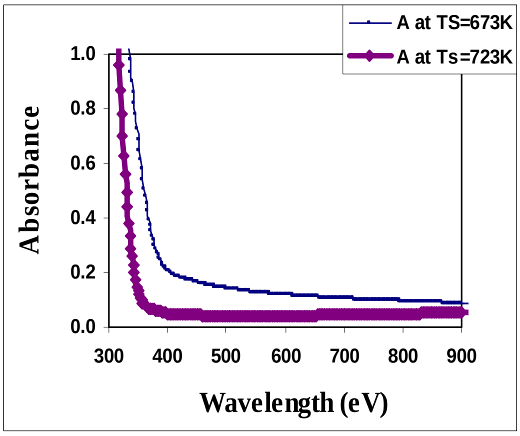

Figure 4: The absorption spectra of ZnS thin films as a function of wavelength prepared at both substrate temperature of 673K and 723K

3-4The reflectance spectra

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 [6], the reflectance (R) of ZnS film can be calculated from the absorbance and the transmittance spectrum using the following relation:

R+T+A = 1 -----------(4)

where A is the absorbance and T is the transmittance of the film.

(Figure 5) shows the reflectance of ZnS film as function of the wavelength, there is a little change in the range 600-900 nm; (2.1-1.8) eV, then rapid reduction will appear in the range 370-500 nm; (3.3-2.5) eV of the photon energy, that mean the absorbance of the film will be very little amount at the photon energy less than the value of the energy gap; hυ< Eg.

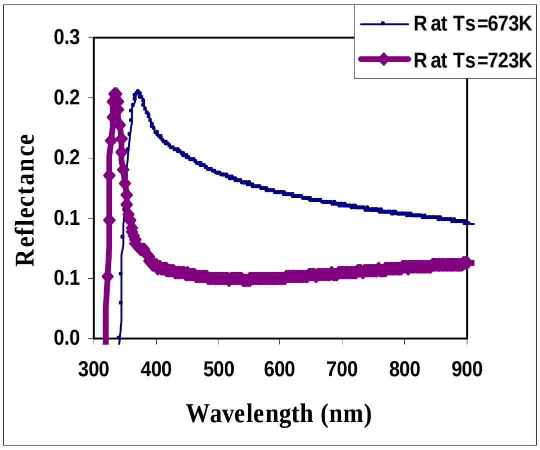

Figure 5: The reflectance spectra of ZnS thin films as a function of the wavelength prepared at both substrate temperatures of 673K and 723K

3-5 Absorption and extinction coefficients

The absorption coefficient of ZnS film was determined from the absorbance measurements, α was calculated using the following equation; α= 2.303A/t where t is the thickness of the film. The absorption coefficient of ZnS film was calculated to be $18\times10^4 cm^{-1}$ and it was decreased when the substrate temperature increased to 723K.

(Figure 6) show 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) at 673K and at 723K.

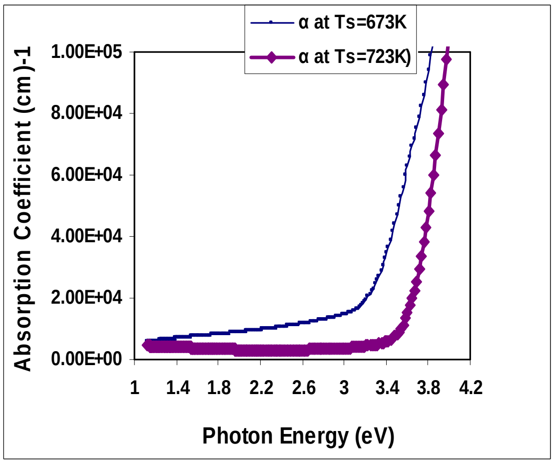

Figure 6: The absorption coefficient of ZnS thin films as a function of wavelength at both substrate temperatures of 673K and 723K

The extinction coefficient (k) can be determined from the absorbance measurements as a function of the wavelength within the range 300-900 nm, it was calculated by using the following equation:

$k = \alpha\ \lambda/4\pi$ ---------------------------------------(5)

where λ is the wavelength.

Extinction coefficient versus wavelength spectra is shown in (Figure 7), 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, and it was decreases with increasing the substrate temperature. The increased extinction coefficient at the wavelengths below 400 nm is due to the high absorbance of ZnS thin films in that region.

