Journal of Basrah Researches ((Sciences)) Vol.( 40). No.( 1) A …… ( 2014 )

Available online at: www.basra-science-journal.org

ISSN -1817 -2695

# Optical constants of Zinc sulphide ZnS thin films for different annealing temperature

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Received 22-4-2013 , Accepted 2-3-2014

## Abstract

Zinc sulphide ZnS thin films were prepared by the spray pyrolysis (SP) technique on glass substrates at different temperatures (450, 500,550 and 600°C). Transmittance and absorbance measurements in the wavelength range (200–1000 nm) were used to calculate the refractive index n and the extinction coefficient k. The optical band gap $E_g(=E_{opt.}^{WD})$, optical conductivity $\sigma_{opt}$, complex dielectric constant $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_\infty$, relaxation time $\tau$, average interband oscillator wave length $\lambda_o$ average oscillator strength $S_o$, N/m*(N the free charge carrier concentration , m* the effective mass of the free charge carrier ) and dissipation factor $\tan\delta$ were determined. The analysis of the optical absorption data indicates that the optical band gap was indirect transitions. According to Wemple and Didomenico method, the optical dispersion parameters $E_o$ and $E_d$ were determined.

**Keywords:** Zinc sulphide; Optical properties; Optical dispersion parameters; Dielectric constant; Relaxation time.

## 1. Introduction

Zinc sulphide thin films have in recent years been rediscovered as a subject of considerable research interest due to their very unique physical properties (piezoelectricity, conductivity, magnetic and optical) and a wide range of possible device application. Special care is directed to optical and magnetic memory devices, laser system, blue light diodes, medicine, environment protection, solar cells (transparent conducting electrodes), displays, ultrasonic transducers and sensor [1-3].

(ZnS) is important semiconductor material with a wide direct band gap $E_g$ = 3.5 eV, high refractive index (2.35 at 632 nm), high effective dielectric constant (9 at 1 MHz). It's optical properties make it useful as a filter reflector and planer wave guide [4]. ZnS has been studied due to its wide applications as phosphors and catalysts [5]. ZnS is also applicable for a variety of other applications such as electro-luminescent devices, solar cells, and many other optoelectronic devices. ZnS has a low exciton Bohr radius (2.5 nm) that makes its nanoparticles interesting as small biomolecular probes for fluorescence and laser scanning microscopy. ZnS is also currently used as a shell or capping layer in core/shell nanoprobes such as CdSe/ZnS core/shell structures[6]. Optical absorption measurements is a standard technique for investigating band structure and it is therefore of interest to study absorption in thin films. The higher energy region (UV) can be useful to manifest the electronic states of the atoms and other important phenomena affected by irradiation [7]. The aim of this study is to measure the optical constants of ZnS thin films such as refractive index n, absorption index k, optical band gap $E_g$ , optical dispersion parameters $E_o$ and $E_d$, complex dielectric constant ($\varepsilon_i$, $\varepsilon_r$), relaxation time $\tau$, dissipation factor tan $\delta$ and optical conductivity $\sigma_t$.

## 2. Experimental

Zns thin films deposited on glass substrate, were prepared and analysis as described in reference [8]. ZnS thin films deposited by spray pyrolysis (SP) technique with glass substrate kept at different temperatures (450, 500,550 and 600 $^o$C). The refractive index n can be calculated by applying the following equations [9]

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad (1)$$

where, R is the reflectance of ZnS thin film

The thickness of the thin film can be calculated by knowing the following equation: [10]

$$d = \frac{\lambda_1 \lambda_2}{2(n_2\lambda_1 - n_1\lambda_2)} \qquad (2)$$

where d is the thickness of the film (the thickness of ZnS films is equal to 283nm) [8], and $n_1$ and $n_2$ are the refractive index at two adjacent maxima or minima corresponding to their wavelengths $\lambda_1$ and $\lambda_2$. Other conditions studies under which the samples ZnS thin films were analyzed by X-ray diffraction pattern for structural analysis were prepared [8].

Samples of ZnS thin films (of different temperatures) were obtained in uv/ vis/ nir region (from 200 to 1000 nm) by using spectrophotometer type (6800 UV/VIS Jenway Double Beam Spectrophotometer –England) with bare (uncoated) slide as the reference. The measurements were done in the wavelength scanning mode under normal conditions .

## 3. Results and discussion

The analysis of the absorption coefficient has been carried out to obtain the optical energy gap $E_g(\boldsymbol{E^{WD}_{opt.}})$ and also, the analysis of the refractive index n with the help of the extinction coefficient k has been carried out to obtain the real and imaginary part of complex dielectric constants ($\varepsilon_r$, $\varepsilon_i$), dissipation factor tan$\delta$, relaxation time $\tau$ and the optical conductivity $\sigma_{opt}$.

The refractive index n and extinction coefficient k were computed from the obtained transmittance T($\lambda$) in the wavelength range (200-1000 nm)of different temperatures (450, 500,550 and 600 $^o$C ) using Swanepoel's method [11]. The spectral distributions of the mean values of n and k versus wavelength $\lambda$ for the investigation for different temperatures are shown in figures(1 and 2) , respectively.

Wemple and Didomenico [11,12] use a single-oscillator description of the frequency-dependent dielectric constant to define a dispersion energy parameters $E_d$ and $E_o$. The refractive index dispersion of ZnS studied can be fitted by Wemple and Didomenico. The dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and in designing devices for spectral dispersion. Although these rules are quite different in detail, one common feature is the over-whelming evidence that both crystal structure and ionicity influence the refractive-index behaviour of solids in ways that can be simply described[12].

