Study the Effect of Annealing Temperature on the Structural, Optical and Electrical Properties of ZnS Thin Films

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Abstract

The structural, optical and electrical properties of ZnS films prepared by vacuum evaporation technique on glass substrate at room temperature and treated at different annealing temperatures (323, 373, 423)K of thickness (0.5)µm have been studied. The structure of these films is determined by X-ray diffraction (XRD). The X-ray diffraction studies show that the structure is polycrystalline with cubic structure, and there are strong peaks at the direction (111).

The optical properties investigated which include the absorbance and transmittance spectra, energy band gab, absorption coefficient, and other optical constants. The results showed that films have direct optical transition. The optical band gab was found to be in the range to (2.96-3.06)eV with increasing annealing temperatures. The electrical properties of these films have been studied, it was observed that D.C conductivity at room temperature decreases with the increase of annealing temperatures, and the mechanism of conductivity occurs in two ranges of temperature, from Hall measurements the conductivity for all samples of ZnS films is n-type.
Keywords: Optical Properties, Structural Properties, ZnS, transparent layer

Introduction

Zinc sulphide (ZnS) is an important semiconductor compound of the II-VI group with excellent physical properties [1], it has a wide band-gap of 3.65eV in the bulk [2]. Recent investigations have evoked considerable interest in ZnS thin films due to their vast potential for use in thin film devices such as photoluminescent and electroluminescent devices. Zinc sulfide has found wide use as a thin film coating in the optical and microelectronic industries. It has high refractive index (2.25 at 632) nm, high effective dielectric constant (9 at 1 MHz) and wide wavelength passband (0.4–13)µm[3] .Its extensively used for optoelectronics application such as filters, display devices and materials for LEDs and lasers [4].ZnS is highly suitable as a window layer in heterojunction photovoltaic solar cells: because the wide band decreases the window absorption loses and improves the short circuit current of the cell [5].

Thin films of ZnS were prepared using many deposition techniques such as vacuum evaporation method [6], chemical bath deposition [7], spray pyrolysis [8], and screen printing method [9-10].

ZnS exists mainly in two forms an α–phase (hexagonal wurtzite structure) and a β-phase (cubic sphalerite structure) [8].In this paper, the influence of annealing temperature on the structural, optical and electrical properties has been studied.

Experimental Part

The ZnS thin films with different annealing temperatures (323, 373, 423) K of thickness (0.5μm) were prepared by vacuum evaporation technique under lower pressure (10^{-6} Torr). The structure of the ZnS thin films grown on glass substrates was examined by a phillips X-ray diffractometer with copper K_α radiation of the wavelength (λ=1.541 **Å**). Spectrophotometer, type Shimadzu and UV-Visible recorder Spectrophotometer UV-160, is used to measure the transmittance and absorbance spectrum in the range (300-1100) nm region for ZnS thin films

The absorption coefficient (α) and the other optical constants which are represented by refractive index (ń), extinction coefficient (k) and the two parts of dielectric constant (ε_1 and ε_2) were calculated from absorpttance spectrum.

The lambert relation between absorption coefficient and incident power intensity on thin films with thickness (t) [11]:

$$I_{(t)}=I_o \exp[-\alpha.t] \text{------------------------------------} (1)$$

Where $I_{(t)}$ is incident photon energy at thickness (t)inside the material, and I_o is incident photon energy at surface of material, the negative signal refers to the decreases in photon energy.

The absorption coefficient (α) considers as function of wavelength of incident radiation and it is very important because it gives absorption range to the radiation. The following relation below is refereed to the absorption:

$$A = 1-(R+T) \text{--} (2)$$

Where R,T is the reflection and transmittance respectively.

The refractive index (n) can be calculated from the equation[11]:

$$n=\left(\frac{4R}{(R-1)^2}-k^2\right)^{1/2}-\frac{(R+1)}{(R-1)} \text{------------------------------} (3)$$

And k represents the extinction coefficient which is calculated by the relation[11]:

$$k=\alpha\lambda/4\pi \text{---} (4)$$

The real and imaginary part of dielectric constant (ε_1 and ε_2) of the films were calculated from the equations [11]:

$$\varepsilon_1 = n^2 - k^2 \quad \text{(real part)------------------------------} (5)$$

$$\varepsilon_2 = 2nk \quad \text{(imaginary part)-------------------------------} (6)$$

The electrical properties of these films have been studied, the D.C conductivity follows the relation**:**

$$\sigma_{R.T} = \sigma_o \exp(E_a/k_B T) \text{--} (7)$$

Where $\sigma_{R.T}$ is conductivity at room temperatures, σ_o is a constant, k_B is a Boltzman constant and E_a is activation energy for conduction.

