Structure and Some Optical Properties of ZnS Thin Films Prepared by Thermal Evaporation Method.

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Abstract:

Zinc sulfide thin films were prepared by thermal evaporation technique, on glass substrate(corning 7059) at different substrate temperatures. Films structure and grain size were determined by X-ray diffraction (XRD) device. Films have cubic polycrystalline structure with lattice constant $a=5.41$ Å . The optical constants (refractive index and absorption coefficient) of the films were derived from optical transmission spectra in the wavelength range 300-700 nm. Data are analyzed by Swanepoel method. Increasing of substrate temperature, the refractive index of films was increased and all films have nearly same refractive index at wavelength about 630 nm. Optical band of prepared films are in the range 3.4-3.62 eV and was increased with increasing substrate temperature. The aim of this study is to obtain matched properties from ZnS thin films to be used in solar cell applications.

Keywords: ZnS thin film, optical and structural properties ,Swanepoel method.

1-Introduction:

The zinc based binary and ternary II-VI compounds (ZnS, $Cd_{1-x}Zn_xS$, ZnSe, and $Cd_{1-x}Zn_x$ Se are of great important in optoelectronic application [1].ZnS is a well known II-VI semiconductor with multi-faceted application and possessing a direct band gap of 3.68 eV, high refraction index (2.25 at 632nm), high transmittance in the visible range, and high effective dielectric constant (9 at 1MHz)[1-3].It an important device material for the detection, emitting and modulation of visible and near ultra violet light [4],and in particular for making high resolution colour electroluminescent and cathodoluminescent display of various types[5].ZnS is believed to be one of the most promising material for blue light emitting laser diode ,and thin film electroluminescent displays[6,7].Furthermore the wide band gap ZnS enjoys the advantage of being highly resistive and UV light sensitive having low dark noise. They are potentially good candidates for visible blind UV imaging material[8]. Considerable effort has been devoted recently to controlling the size and the shape of ZnS nanofilaments so that size and shape dependent properties can be studied, e.g, ZnS nanobelts with wurtzite structure that is grown by thermal evaporation methods[9]. Our interest in this material lies behind its use as n-window layer on different window layers for CdTe and CuInSe group (CIS) base solar cell due to large band gap, for the construction of colour electroluminescent display device, also for the construction of room temperature antiferromagnetics alloy and as IR window in IR sensor. A variety of preparation techniques has been reported so far to obtain ZnS thin films, some of them are: Chemical bath deposition (CBD) that is used due to the possibility of large area deposition[1,3,10,11]. Sol-gel method that is employed in industrial manufacturing to obtain stable electroluminescent (EL) and photoluminescent (PL) properties[12]. Electron beam evaporation (EBE) that has fast grown thin films[5,13]. Pulsed laser vaporization: that is fast thin film evaporation techniques [2]. Wurtzite thin film structure can be obtained by vapour-liquid-solid (VLS) process[14,15]. Metal organic chemical vapour deposition (MOCVD) system used to obtain quantum dot composites of ZnS[16]. Molecular beam epitaxy (MBE) system is also used to prepare high

quality thin films[8]. Simplest and cheap way to obtain thin films of ZnS is by resistive heating technique[4,17], that we used to prepare ZnS thin films in this work.

2-The experimental:

ZnS thin films were deposited on clean glass substrates by thermal evaporation technique, vacuum evaporator (Varian 3117) was used to prepare ZnS thin films, and a tantalum boat was used as a support to evaporate ZnS .The distance between the boat and substrate was (20 cm). Temperature controller type (CXTA-3000) was used to control the substrate temperature. The substrate temperature was selected at (Room temperature(R.T), 100,150,200) C. The rate of deposition was varied from 1-3 ($\mathring{A}$ /s).