According to the single-effective oscillator model proposed by Wemple and Didomenico [12,13], the optical data can be described to an excellent approximation by the relation:

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \qquad 3$$

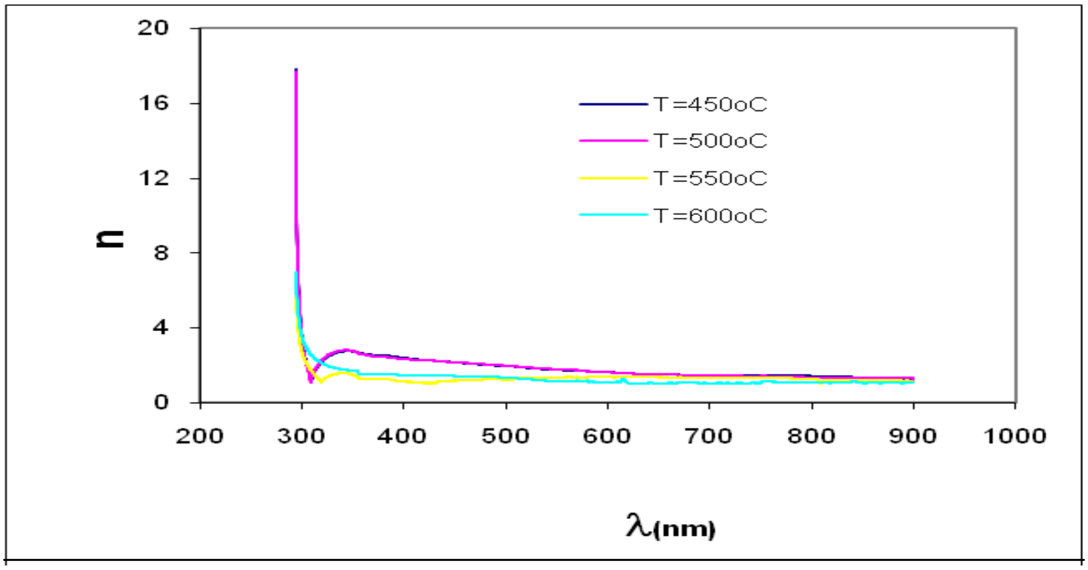


**Fig.(1):Dependence of the mean values of the refractive index non the wavelength λ for ZnS thin films at different temperatures(450,500,550 and 600)°C.**

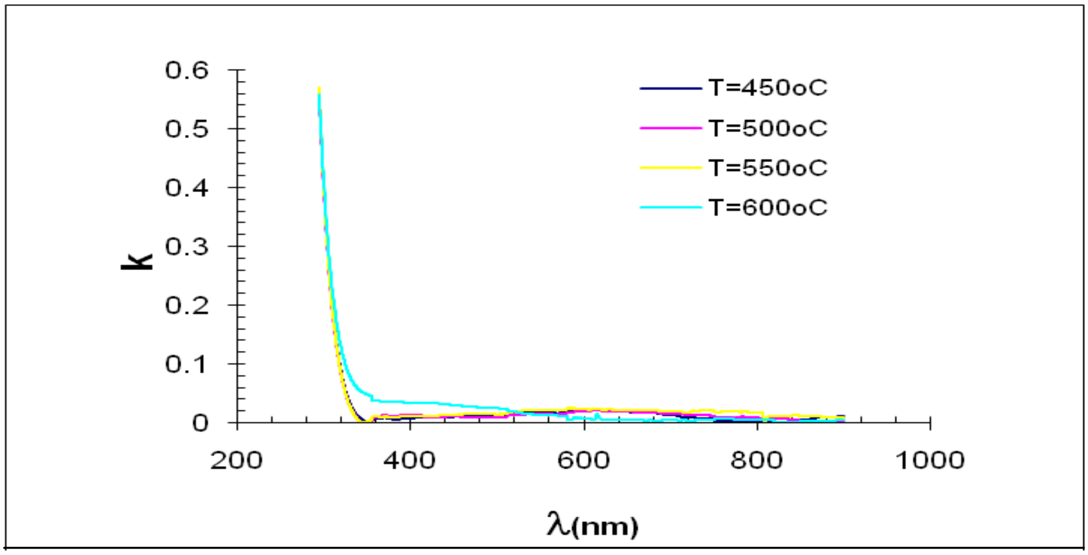


**Fig. (2): Dependence of the mean values of the absorption index k on the wavelength λ for ZnS thin films at different temperatures(450,500,550 and 600)°C.**

where E(=hν) is the photon energy, n is refractive index, $E_d$ is the single-oscillator constants, $E_o$ is the energy of the effective dispersion oscillator, $E_d$ the so-called dispersion energy, which is a measure of the average strength of interband optical transitions. The oscillator energy $E_o$ is an average of the optical band gap, $E_g$, can be obtained from the Wemple–Didomenico model.

