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Preperation and study optical trasnpraency of spray deposted ZnS films with different annealing temperatures

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Abstract:

The article reports the preparation of ZnS films prepared by chemical method, The band gap of ZnS films is calculated theirs value are nearly of (4 eV) for all samples The experimental diffraction angle θ and d- spacing values are in a well agreement with the standard ASTM data at all annealing temperature used (450,500,550,600 oC) of ZnS thin films. The grain size (D) increases with increasing temperature. The increase in the temperature of annealing leads to lower peaks of x- ray diffraction pattern for structural analysis. . The thickness of the prepared film is around (283nm).

Keywords: Zinc sulphide; spray pyrolysis, thin films, UV spectrophotometer, Optical properties, X- ray diffraction.

1. Introduction:

ZnS is today clearly regarded as thin films materials. ZnS sintered film may be suitable for solar cells, Wide band gap window material and other photovoltaic devices. The analysis of the optical film properties naturally enforces the application of the theoretical and experimental skills of thin film optics to the mentioned molecular system [1-3]. Another important fact emphasizes the significance of thin film spectroscopy in application to condensed molecular matter. The point is, that due to the weak Van der Waals interaction between molecules in comparison with the free molecule [2-4]. ZnS is exceptionally interesting for the photo-induced nonlinear optical effects[5], and it possesses a specific number of defect states which may be of interest for the different applications [6] These materials are generally n-type semiconductors and have the advantage of being sufficiently stable towards chemical and thermal treatment. They can easily be sublimed and resulting in high purity thin films without decomposition.

There are several methods for depositing ZnS thin films, such as; spin coating (VE) [7-9], chemical bath deposition (CBD) [7,10-13], spray pyrolysis (SP) [14- 18], etc. However, the SP technique is a very low cost and simple technique that enables intentional doping and getting large area and uniform thin films [14].

(ZnS) is an n-type semiconductor with a wide band gap about (4.07) eV, it shows high optical transmittance and a wide range of electrical conductivity values simultaneously. ZnS is used in many different applications in both microelectronic and optoelectronic devices. As a consequence of it direct energy gap. Furthermore ZnS can be used as semiconducting gas sensor [19] due to conductivity changes it exhibits when exposed to oxidizing gases such as ozone.

The main aim of the paper is the preparation ZnS as thin films used in the application in the photovoltaic conversion of solar energy and important investigations of novel materials and structures. Photovoltaic are the most fascinating ways of direct solar energy conversion. ZnS thin film solar cells give hope to meet the cost goals, which are necessary to provide the needs for the energy production by photovoltaic.

In the present paper, ZnS nanoparticles are synthesized by using spraying pyrolysis method then, deposited on glass substrate. ZnS thin films were analyzed by X-ray diffraction. The optical absorption spectra of the ZnS were measured using a UV-V spectrophotometer.

2. The synthesis of Zinc Sulphid (ZnS)

The Zinc Sulphid (ZnS) thin films were prepared by using Zinc Chloride ($ZnCl_2$) of molecular weight (136.28 g/mol) and purity of (99%) equipped by (General Purpose Reaent BDH-Limited Pool England) (0.681 g) of ($ZnCl_2$) was dissolved in (50 ml)of distilled water but the dissolution was not completed because of the existence of plankton in the solution and for the dissolution to be done completely and quickly drops of hydrochloric acid (HCl) was added in order to dissociate the chlorides bonds that exist in the solution with that the solution became clear and colorless and was put on the magnetic stirrer for (15 min.) to make sure that the material was completely dissolved in the distilled water and with that we get a homogeneous solution of ($ZnCl_2$) which is the source of the Zinc ion (Zn^{+2}) whereas the source of Sulphid ion (S^{-2}) Thiourea ($CS(NH_2)_2$) in which its weight was (0. 38 g) . After that (50 ml) of (ZnS) is mixed with (50 ml) of ($CS(NH_2)_2$

$$\mathbf{ZnCl_2 + CS(NH_2)_2 + 3H_2O \rightarrow 2NH_4Cl + ZnS + CO_2\uparrow + H_2O}$$