XRD measurements techniques have been used to determine the crystal structure of ZnS thin films, X-ray diffraction spectra were recorded with PHILIPS (PW 1053) X-ray diffractometer with CuKα radiation(40KV and 20mA) for 2θ values over 20-40^0.Optical measurements of all thin films samples were carried out using UV-VIS spectrophotometer type (Thermo spectronic) in the range 300-800nm at room temperature, to obtain the absorbance and transmission spectra at room temperature. (All measurements were carried out in Basrah university-college of science-physics department)

3: Results and discussion:

3.1: Structural properties:

The XRD patterns show that the ZnS films deposited by thermal evaporation onto glass substrate have polycrystalline structure and reveal only one peak that coincides with the position for (111) diffraction line for zincblende crystal structure or (002) diffraction line for wurtzite structure .So it is possible to conclude that films have the cubic crystal structure with the preferred orientation in the <111> direction **(Fig.(1))** as it was observed in Ref.[18].

Lattice parameter of ZnS thin films were calculated using the relation (1)and it was 5.41 $\mathring{A}$ that was very close to that of powder source.

$$d_{(hkl)}=[(h^2+k^2+l^2)/a^2] \quad \text{.....(1)}$$

Where $d_{(hkl)}$ is the planner distance of the preferred peak of ZnS ,h,k,l are the miller index a is the lattice parameter of ZnS. Grain sizes of thin films were estimated according to line broadening analysis of the one strong peak of ZnS thin films on X-Ray pattern, and because it is impossible to eliminate the effects of strains and sizes on line broadening, these values of grain sizes were done approximately by using Sherrer equation:

$$D=1.155\,\lambda/H\cos(\theta) \quad \text{.....(2)}$$

Where θ is a Bragg angle, H is integral breadth, and λ is a wavelength of X-ray source.

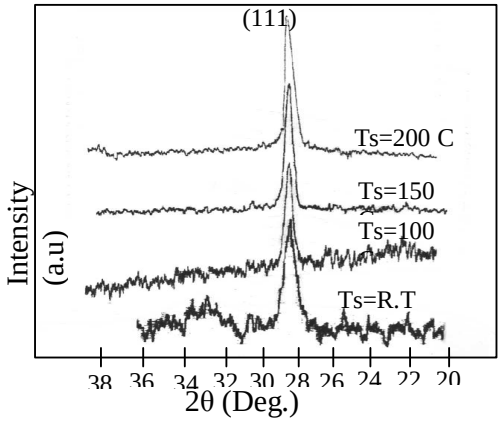

Fig. 1. XRD patterns of ZnS thin films prepared at different substrate temperatures

2 θ	Int.	hkl
28.558	100	111
33.089	10	200
47.515	51	220
56.289	30	311
59.136	2	222
79.155	2	420
95.539	5	511

Table[1] ASTM card No.05-0566 for Sphalerite ZnS powder

The results of evaluations are shown in table [2] ,from the table the grain sizes of the ZnS films are increased with increasing of substrate temperature and we note that the increase is not large due to decreasing of films thickness with increasing of substrate temperature .

Table [2]: grain size, energy gap and thickness varied substrate temperature for ZnS thin films.

Substrate temperature(Ts) C	Grain size (D) (nm)	Energy gap(eV)	Thickness (nm)	
R.T	17.5	3.4	1100	Present work
100	23	3.44	800	
150	24.4	3.56	1000	
200	27.6	3.62	300	
-	bulk	3.68	-	Ref.[9]

3-2: Optical properties:-

3-2-1: Determination of optical constants:

The transmittance spectrum of all ZnS thin films prepared, exhibits peaks and valleys that are associated with interference effects (see Fig.2**)** .The interferences are fully coherent, and then the locations of the interference maxima and minima are related to the real part n (λ) of the complex refractive index[19]:

$$n^*(\lambda) = n(\lambda)+ik(\lambda) \quad \text{..... (3)}$$

Where n (λ), is the refractive index, and k (λ) the extinction coefficient.

For the method proposed by Swanepole, the optical constants are deduced from the finger patterns in the transmittance spectrum[19].The practical situation for a thin film on a transparent substrate is shown in Fig (3)[20].The film has thickness d and complex refractive index n(λ) :

$$2d\, n(\lambda) = m\lambda \quad \text{..... (4)}$$

Where m is the interference order and d is the film thickness .The values of m takes integer number for maxima and half integer for minima. The questions, therefore, arises concerning the determination of n (λ) and d only from transmittance data[21].