Results and Discussions

The results and analysis of the experimental measurements and test of the structural, optical and electrical properties of ZnS films of thickness (0.5) µm on glass substrates at annealing temperatures (323, 373, 423) K have been presented.

Structural Properties

Fig.(1) shows the X-ray diffraction for ZnS un annealed and annealed films at (323, 373, 423)K. The figure showed that all the layers grown at room temperature and annealed at different annealing temperatures had only (111) plane and exhibited cubic structure according to ASTM cards.The presence of a single peak at $2\theta \approx 28.6^0$ indicated that the layers had a highly preferential growth along the (111) direction.

The increase of T_a improves the crystal structure by increasing the intensity of the planes. Such improvement in crystal structure could be attributed to the increase in crystallite size as the small crystallites join each other in the planes by increasing heat treatments, and this behavior is similar to the work of [10-14].The structural parameters such as inter planar spacing, lattice constant, crystallite size, strain and dislocation were determined as given in Table (1).It is clear from this table that the lattice constant decreases with the increase of the annealing temperatures , this occurs because the strain decrement in the films treated at different T_a as well as dislocation density values are found to decrease with increase of annealing temperatures. The grain size increases with the increase of annealing temperatures.

Optical Properties

The absorbance spectra for ZnS thin films as deposited and at different annealing temperatures (323, 373, 423) K, are shown in Fig. (2). This figure indicates that the films have low absorbance in the visible and near infrared regions. It is observed that the maximum absorption peak shifts slightly towards the smaller wavelength with the increase of annealing temperature. This suggests the increase in the band gap with the increasing of T_a as given in Table (2). The over all absorbance decreases with the increase of T_a but not systemically in all regions of the spectrum. This is because of the characteristics of ZnS structure [10-14]. Also we studied the spectrum of transmittance as shown in the Fig. (3), it is obvious that its behavior is opposite to that of the absorpttance spectrum. The optical transmittance spectra for ZnS thin films, having different T_a are shown in Fig.(3) . All the films demonstrate that more than 60% transmittance occurs at wavelengths longer than 0.4 µm. Below 0.4 µm there is a sharp fall in transmittance of the films, this because of its high energy gap value which renders strong absorbance of the films in this region. It is observed that the over all transmittance increases with the increase of the T_a. Similar results have been pointed out and referred the overall decrease in the absorbance with the increase of T_a [12]. A usual interference in the transmittance above 0.4 µm is observed which proves the uniformity of the thin film and the substrate. However variations in the transmittance have been observed to increase with the increase of T_a.

The absorption coefficient (α) was determined from the region of high absorption at the fundamental absorption edge of the film, using equation (1).Fig.(4) shows the absorption coefficient (α)of ZnS films of thickness(0.5)µm with different annealing temperatures (323, 373, 423)K.From this figure, α decreases with the increase of annealing temperatures for all samples as shown in Table(2), and this is due to the increasing value of energy gap with annealing temperatures. Our value of α which varies between $(1.22\text{-}0.599)\text{x}10^4 cm^{-1}$ nearly agrees with [12-13].

To determine the type of optical transition, we have examined $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{1/3}$, $(\alpha h\nu)^{2/3}$, $(\alpha h\nu)^{2}$, versus hν and found that the last relation yielded a linear dependence, which describes allowed direct transitions. From Fig. (5) the energy gap is determined by plotting Tauc equation, and taking the extrapolation of the linear portion where ($\alpha \geq 10^4$ cm^{-1}) of the $(\alpha h\nu)^2$ as a function of hν curve to α=0 .The direct energy gap value was found to be as shown in the Table(2), which is nearly in agreement with the other literatures[10-13]. The value of optical energy gap increases with the increase of annealing temperature for all samples as shown in Table(2) and Fig.(5), and this is due to the growth of grain size and the decrease in defect states near the bands and this turn increased the value of E_g^{opt}.

The density of localize states in the band can be evaluated from the Urbach energy (E_u) at $\alpha < 10^4 cm^{-1}$ which is referred to absorption tails at energies smaller than the optical energy gap, by ploting Ln α as a function of hν, and the reciprocal slope of the linear part give the value of E_u. We can see from Table (2) that E_u decreases from (0.567 to 0.279)eV with increasing annealing temperature and this may be attributed to improvement in the structure by annealing and decreasing the degree of amorphous films leading to decrease the localized states .