Experimental verification of equation (3) can be obtained by plotting $(n^2-1)^{-1}$ against $E^2$ as illustrated in figures(3) for ZnS thin films, which gives the oscillator parameters by fitting a straight line for normal behaviour having the slope $(E_oE_d)^{-1}$ and the intercept with the vertical axis equal to $(E_o/E_d)$. But the obtained curves in figures(3), show positive deviation from linearity at different temperatures (450, 500, 550 and 600 $^o$C). A positive curvature deviation [13] from linearity at longer wavelength is usually observed due to the negative contribution of lattice vibrations on the refractive index. The values of the parameters $E_o$ and $E_d$ can be estimated from figure ( 3) as listed in table(1). Furthermore, the values of the static refractive index ($n_o$) can be calculated by extrapolating the Wemple - Didomenico dispersion equation to E approach to zero

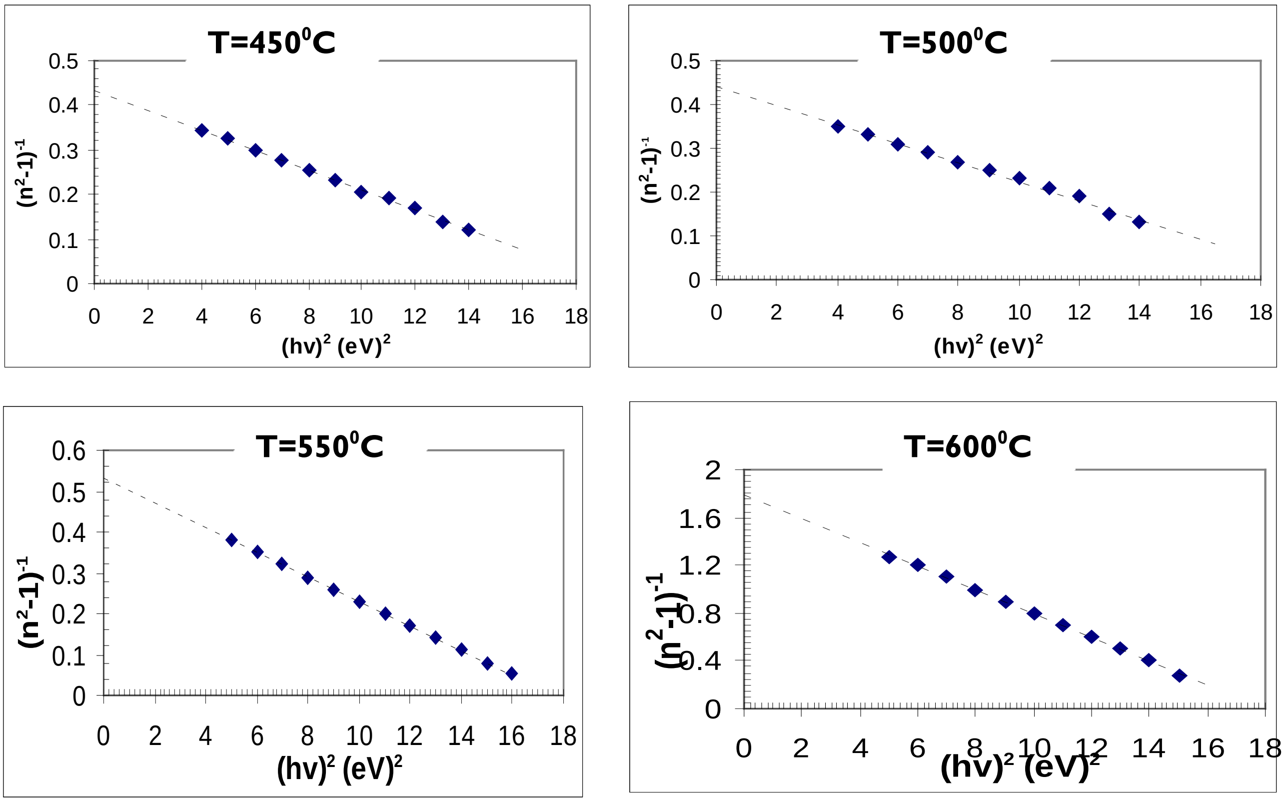


**Fig. (3):Plots of $(h\nu)^2$against$(n^2-1)^{-1}$ for ZnS thin films at different temperatures (450,500,550 and 600)$^o$C.**

The calculated values of $n_o$ are shown in table(1) . The obtained data of refractive index n can be analyzed to obtain the high frequency dielectric constant via two analysis [14]: the first procedure describes the contribution of the free carriers and the lattice vibration modes of the dispersion. The second analysis, however, is based upon the dispersion arising from the bound carriers in an empty lattice. To obtain a reliable value for the high frequency dielectric constant $\varepsilon_{\infty}$, we employed both procedures. The following equation can be used to obtain the high frequency dielectric constant [14]:

$$\varepsilon_r = \varepsilon_{\infty(1)} - B\lambda^2 \ , \qquad (4)$$

where

$$B = e^2 N / 4\pi^2 c^2 \varepsilon_0 m \qquad (5)$$

where $\varepsilon_r$ is the real part of dielectric constant, $\varepsilon_{\infty(1)}$ the lattice dielectric constant or (the high frequency dielectric constant) according to the first analysis, $\lambda$ the wavelength, N the free charge carrier concentration, $\varepsilon_o$ the permittivity of free space (8.854×10−12 F/m*), m* the effective mass of the charge carrier and c the velocity of light. The real part of dielectric constants $\varepsilon_r = n^2$ was calculated at different values of $\lambda$. Then, the obtained values of $\varepsilon_r$ are plotted as a function of $\lambda^2$ at different temperatures (450,500,550 and 600 $^o$C) as shown in igure(4).

It is observed that the dependence of $\varepsilon_r$ on $\lambda^2$is linear at longer wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives the value of $\varepsilon_{\infty(1)}$ and from the slopes of these lines, values of N/m* for the investigated ZnS were calculated according to the Equation (4) of the constant B. The obtained ZnS values of $\varepsilon_{\infty(2)}$ , N/m$^*$ are given in table (1).