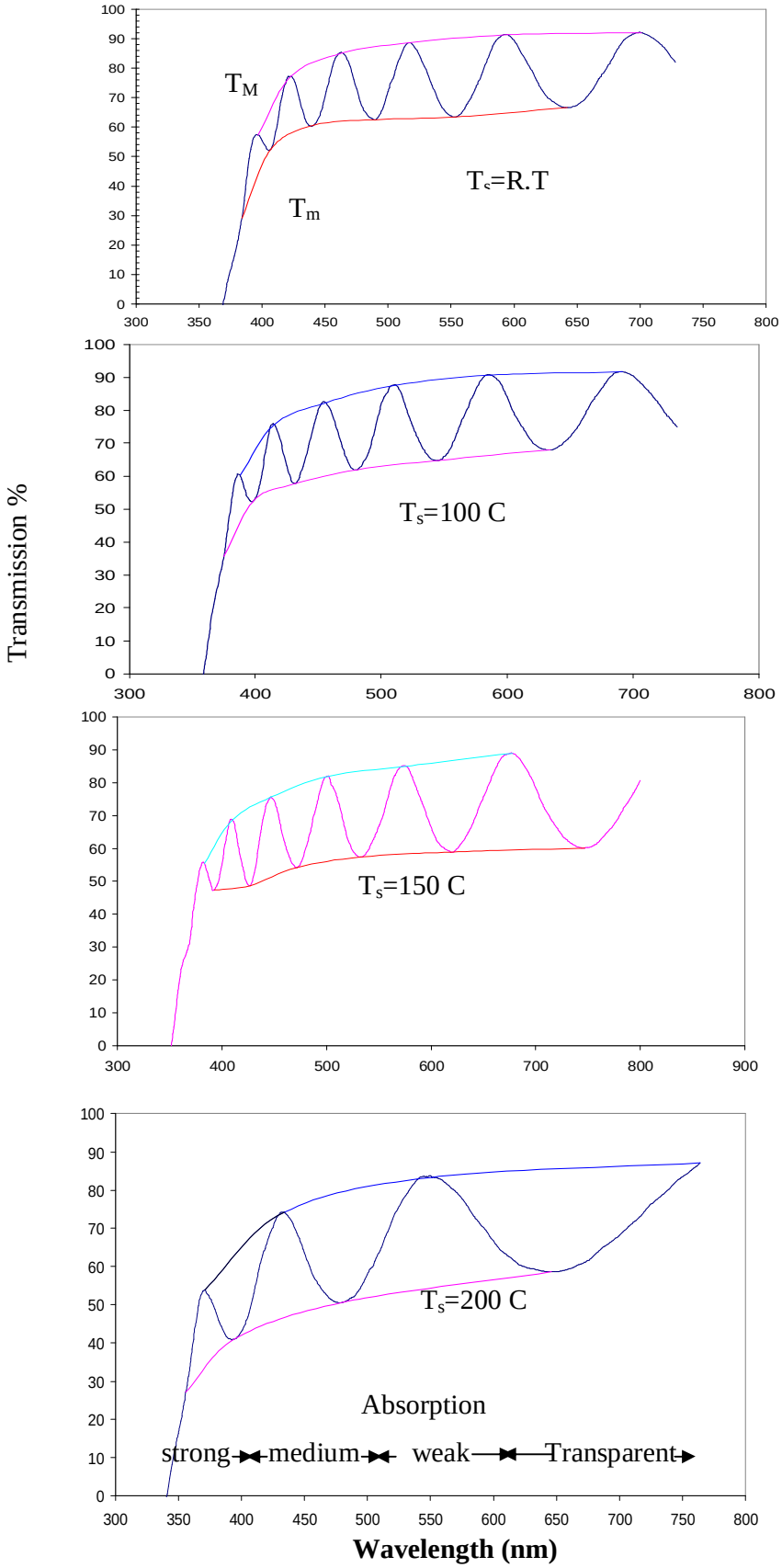

Figure 2. Four typical transmission spectra for prepared samples of different substrate temperatures