When depositing Ammonium Chloride (NH_4Cl) is dissociated at a temperature of (350 ^{0}C) to Ammonium gas (NH_3) and Hydrogen Chloride gas (HCl) , and with that, we have a thin film of (ZnS) material on the surface of the substrate according to the following reaction:

$$\mathbf{2NH_4Cl+ZnS+H_2O \xrightarrow{350^oC} 2\,NH_3\uparrow 2HCl\uparrow ZnS+ H_2O\uparrow}$$

The thin films were deposited on glass substrate with dimensions of (2.5X1 cm^2) and thickness of (0.1 mm) and it bears high temperature without breaking because of its thin layer and also provides high homogeneous in spreading the heat, which is Iraqi made. For the purpose of cleaning it is put in a beaker of distilled water and then it is put in acetone and then dried with filtering paper.

3. Preparation of thin films by heat solution

The hot plate is prepared for the purpose of depositing the thin films by feeding it with electricity current for (one hour) until it gets to the required temperature for the solution which is (350 ^{0}C).

After that the analyses device is put in a vertical way towards the substrates at a distance of (320 ± 10 mm) . Then the required solution to deposit the thin films is put in the tank of the analyses device and the glass valve is opened in the analyses device, so the solution flows as drops of (ZnS) material . After that the electric pump is opened, so the drops are turned into very tiny drizzle. Then the glass put under the analyses device is moved for (10 s), then it is returned to the bottom or the spray device and the electric pump is closed to stop for (3 min) to increase the temperature of the substrate which that decreased because of the cold drizzle are back to its first valve.

Within the process of analyses the hot plate turns in a circular way to ensure the homogeneous deposition. After the idle period the process is repeated several times until it gets to the required thickness. When finished the thin films are left on the hot plate for (5 min).

The process of the crystal growth would be done well, after that the electricity current is turned off and the thin films are left on it to cool down. The process of exposing the films to a certain temperature and for a specified time is called heating treatment. Annealing process effects the crystal form and electronic transportations and leads to decreasing the levels in the non-crystals substances, whereas, in the crystal defects where it either gives the atoms the kinetic energy required to rearrange itself in the crystal lattice and we used an electric oven (Sx-5-12-Box-Resistance Furnaces controller Box) equipped by (Instrument Co. LTD Tianing Taisite CHINA) where its temperature reaches (1200 ^{0}C) with the presence of air by annealing the thin film with temperatures of (450, 500, 550, 600 ^{0}C) and for half an hour for every (25 ^{0}C) then the thin film is left in the oven to cool down.

4. Results and discussion

The deposited ZnS thin films were analyzed by X-ray diffraction pattern for structural analysis by using Philips X-ray diffractometer CuKα radiation with the help of Philip X-ray diffract meter. The peak broadening in the XRD patterns clearly indicates the formation of ZnS crystal with small size as shown in Figure (1 A-D) which shows the x- ray at different temperature (450, 500.550,600 ^{o}C) respectivily. The d-values were calculated by calculating θ values from the peaks of the X-ray spectrum by using Bragg's relation (2dsinθ = n λ), **(**n=1 in the present study and used K-Alpha1 wavelength = "1.54060"A^{0}). These d values were compared with the standard ASTM data to confirm the structure of ZnS table (I).

The peak broadening at lower angle is more meaningful for the calculation of particle size, therefore size of crystals has been calculated using Debye-Scherrer formula [20] using (111) reflection from the XRD pattern. Debye-Scherrer formula for crystallite size determination is given by:

$$D = \frac{0.94\lambda}{\beta cos\theta} \qquad (1)$$

Where D is the crystallite size (grain size), λ is the wavelength of x-ray, β is the Full Width at Half Maximum (FWHM) after correcting the instrument peak broadening (β expressed in radians), and θ is the Bragg's angle. The values of particle size obtained from XRD for different molar are listed in table (1).From table (1), it is clear that the particle size increases when temperature increases , because increasing temperature lead to increase intra-distance between molecules[21].