The dielectric constant of a material could be calculated using the dispersion relation of incident photon. The refractive index was also fitted using a function for extrapolation towards shorter wavelengths.

The properties of the investigated ZnS could be treated as a single oscillator at wave length $\lambda_o$ at high frequency. The high frequency dielectric constant can be calculated by applying the following simple classical dispersion relation[14]:

$$\frac{n_o^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2 \qquad (6)$$

where $n_o$ is the refractive index at infinite wavelength $\lambda_o$ ($\lambda_o$ is the average interband oscillator wavelength), n the refractive index and $\lambda$ the wavelength of incident photon. Plotting $(n^2\text{-}1)^{-1}$against $\lambda^{-2}$ which showed linear part, was below

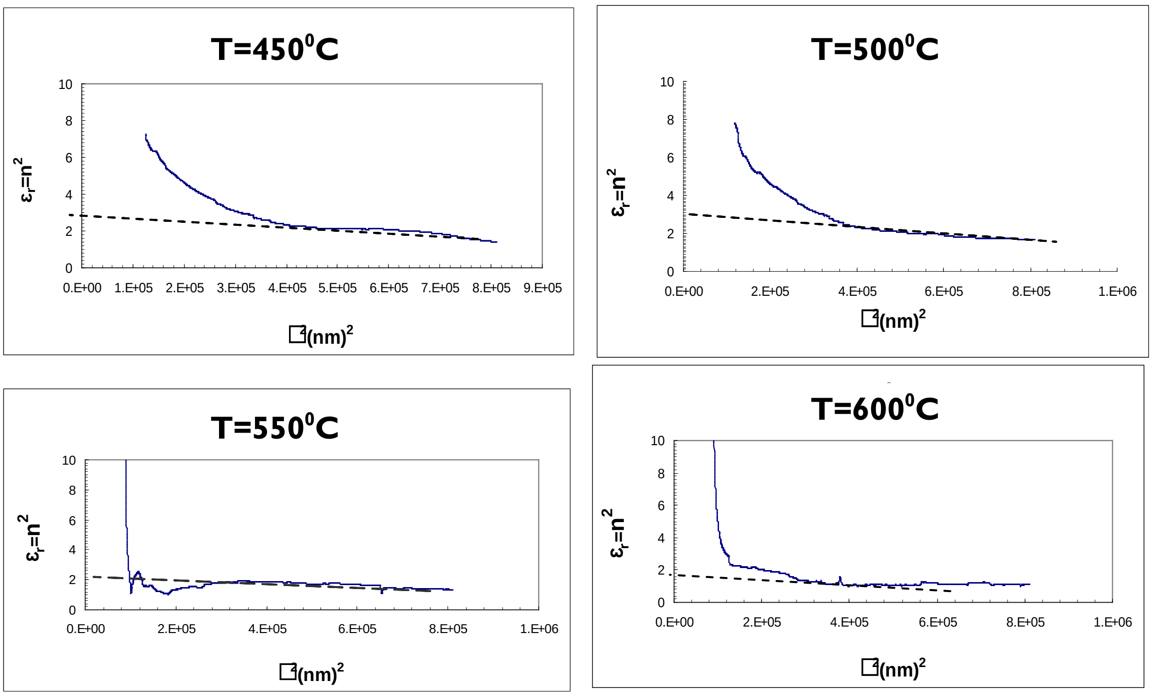

**Fig.(4): Plots of $n^2=\varepsilon_r$ as a function of $\lambda^2$ for ZnS thin films at different temperatures (450,500,550and 600)°C.**

the absorption edge as shown in figure(5) .