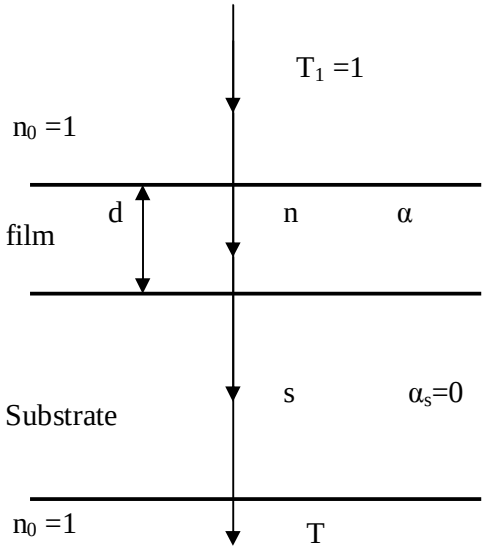

Figure 3. System of an absorbing thin film on thick finite transparent substrate.

Swanepoel method[22,23]

The transmission spectrum can be roughly divided into four regions Fig. (2). In the transparent region (α=0) the transmission is determined by n (refractive index of film) and s (refractive index of transparent substrate) through multiple reflections. In the region of weak absorption region α is small and the transmission begins to decrease .In the medium absorption region α is large and transmission decreases mainly due to the effect of α .In the region of strong absorption the transmission decreases drastically due to almost exclusively the influence of α [22-24].

The transmission T for the case of Fig.(2) is a complex function and is given by :

$T=T(\lambda,s,n,d,\alpha)$ .....(5)

And for convinces, equ. (5) can be written in terms of n(λ) and absorbance x(λ)[24]:

$$T=\frac{AX}{B-CX\cos\phi+DX^2} \quad \text{..... (6)}$$

Where:

$A=16n^2s$ ..... (6a)

$B=(n+1)^3(n+s^2)$ .....(6b)

$C=2(n^2-1)(n^2-s^2)$ .....(6c)

$D=(n-1)^3(n-s^2)$ .....(6d)

$$\Phi=\frac{4\pi nd}{\lambda} \quad \text{.....(6e)}$$

$X=\exp(-\alpha d)$ .....(6f)

Now if T_M and T_m are maximum and minimum values of the envelope function of the transmission and T_s is the maximum value of the transmission in the absence of the film, then substrate refractive index s , T_M and T_m are given by the following equations:

$$s=\frac{1}{T_S}+\left(\frac{1}{T_S^{\,2}}-1\right)^{\frac{1}{2}} \quad \text{..... (7)}$$

$$T_M=\frac{AX}{B-CX+DX^2} \quad \text{..... (8)}$$

$$T_m=\frac{AX}{B+CX+DX^2} \quad \text{..... (9)}$$

For further analyses T_M and T_m are now considered to be continuous functions of λ and thus of n(λ) and X(λ) as shown in the envelopes in Fig(2**)**.For any λ ,T_M has a corresponding value T_m, The absorption coefficient α for the regions of medium absorption will be non-zero. From equations (8) and(9)can be obtained an equation that is independent of X[20].:

$$\frac{1}{T_M}-\frac{1}{T_m}=\frac{2C}{A} \quad \text{..... (10)}$$

The determination of the envelopes are based on the parabolic interpolation between three nearest adjacent maximum(T_M) or minimum(T_m) for any λ ,T_M has corresponding value T_m ,and T_m has corresponding value T_M , substituting equations (6a-6f) into (10) and solving for n(λ) yields:

$n(\lambda)=[N+(N^2-s^2)^{1/2}]^{1/2}$ .....(11)

Where

$$N=2s\frac{T_M-T_m}{T_M T_m}+\frac{s^2+1}{2} \quad \text{..... (12)}$$

The film thickness can be determined if we assume n_1 and n_2 the refractive indices for two adjacent maxima(or minima) at λ_1 and λ_2 then the film thickness is given by:

$$d=\frac{\lambda_1\lambda_2}{2(\lambda_1 n_2-\lambda_2 n_1)} \quad \text{..... (13)}$$