The optical behavior of materials is generally utilized to determine its optical constants for example the refractive index (n) which is calculated from equation (3). Fig.(6)and Table (2) showed the variation of refractive index at deposited and annealed films. It is interesting to see that n decreases with the increase of annealing temperatures from (4.956 -1.52). The decrease is due to the over all decrease in the reflectance with the increase of T_a, also this behavior is may be due to increase in energy gap which causes to expand the lattice and grow the grain size and decreases the defect which means increasing the absorption and decreasing the reflection which the refractive index depend on it and this is in agreement with [10-17].

The behavior of extinction coefficient (k) which is calculated from equation (4) is nearly similar to the corresponding absorption coefficient at different T_a, we can see from Table (2) and Fig.(6) that k decreases with the increase of T_a from R.T to 423K ,this attributed to the same reason, which mentioned previously in absorption coefficient.

Fig. (7) shows the variation of (ε_1, ε_2) which is calculated from equation 5& 6 respectively with different annealing temperatures. The behavior of ε_1 is similar to refractive index because the smaller value of k^2 comparison of n^2, while ε_2 is mainly depends on the k values, which are related to the variation of absorption coefficient. It is found that ε_1 and ε_2 decrease with the increase of T_a and this is in agreement with [14-17].

The imaginary part represents the absorption associated of radiation by free carriers [16]. Table (2) gives values of the real and imaginary parts of the dielectric constant at wavelength equal to 0.4 μm.

Electrical Properties

The electrical conductivity of ZnS thin films was calculated using equation (7), Fig.(8) showed the variation of lnσ as a function of 1000/T, the room temperature conductivity decreases with increases of annealing temperature as shown in table (3). The decreases in the $\sigma_{R.T}$ with the increase of annealing temperatures is attributed to decrease in the defect state which leads to increase in the mobility and energy gap and this is in agreement with [15, 18].

Also it can observe two transport mechanisms for all samples, the activation energies (E_{a1}) and (E_{a2}) have been determined as in Table(3). The first activation energy, at (393-493) K, represents transition process for carriers within localized states in the energy gap and this suggests the existence of high density of localized states in the energy gap. The second activation energy at (303-393) K represents the carriers transport across the grain boundaries by thermal excitation.

As given in Table (3), in general, the value of activation energy increases as the T_a increases and this is because of the improved crystallinity with the increase of the grain size and to elimination of some defects from the films. Fig.(9) Shows the plot of Hall voltage versus the current for ZnS thin films for various annealing temperatures. By using the slope of the figure for each T_a, Hall coefficient (R_H) was calculated and the conductivity for all samples of ZnS films is n-type, then carrier concentration has been calculated and its decreases with the increase of annealing temperatures. Carrier mobility was determined for all samples. All these parameters are shown in Table (3). It can be observed from the Table that carrier mobility increases with the decrease of the carrier concentration and with the increase of annealing temperatures and this is in agreement with [15,18] .

Conclusions

From the data of the present work, we can conclude that:-

1. The ZnS films of thickness (0.5)μm on glass substrate at annealing temperature (323, 373, 423)K have been prepared successfully by vacuum evaporation technique.
2. The XRD tests of these films at different T_a showed that the structure is polycrystalline with cubic structure (FCC) and there are strong peaks at (111) direction, the intensity and the grain size increases with the increase of annealing temperatures.
3. From the absorbance spectra for ZnS thin films, we observed that the maximum absorption peaks shift towards the smaller wavelength with the increase of annealing temperatures. And the value of absorption and reflection decreases with the increases of annealing temperatures whereas the transmission is increased.
4. The optical energy gap for ZnS increases with the increase of annealing temperatures**.**
5. The absorption coefficient, extinction coefficient, refractive index and the (real, imaginary) parts of dielectric constant decrease with the increase of annealing temperatures for ZnS films.
6. The room temperature conductivity decreases with the increases of annealing temperature, there are two transport mechanisms for conduction, the conductivity for ZnS films is n-type.
7. The carrier concentration decreases with the increase of annealing temperatures, and the carrier mobility increases with the increase of annealing temperatures.

References

1.Eid, A.H.; Salim, S.M.; Sedik, M.B.; Omar, H.,T.Dahy and Abou-Elkhair, H.M. (2010), Preparaition and characterization of ZnS thin films, Journal of applied sciences research,6(6):777-784.

2.Ben Nasr, T.; Kamoun, N.; Kanzari, M. and Bennaceur, R.,(2006), Effect of pH on the properties of ZnS thin films grown by chemical bath deposition, Thin Solid Films, 500:4-8.

3.Ubale, A.U. and Kulkarni, D.K.,(2005), Preparation and study of thickness dependent electrical characteristics of zinc sulfide thin films, Bull. Mater. Sci., 28(1) : 43-47.