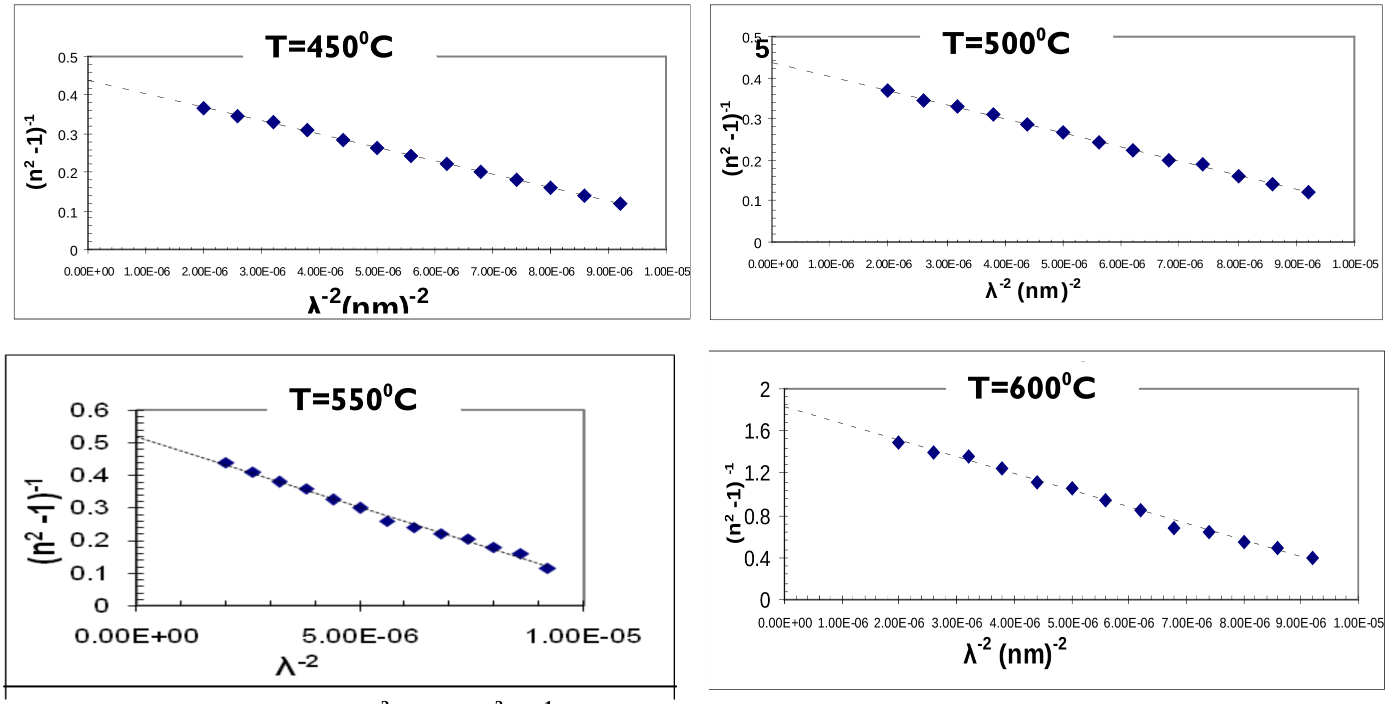


**Fig. (5):Plots of $\lambda^{-2}$against$(n^2-1)^{-1}$ for ZnS thin films at different temperatures (450,500,550, and 600)°C.**

The intersection with $(n^2-1)^{-1}$ axis is $(n_o^2-1)^{-1}$ and hence $n_o^2$ at $\lambda_o$ equal to $\varepsilon_{\infty(2)}$ (high frequency dielectric constant). Values of $\varepsilon_{\infty(2)}$ for ZnS thin films at different temperatures (450,500,550 and 600)°C are given in table(1). The simple classical dispersion relation (equation 6) can be written as[15]:

$$n^2-1=\frac{S_o\lambda_o^2}{1-\frac{\lambda^2}{\lambda_o^2}} \qquad (7)$$

where $S_o$ is the average oscillator strength which is equal to:

$$S_0=\frac{n_0^2-1}{\lambda_0^2} \qquad (8)$$

The obtained values of $\mathbf{S_o}$ and $\boldsymbol{\lambda_o}$ are given in table(1).

**Table(1): The values of optical parameters for ZnS thin films at different temperatures (450,500,550 and 600)°C.**

| T °C / Parameters | T=450°C | T=500 °C | T=550 °C | T=600 °C |
|---|---|---|---|---|
| $E_0$(eV) | 4.406 | 4.519 | 4.203 | 4.243 |
| $E_d$(eV) | 10.178 | 10.245 | 7.93 | 2.369 |
| $E_{opt.}^{WD}(eV)$ | 2.203 | 2.259 | 2.101 | 2.121 |
| $\varepsilon_{\infty(1)}=n^2$ | 2.85 | 2.6 | 2.2 | 1.6 |
| $\varepsilon_{\infty(2)}=n_o^2$ | 3.390 | 3.288 | 1.192 | 1.549 |
| $\lambda_o$ (nm) | 91 | 91.82 | 93.2 | 92.9 |
| $S_o$ ($m^{-2}$) | $2.9\times10^{13}$ | $2.9\times10^{13}$ | $2.3\times10^{13}$ | $6.4\times10^{13}$ |

| | | | | |
|---|---|---|---|---|
| **N/m*($m^{-3}kg^{-1}$)** | $5.22x10^{56}$ | $14.7x10^{56}$ | $11.1\ x10^{56}$ | $77.4\ x10^{56}$ |

The complex refractive index ñ = n + ik and the complex dielectric function $\varepsilon = \varepsilon_r + i\varepsilon_i$ characterize the optical properties of any6 solid material. The real part of the dielectric constant shows how much it will slow down the speed of light in the material, whereas the imaginary part shows how a dielectric material absorbs energy from an electric field due to dipole motion. The knowledge of the real and the imaginary parts of the dielectric constant provides information about the loss factor(tan δ) which is the ratio of the imaginary part to the real part of the dielectric constant. The real and imaginary parts of dielectric constant of thin films can be determined using the following relations [16,17]:

$$\varepsilon_r = n^2 - k^2 = \varepsilon_\infty - [\frac{e^2 N}{4\pi^2 c^2 \varepsilon_0 m^*}]\lambda^2 \quad (9)$$

$$\varepsilon_i = 2nk = [\frac{\varepsilon_\infty w_p^2}{8\pi^2 c^3 \tau}]\lambda^3 \quad (10)$$

where $\varepsilon_r$ is the real part, $\varepsilon_i$ the imaginary part of the dielectric constant, $\varepsilon_\infty$ is the high frequency dielectric constant, $w_p$ is the plasma frequency, τ the optical relaxation time and k = (αλ/4π).

The real and imaginary parts of the dielectric constant can be calculated as it is directly related to the density of states within the forbidden gap of the investigated ZnS [15,16]. The variation of the real and imaginary parts of the dielectric constant as a function of photon energy for ZnS thin films at different temperatures is (450,500,550 and 600) $^o$C.

It can be seen clearly from figures (6 and 7) that both the real $\boldsymbol{\varepsilon_r}$ and imaginary $\boldsymbol{\varepsilon_i}$ parts of the dielectric constant decrease with increasing photon energy for ZnS thin films at different temperatures (450,500,550, and 600) $^o$C The real and imaginary parts follow the same pattern and it is seen that the values of real part are higher than the imaginary parts.