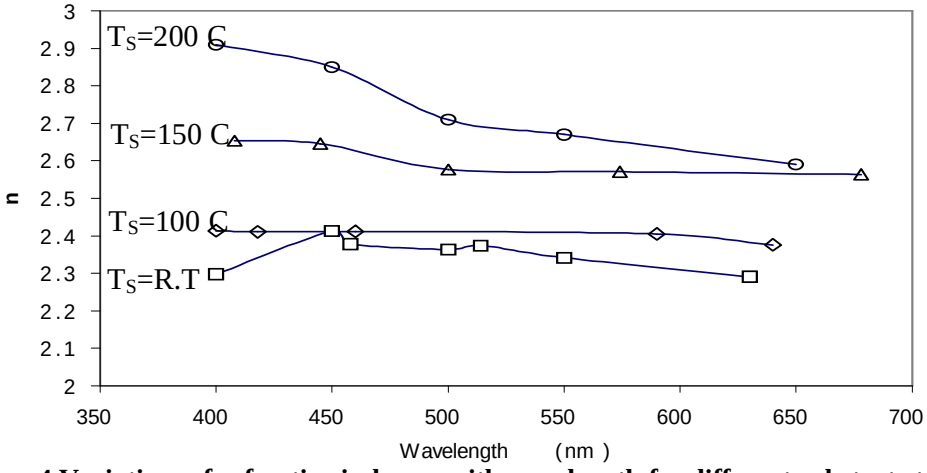

Figure 4.Variations of refractive index n with wavelength for different substrate temperatures

From the Fig. (4), the refractive index, n, is found to decrease with the increasing in the wavelength of incident photon for all samples, and tends to be constant at higher wavelengths. And also note that refractive index, n, increases with increasing in substrate temperature of films and become nearly equal near 600 nm for all films, the increases of n with substrate temperature may be attributed to the increasing of particle size of these films. The calculated films thickness obtained by using equ.(13) was tabled in table[1].The thickness of thin films decreased with the increasing substrate temperature.

3-2-2: Optical band gap:

The transmission spectra of the ZnS thin films that are shown in Fig(2) showed transmission of more than 80% in the visible range .The high transparency in the visible region is consequence of the wide band gap of the films.The optical absorption coefficient **α** was deduced from the transmission spectra using the relation:

$$I = I_o \exp(-\alpha d) \qquad \text{.....(14)}$$

Where d is the thickness of the film**, I** ,**Io** are the intensities of the transmitted and incident light respectively.

ZnS is a direct band gap semiconductor (see fig.5), the band gap of the films was calculated by plotting the value of $(\alpha h\nu)^2$ against photon energy . The straight line portion and the intercept of this liner portion on the energy axis at $(\alpha h\nu)^2$ equal to zero gives the band gap[10]. The $(\alpha h\nu)^2$ against **hν** plots of the ZnS films are shown in Fig(6),the band gap values of the ZnS thin films at different substrate temperature are shown in table[1],it can be noted that band gap value of the films are increased with increasing of the substrate temperature and reaching to the value of ZnS bulk material.