4.Salleh, S.; Dalimin, M.N. and Rutt, H.N.,(2010), proceeding of ICSSST, 3rd international on solid state science & technology,Kuching, Sarawak, Malaysia, Structural and surface characterization of cold deposited zinc sulfide thin films, conference.

5.Shaban, S.M.; Saeed, N.M. and Al-Haddad, R.M.,(2011), Fabrication and study zinc sulfide schottky barrier detectors, Indian Journal of Science and Technology, 4(4):384-386.

6.Kumar, P.;Kumar, A.;Dixit, P.N.and Sharma, T.P.,(2006), Optical,structuraland electrical properties of zinc sulphide vacuum evaporated thin film, Indian Journal of Pure& Applied Physics, 44: 690 – 693.

7.Ubale, A.U.; Sangawar, V.S.and Kulkarni, D.K.,(2007), Size dependent optical characteristics of chemically deposited nanostructured ZnS thin films, Bull. Mater. Sci., 30(2):147-150.
8.Nithyaprakash, D.;Ramamurthy, M.; Thirunavukarasu, P.; Balasubramaniam, T.; Chandrasekaran, J. and Maadeswaran, P.,(2009), Effect of substrate temperature on structural ,optical and thermal properties of chemically sprayed ZnS thin films, Journal of Optoelectronic and Biomedical Materials, 1(1): 42-51.
9.Kumar, V.; Sharmam, M.K.; Gaur, J.and Sharmam, T.P.,(2008), Polycrystalline ZnS thin films by screen printing method and its characterization, Chalcogenide letters, 5(11): 289-295.
10.Rezagholipour, Dizaji, H.; Jamshidi, Zavaraki A.and Ehsani M. H.,(2011), Effect of the thickness on the structural and optical properties of ZnS thin film prepared by flash evaporation technique equipped with modified feeder, Chalcogenide Letters, 8(4) : 231 – 237.
11. Sze, S.M., (1981), Physics of Semiconductor Devices,,2nd ed, John Wiley & Sons , NewYork.
12. Ruhul, Amin Bhuiyan, M.; Monjarul, Alam, M.and Abdul Momin, M., (2010), Effects of substrate temperature and annealing on the structure and optical properties of ZnS film, Turk J. Phys, 34:1-7.
13. Ashraf, M.; Akhtar, S.M.J.; Ali, Z.and Qayyum, A.,(2011), The influence of substrate temperature on the structural and optical properties of ZnS thin film, Semi Conductor-Vabrication Treatment and Testing of Material and Structure, 45(5):708-711.
14. Sabaan, S. M.,(2007),Investigation of some physical properties of ZnTe/GaAs and ZnS/GaAs heterojunction, college of science, Baghdad University, Physical department.
15. .Shinde, M.S; Ahirrao, P.B.and Patil, R.S.,(2011), Structural, Optical and Electrical properties of nanocrystalline ZnS thin films deposited by novel chemical route, Archive of applied science research, 3 (2):311-317.
16. Nadeem, M. Y.and Ahmed, W.,(2000), Optical properties of thin films, Turk J.Phys, 24:651-659.
17. Xiaochun, Wu; Lai, F.; Lin, Y.; Huang Z.and Chen, R., (2007), Effects of substrate temperature on the structural and optical properties of ZnS thin film, Proc of SPIE, 6722:1-6.
18. Ubale, A.U.and Kulkarni, D.K.,(2005), Preparation and study of thickness dependent electrical characteristics of zinc sulfide thin films, Bull.Mater.Sci, 28(1):43-47.

Table (1): Structural parameters of ZnS thin films formed at different annealing temperatures

T_a(K)	2θ (deg.)	d (Å)	hkl	a (Å)	Grain size (nm)	Dislocation$\times 10^{11}$ Lines/m^2	Strain$\times 10^{-3}$
R.T	28.6	3.119	111	5.403	12.31	6.589	2.80
323	28.65	3.114	111	5.393	13.67	5.351	2.53
373	28.7	3.108	111	5.384	14.49	4.762	2.39
423	28.8	3.098	111	5.365	18.9	2.799	1.82

Table (2) :The optical constants of ZnS thin films formed at different annealing temperatures

λ=0.4μm							
T_a (K)	E_g^{opt}(eV)	E_u(eV)	$\alpha x10^4 cm^{-1}$	N	k	ε_1	ε_2
R.T	2.96	0.5678	1.220	4.956	0.0430	24.500	0.433
323	3.01	0.3993	0.944	3.196	0.0300	10.200	0.19
373	3.02	0.3992	0.829	2.500	0.0264	6.69	0.13
423	3.06	0.2798	0.599	1.520	0.0189	2.312	0.057