At temperatures (450 and 500)$^o$C the real and imaginary parts of the dielectric constant decrease sharply with increasing photon energy in the lower photon energy region, but decrease slowly in the higher photon energy region[as shown in figures (6 and 7)], whereas at temperatures (550 and 600)$^o$C the real and imaginary parts of the dielectric constant decrease slowly with increasing photon energy in all photon energy region.

These results indicated that in ZnS thin films the dissipation factor(loss factor) (tan δ) increase with increasing photon energy.

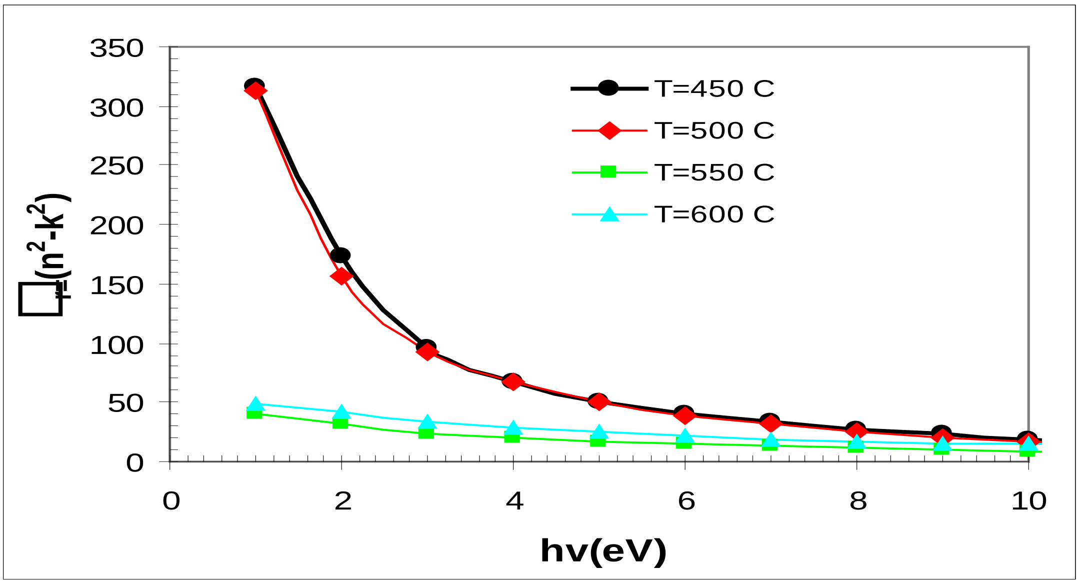


**Fig. (6): Plots of $\varepsilon_r$ as a function of hν at different temperatures (450,500,550 and 600)$^o$C for ZnS thin films.**

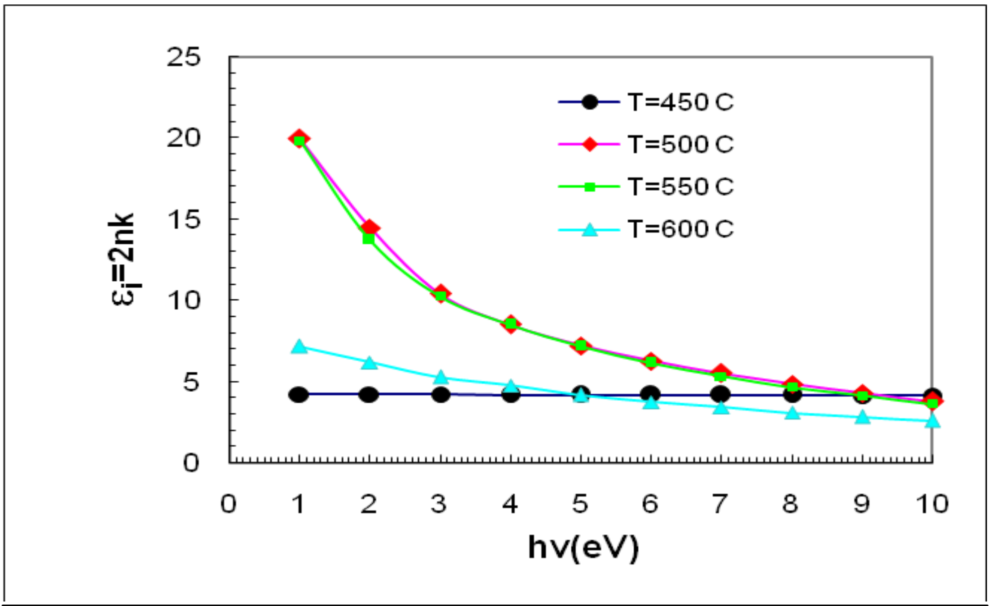


**Fig.(7): Plots of $\varepsilon_i$ as a function of hν at different temperatures (450,500,550 and 600)$^o$C for ZnS thin films.**

Figure(8) shows the dielectric relaxation time τ as a function of photon energy E(=hν) for ZnS thin films. This figure showed that the relaxation time increases with increasing the photon energy.