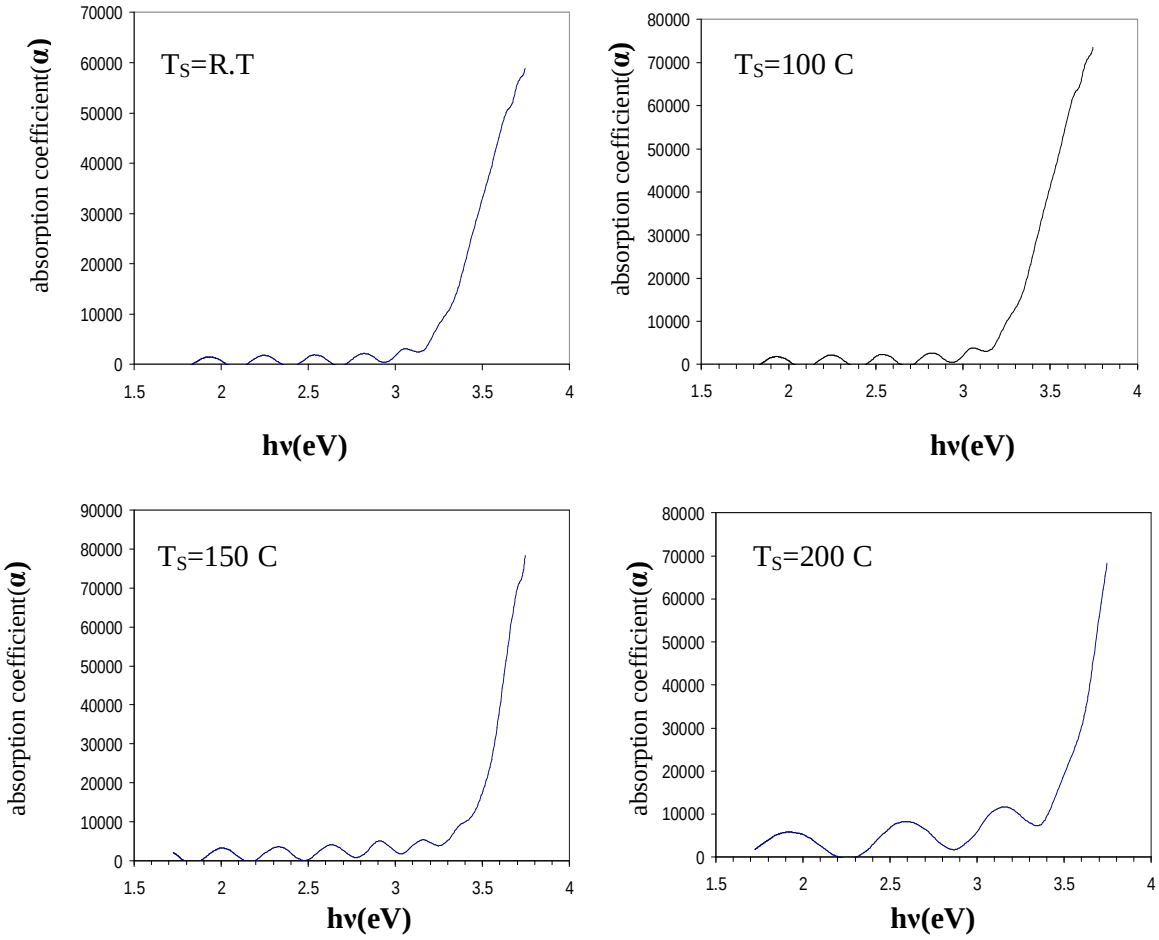

Fig. 5. absorption coefficient (α)vs. photon energy (hν(eV))for different substrate temperature .