Table (3): The electrical measurements of ZnS thin films formed at different annealing temperatures

T_a(K)	$\sigma_{R.T}$ x10^{-5} $(\Omega.cm)^{-1}$	(393-493)K E_{a1}(eV)	(303-393)K E_{a2}(eV)	n_H x10^{15} (cm^{-3})	μ_H x10^{-3} cm^2/V. s.
R.T	5.18	0.6313	0.0644	1085.8	0.298
323	2.6	0.6816	0.0615	456.49	0.356
373	1.56	0.6433	0.0886	81.601	1.195
423	1.11	0.6677	0.0989	22.819	3. 04

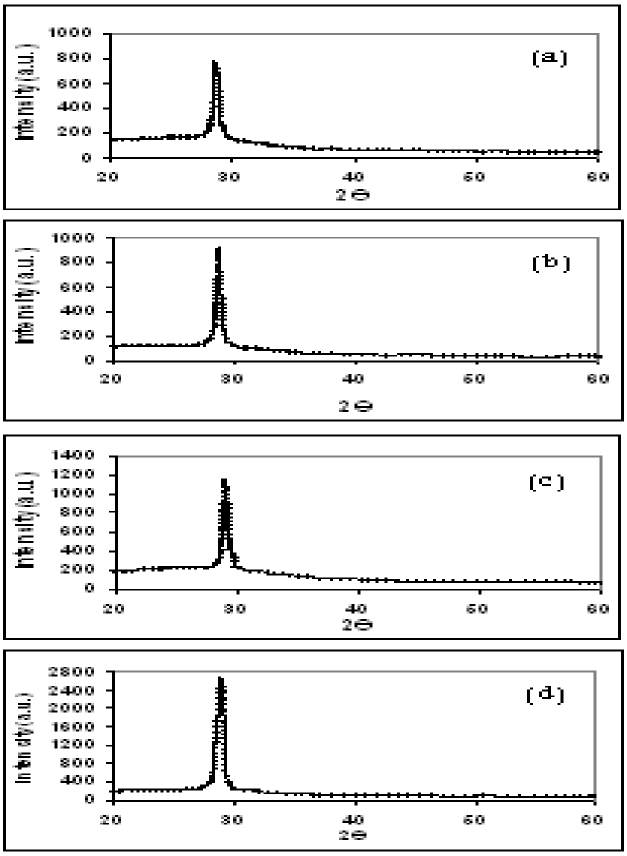

Fig.(1):The X-ray diffraction for ZnS thin films at different annealing temperatures. (a) R.T, (b) 323K, (c) 373K , (d)423K

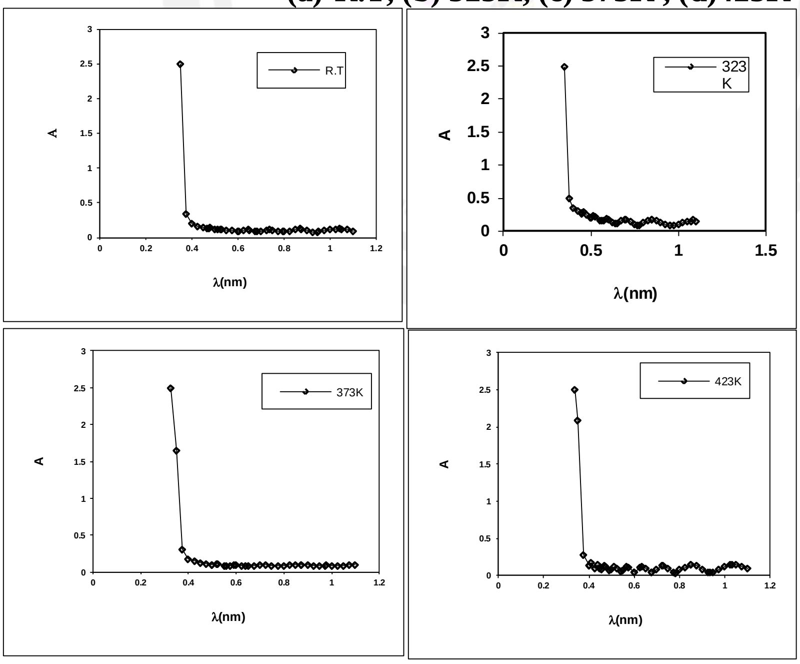

Fig.(2):The absorptance spectrum of ZnS thin films with different annealing temperatures