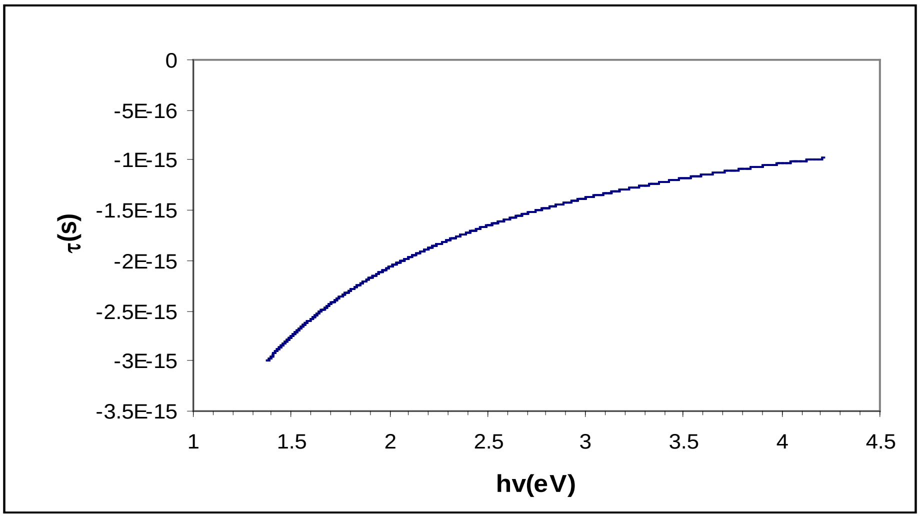


**Fig.(8):Dependence of relaxation time τ on the photon energy hν at different temperatures (450, 500,550 and 600 $^{o}$C) for ZnS thin films.**

The dissipation factor (tan δ) is a measure of loss-rate of power of a mechanical mode, such as an oscillation, in a dissipative system. For example, electric power is lost in all dielectric materials, usually in the form of heat. The dissipation factor tanδ can be calculated according to the following equation [18]:

$$\tan\delta = \frac{\varepsilon_i}{\varepsilon_r} \qquad (11)$$

The variation of dissipation factor of the investigated films with frequency f is shown in Figure(9). It is found that the dissipation factor increases with increasing frequency ( i.e. photon energy) in the absorption region.

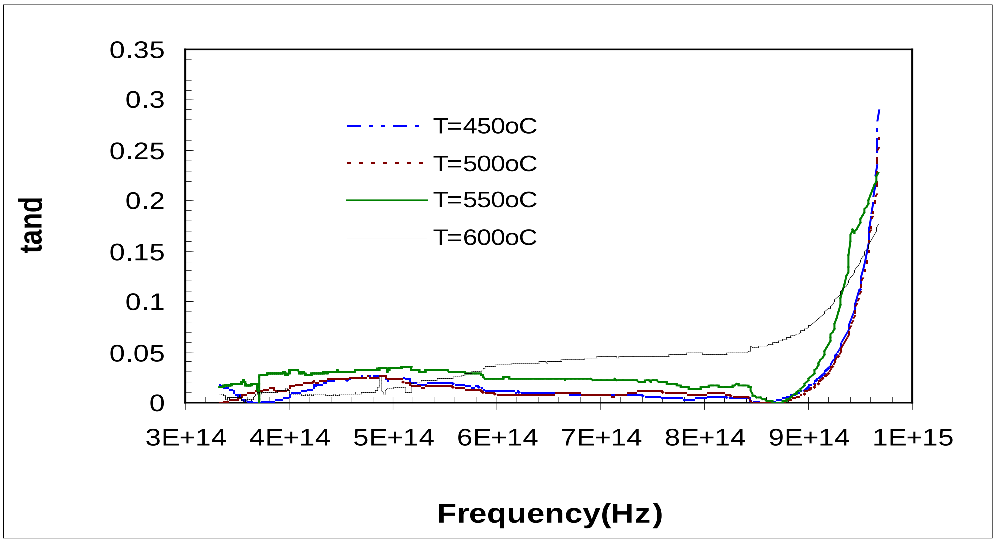


**Fig.(9): Dependence of dissipation factor tanδ on the Frequency at different temperatures (450, 500,550 and 600 $^{o}$C) for ZnS thin films.**

The optical response of a material is mainly studied in terms of the optical conductivity $\sigma_{opt}$ which is given by the relation[17,19]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \qquad (12)$$

where α is the absorption coefficient ,c the velocity of light and n the refractive index. Figure(10) shows the variation of optical conductivity $\sigma_{opt}$ as a function of photon energy E(=hν) for the ZnS thin films at different temperatures (450, 500,550, and 600

°C), it can be seen clearly from the figure that the optical conductivity increase abruptly after (~4)eV for all ZnS samples under investigation. The sudden increase in optical conductivity can be attributed to the increase in absorption coefficient of ZnS thin films and also may be due to the electron excited by photon energy [14].