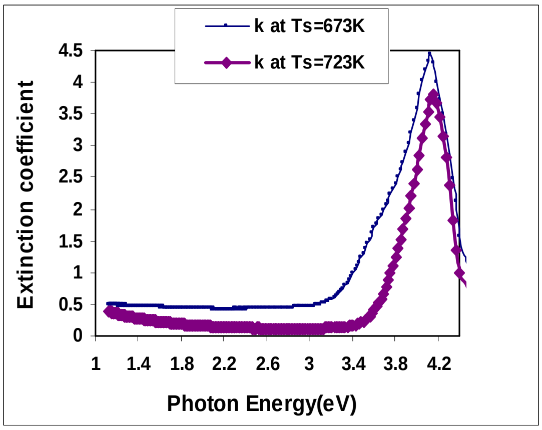

Figure 7: The extinction coefficient of ZnS thin films as a function to the photon energy at both substrate temperatures of 673K and 723K

3-6: The optical energy gap

The optical energy gap for the direct allowed transition between valence band and conduction band of ZnS thin films was calculated from equation -2 using r=1/2.

The values of the band gap for the direct transition can be determined by extrapolating the straight line portion of the $(\alpha h\upsilon)^2$ versus $h\upsilon$ graphs for ZnS thin films deposited with both substrate temperatures was shown in (Figures 8-a and 8-b).

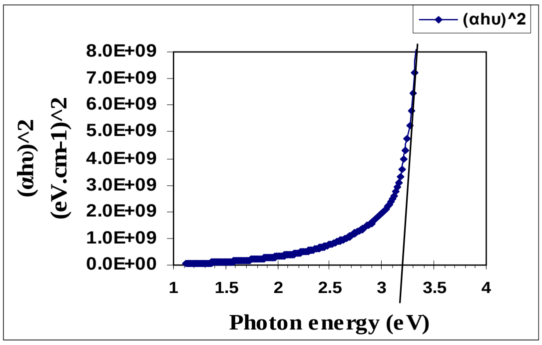

Fig.8-a: The optical energy gap for the direct allowed transition of ZnS thin films at substrate temperatures 673K

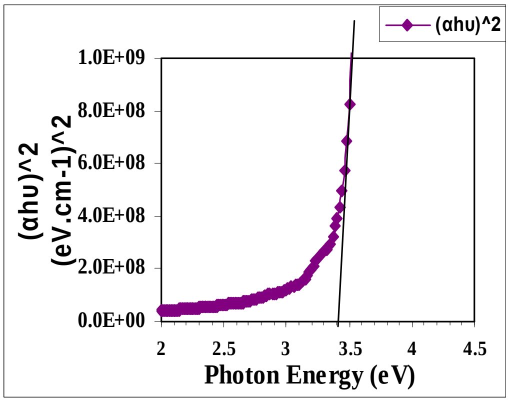

Figure8-b: The optical energy gap for the direct allowed transition of ZnS thin films at substrate temperatures 723K

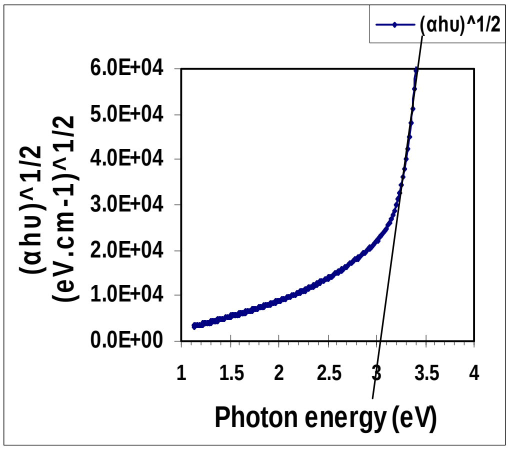

Figure 9-a: The optical energy gap for the indirect allowed transition of ZnS thin films at substrate temperatures 623K

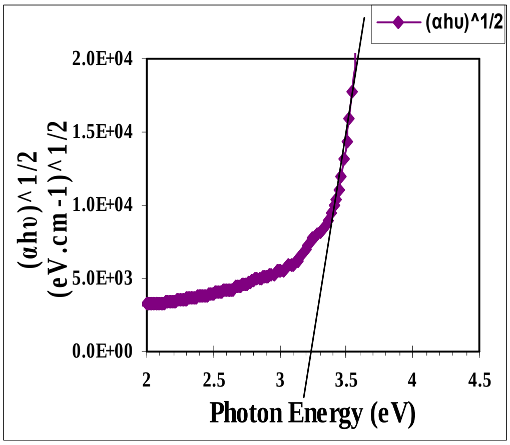

Figure 9-b: The optical energy gap for the indirect allowed transition of ZnS films at substrate temperatures 723K

From these figure it is clearly observed that the direct band gap increases as the deposition substrate temperature increases. Direct band gap energy of ZnS thin films increases from 3.2 eV to 3.4 eV as the substrate temperature increases from 673K to 723K. The value of the optical energy gap for the direct allowed transition of ZnS thin films prepared at T_S= 723K is in good agreement with previously reported value of ZnS thin film [3, 7].