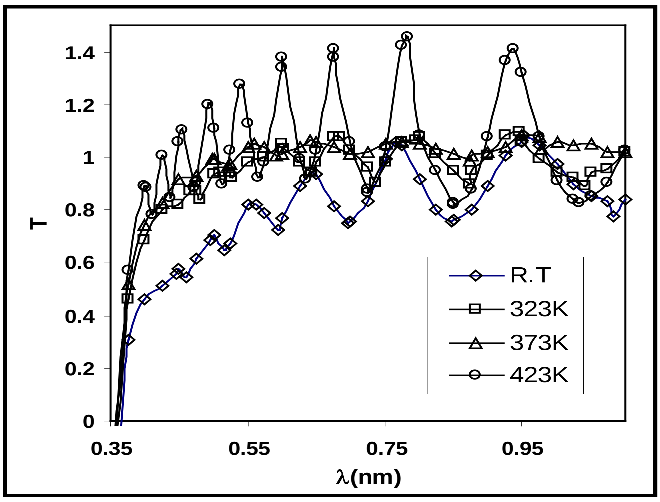

Fig.(3):The transmittance spectrum of ZnS films with different annealing temperatures

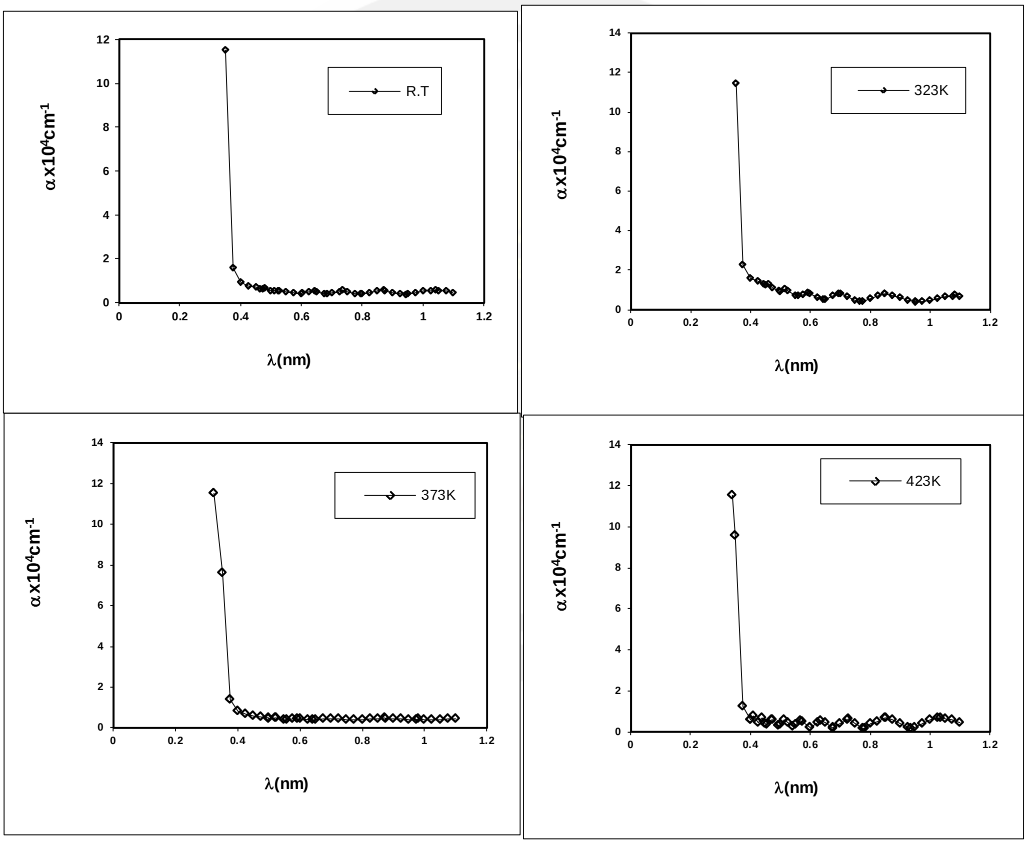

Fig.(4):The absorption coefficient of ZnS films with different annealing temperatures