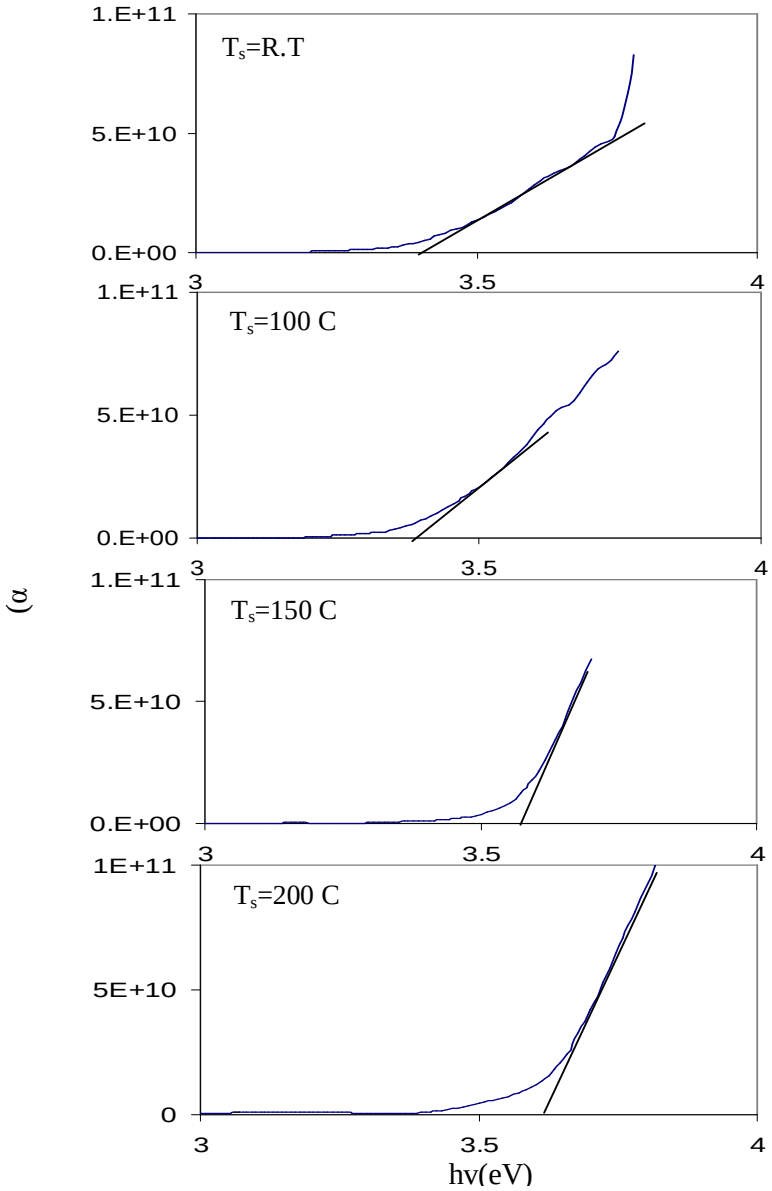

Fig. 6. $(\alpha h\nu)^2$ vs. hν plots of ZnS thin films for different substrate temperature .

4- conclusions:

A series of the ZnS thin films with different substrate temperature are prepared by thermal evaporation technique. In this study, the influence of substrate temperature on the structural and optical properties of ZnS thin films was investigated. The X-ray diffraction (XRD) patterns analysis indicates that the crystal structure transfers from wurtzite in powder material to zincblend structure in thin films form, and reveals that these films have polycrystalline nature with lattice parameter a= 5.41 $\overset{o}{A}$ .As the substrate temperature increases from R.T to 200C, the average grain size increases from 17.5 nm to 27.6 nm.

The concepts of the Swanepoel method for the determination of optical properties of thin films were evaluated .The refractive index, thickness, absorption index; extinction coefficient and optical band gap of thin films deposited on transparent substrate several orders of magnitude thicker than the films. We showed that the application of the Swanepoel method is straightforward.

Optical properties analysis of all the films by using Swanepol methods indicates that with the increasing substrate temperature the refractive index of films increases and all films have nearly the same refractive index at wavelength about 630 nm. Band gaps values increased and reached the value of bulk material .The transmission of all samples was high in visible range.

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الملخص:

حضرت أغشية كبريتيد الخارصين بوساطة تقنية التبخير الحراري بالفراغ على قواعد من الزجاج(corning 7059) وعند درجات حرارة قاعدة مختلفة.التركيب البلوري والحجم الحبيبي حسب بأستخدام تقنية الاشعة السينية(XRD) .الاغشية المحضرة تملك تركيباً مكعباً متعدد التبلور وبثابت شبيكي قدره

$a=5.41\ \text{Å}$

الثوابت الضوئية(معامل الانعكاس ومعامل الامتصاص) لهذه الاغشية استحصلت من طيف النفاذية في المدى -300 700 nm .بيانات النفاذية حللت بأستخدام طريقة Swanepoel.حيث ان معامل الانعكاس يزداد مع زيادة درجة حرارة قاعدة اترسيب وجميع الاغشية المحضرة تملك تقريباً نفس معامل الانعكاس بالقرب من الطول الموجي 630 nm .فجوة الطاقة للاغشية المحضرة تتراوح بين 3.4-3.62 eV حيث انها تزداد مع زيادة حرارة قاعدة الترسيب .الهدف من الدراسة هو الحصول على اغشية ZnS ذات خصائص ملائمة لاستخدامها في تطبيقات الخلايا الشمسية.