The optical energy gap for the indirect allowed transition of ZnS thin films was calculated from equation -2 using r= 2, as show in (Figure 9-a and 9-b), it was 3.0, 3.2 eV at substrate tempeterure 673K and 723K respectively.

The variation observed in the energy band gap could be attributed to changes in the grain size of the deposits films at high substrate temperature. 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 improve the short circuit current of the cell.

3-7 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 by using equation -1.

The refractive index of the prepared film at T_S=673K was calculated in the visible region, it was 2.45 at wavelength 500 nm and 2.21 at 700 nm, the refractive index changes slightly and steadily from 500 to 900 nm , as shown in (Figure 10).

The value of the refractive index is in good agreement to the reported value which is 2.35 in the visible range [4, 5**]**, also it was observe that the refraction index decreasing in visible region when the substrate temperature increased. The decrease in the refractive index is due to the increase in the reflectance of the films at the highest substrate temperature [7].

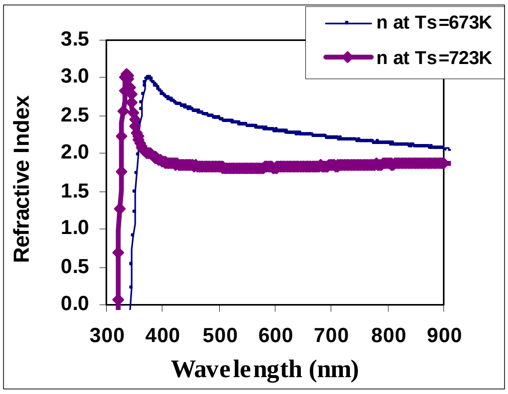

Figure10: The refractive index of ZnS thin films for both substrate temperatures of 673K and 723K

3-8 Optical conductivity (σ) and dielectric constant (ε)

The optical conductivity was calculated by using the equation:

$$\sigma = \varepsilon_i \, \omega \, \varepsilon_o \quad \text{-----(6)}$$

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

The imaginary parts of dielectric constant **(ε_i)** can be calculated from the relation [12]:

$$\varepsilon_i = 2nk \quad \text{-----(7)}$$

where n is represent as the refractive index , k is the extinction coefficient.

(Figure 11) shows the plot **ε_i** against the photon energy, the value of **ε_i** are decreased at T_S=723K. The optical conductivity was also decreased at Ts=723K, as shown in (Figure 12). It was observed that the optical conductivity increase at high photon energy.

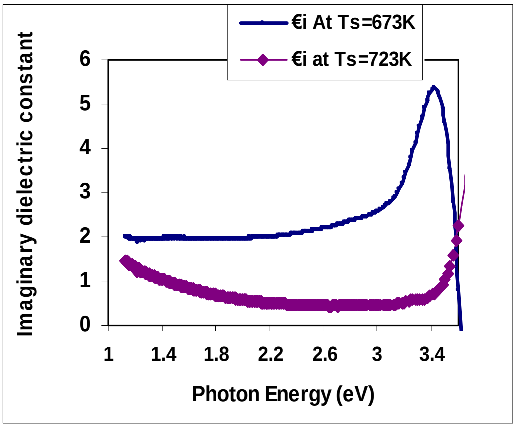

Figure 11: The imaginary parts of dielectric constant for both substrate temperatures of 673K and 723K

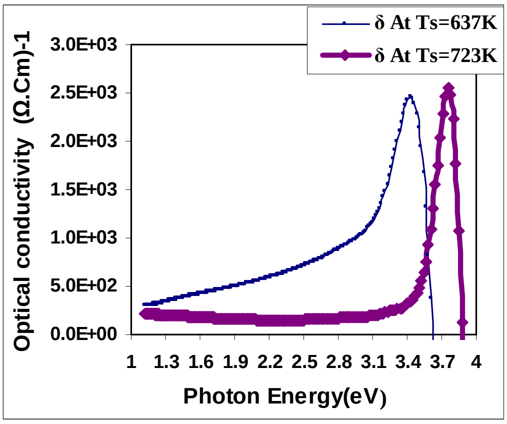

Figure 12: The optical conductivity of ZnS thin films for both substrate temperatures of 673K and 723K

4. Conclusions:

Zinc sulfide thin films were successfully deposited onto glass substrate by using spray pyrolysis technique. The film has a good optical transparency at substrate temperature of 723K, it was about 90 % in the visible region, so it can be used as a transparent dielectric material.

The improvement of the optical properties of the film at the highest substrate temperature is due to the improvement of the crystal structure.

The prepared films have wide direct energy gap, the wide band gap makes these films good material for optoelectronic devices such as a window layer in photovoltaic cells.

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