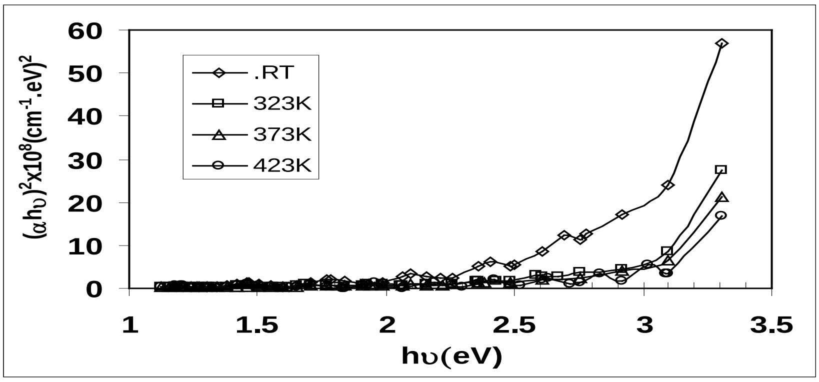

Fig.(5):(αhv)^2 as a function of αhv for ZnS thin films with different annealing temperatures

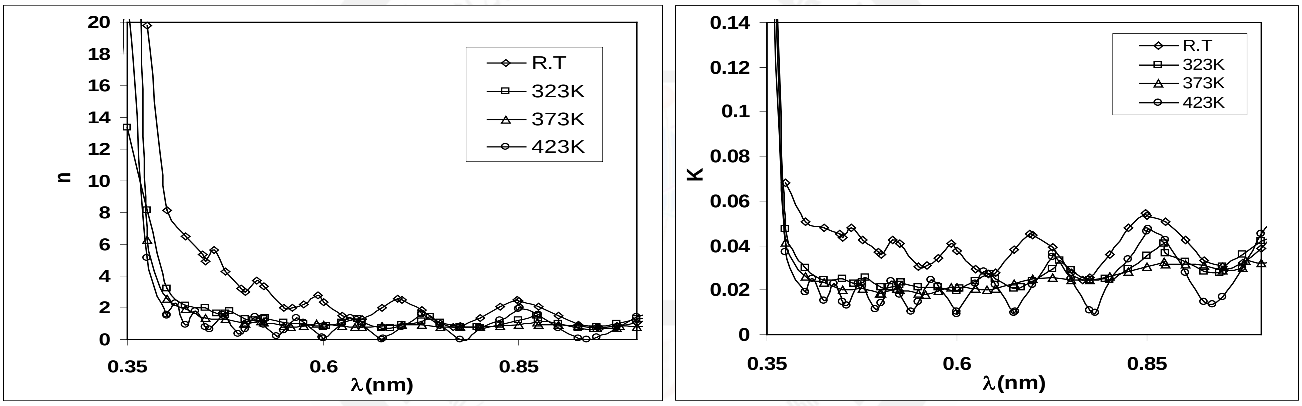

Fig.(6):The refractive index(n) and extinction coefficient(k) of ZnS thin films

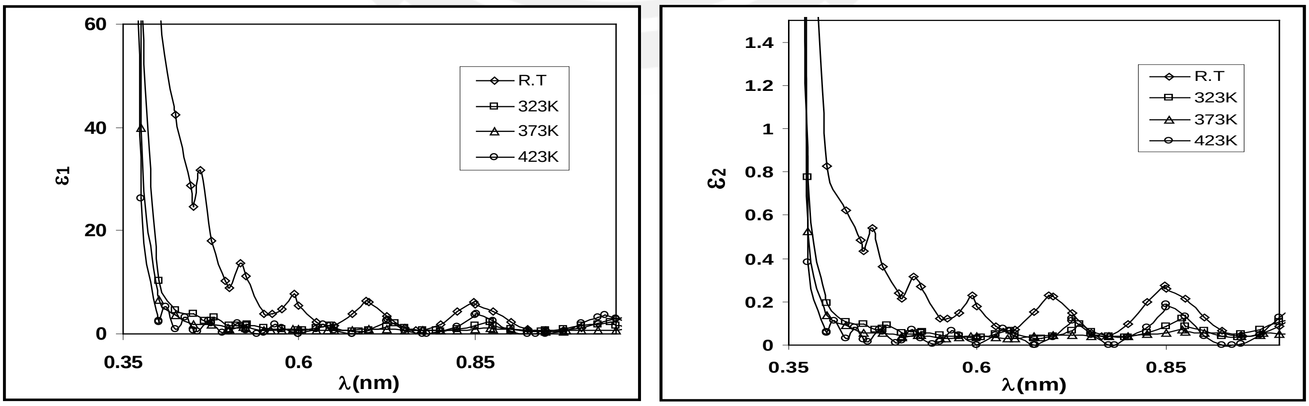

Fig.(7):The real and imaginary part of the dielectric constant of ZnS thin films

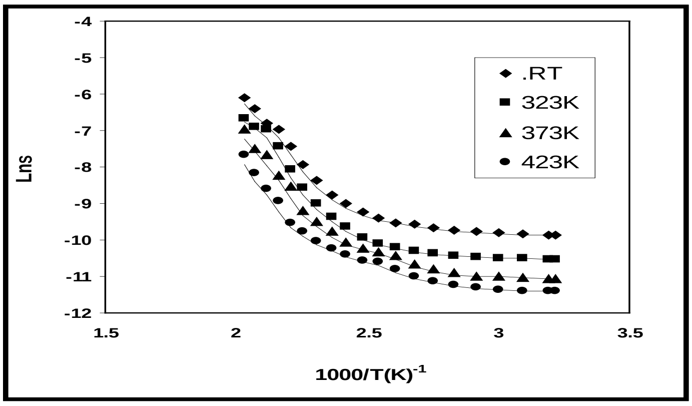

Fig.(8): The variation of lnσ as a function of 1000/T at different annealing temperatures

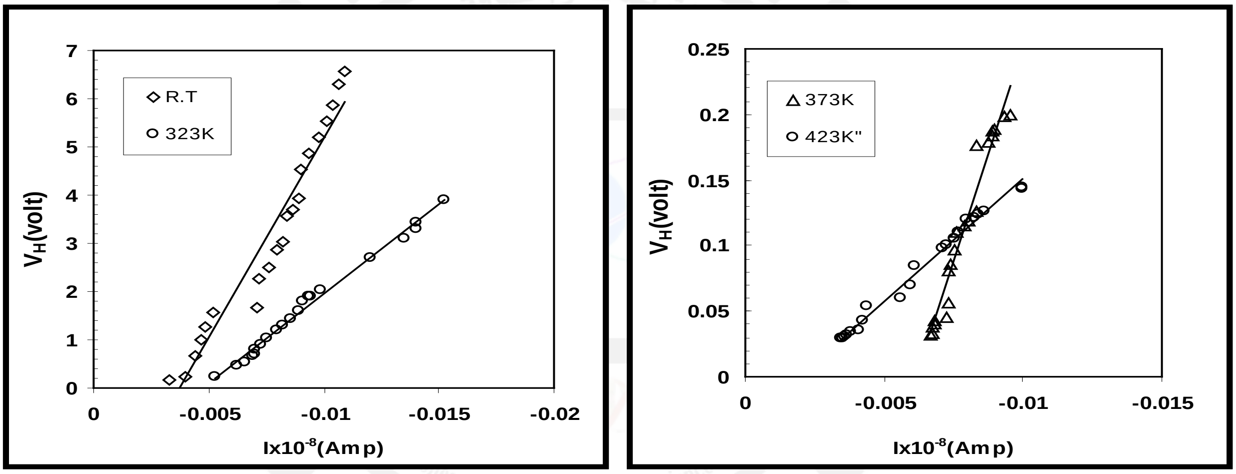

Fig. (9): Hall voltage as a function of the current for ZnS thin films.

دراسة تأثير درجة حرارة التلدين في الخصائص التركيبية، البصرية والكهربائية لاغشية ZnS الرقيقة

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الخلاصة