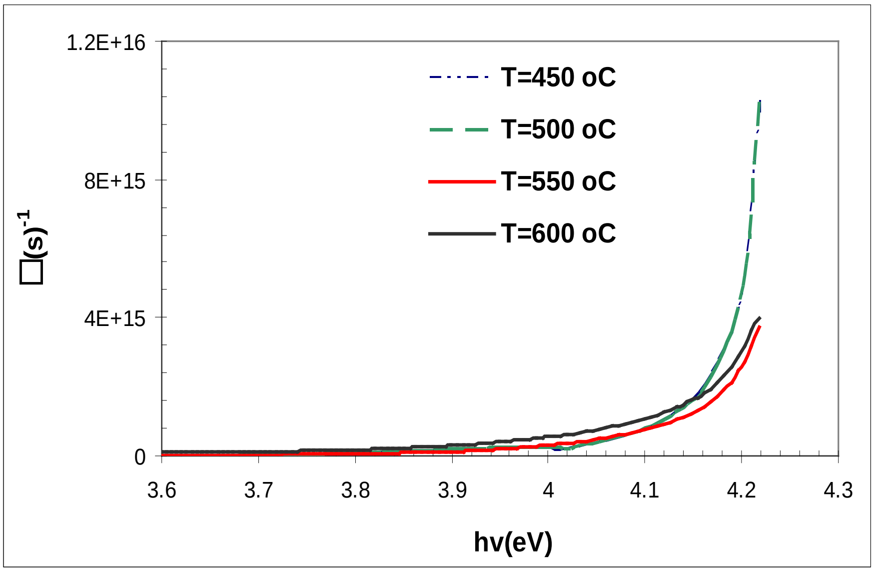


**Fig.(10): Dependence of optical conductivity $\sigma_{opt}$ on the photon energy hv at different temperatures (450, 500,550 and 600 °C) for ZnS thin films.**

## 4. Conclusions

The refractive index n and extinction coefficient k were computed from the obtained T(λ) using Swanepoel's method. The refractive index and absorption index decreased with the increase in wavelength and the absorption edge was observed in all samples. The decrease in refractive index with increase in the wave length indicates that the(SP) technique for ZnS films on glass substrates shows normal dispersion behaviour. The values of the static refractive index obtained for all samples were in the range of the reported values. The real and imaginary parts of the dielectric constant decrease with the increase in photon energy. The loss factor tanδ increase with photon frequency (i.e. photon energy).On the basis of the optical investigations of the films, the following results were obtained. The relaxation time τ increased with increasing the photon energy. Finally the optical conductivity $\sigma_{opt}$ increased with increasing the photon energy and this can be attributed to the increase in absorption coefficient with the increase in photon energy.

## References:


[1] Hickernell F. S,: IEEE Trans MTT 17, 957 (1969).

[2] Campbell C. : Surface Acoustic Wave Devices and Their Si Processing Applications, San Diego, Academic Press, (1989).

[3] Kozak O. , Praus P. and Dvorsky R. , Chalcogenide letters, 9(10)413,(2012).

[4] Suhail M.H. , Indian Journal of pure & applied physics, 50 380,(2012).

[5] Zhu Y.C., Bondo Y. and Xue D.F., Appl. Phys. Lett. 82 1769, (2003) .

[6] Thakur A. and Fradin C., Can. Undergraduate Phys. J. 3 7,(2005).

[7] Madi N. K, Kassem M. E., Abdel Rehim and Abu Taleb W. M., Mater.Lett. 19 87, (1994).
[8] Hussein H. F., Bakr H. and Abul-Hail R. CH., Journal of Basrah Researches/ Science,39-4A.33 (2013).
[9] Palewicz M., Iwan A., Doskocz J., strek W., Sek D. Kaczmarczyk B. and Mazurek B., Polym. Bull.,66 65, (2011).
[10] Swanepoel R., J. Phys. E: Sci. Instrum. 16 1214, (1983).
[11] Priyamvada Bhardwaj, Shishodia P. K. and Mehra R. M., J.Optoelectron. Adv. Mater. 3 319, (2001).
[12] Didomenico M. and Wemple S.H., J. Appl. Phys. 40 720,(1969).
[13] Wemple S.H. and Didomenico M., Phys. Rev. B 3 1338, (1971).
[14] Zeme J. N. l, Jensen J.D. and Schoolar R.B., Phys. Rev. A 140 330 (1965).
[15] El-Korashy A., El-Zahed H. and Radwan M., Phys. B 334 (2003) .
[16] Wakad M. M., Shokr E. Kh. and Mohammed S. H., J. Non-Cryst. Solids 265 157 (2000).
[17] Bakr N.A., Funde A.M., Waman V.S., Kamble M.M., Hawaiter R.R., Amalnerkar D.P., Gosavi S.W. and Jadkar S.R., Indian academy of sciences, 76(3)519, (2011).
[18] Pankove J. I., Optical Processes in Semiconductors, Dover Publications Inc., New York, , pp. 91,(1975).
[19] Yakuphanoglu F., Cukurovali A. and Yilmaz I., Opt. Mater. 27 1366 ,(2005).

## الثوابت البصرية لأغشية كبريتيد الخارصين ZnS الرقيقة لدرجات حرارة تلدين مختلفة

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**المستخلص**

تم تحضير اغشية رقيقة لكبريتيد الخارصين ZnS بتقنية الرش الكيميائي الحراري على قواعد زجاجية ولدرجات حرارة تلدين مختلفة ( 450 , 500 , 550 , 600 ) درجة سيليزية . تم قياس طيف الامتصاصية والنفاذية لمدى من الاطوال الموجية (200 – 1000) نانومتر. معامل الانكسار n ومعامل الخمود k وفجوة الطاقة $E_g$ والتوصيلية الضوئية $\sigma_{opt}$ وثابت العزل المعقد $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_\infty$ وزمن الاسترخاء $\tau$ والطول الموجي لمعدل التذبذب $\lambda_o$ ومعدل قوة التذبذب $S_o$, N/m* تركيز حاملات الشحنة الحرة, m* الكتلة المؤثرة لحاملات الشحنة الحرة) ومعامل التشتت $\tan\delta$ تم حسابها.

من تحليل قيم الثوابت البصرية تبين ان فجوة الطاقة ذات انتقالات غير مباشرة. تم حساب معاملات التشتت البصرية $E_d$ , $E_0$ طبقاً لطريقة الباحثان ونبل و دايدومنيكو.