درست الخصائص التركيبية، البصرية والكهربائية لأغشية ZnS المحضرة بتقنية التبخير الحراري في الفراغ على قواعد زجاجية عند درجة حرارة الغرفة ،وبدرجات حرارة تلدين مختلفة K(323, 373, 423) بالسمك μm(0.5). حدد تركيب تلك الاغشية بوساطة حيود الاشعة السينية. بينت نتائج حيود الاشعة السينية أن التركيب من نوع متعدد البلورات ذي التركيب المكعبي وهناك قمة واضحة بالاتجاه (111) . تشمل دراسة الخصائص البصرية دراسة اطياف الامتصاصية، والنفاذية،وفجوة الطاقة البصرية ،ومعامل الامتصاص، وبقية الثوابت البصرية. وبينت النتائج امتلاك جميع الاغشية المحضرة انتقالا بصريا مباشرا.ووجد ان فجوة الطاقة المقاسة تتراوح ضمن المدى eV(2.96–3.06) بزيادة درجة حرارة التلدين. درست الخصائص الكهربائية ولوحظ أن التوصيلية المستمرة عند درجة حرارة الغرفة تقل بزيادة درجة حرارة التلدين، وهناك ميكانيكيتان للتوصيل. ومن خلال قياسات هول وجد أن جميع الاغشية المحضرة هي من نوع n–type.
الكلمات المفتاحية:الخصائص البصرية، الخصائص التركيبية،كبريتيد الخارصين،طبقة شفافة.