The optical absorption spectra of the crystallites were measured using a (6800 UV/VIS Jenway Double Beam Spectrophotometer –England) UV-V is spectrophotometer. The ZnS films has been recorded at room temperature over the range (250 to 700) nm, at different annealing temperatures
(450, 500, 550, and 600 ^{o}C), as shown in figure(2). The absorption spectra of these samples is clear from that all thefour samples have absorption peak at wavelength of (300 nm). All samples have small shift of the absorption edges for different temperature arises.
The relation between the absorption coefficient (α) and the incident photon energy (hν) can be written as [22]:

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

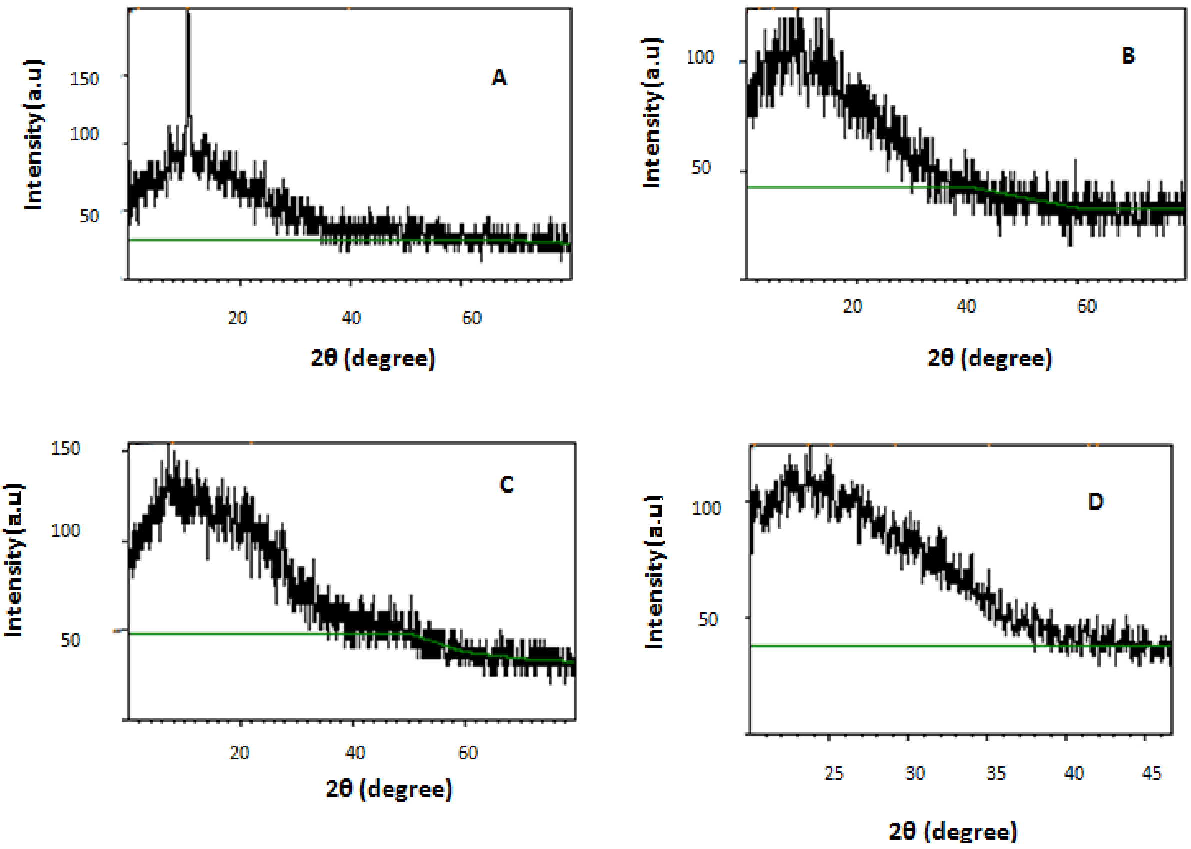

Fig.(1): x-ray at different annealing temperature(A- 450oC, B- 500^{o}C, C-550^{o}C, and D-600^{o}C) between (2θ) and counts/sec

Table(I): the X-ray analysis of sintered ZnS film, all the value were in well agreement with the standard ASTM data at different temperature.

T °C	ASTM (2θ) degree	Observed 2θ (degree)	ASTM d-spacing A°	Observed d-spacing A°	FWHM	D grain size nm
450	25.4281	25.3842	3.5052	3.50886	0.1574	28.18
500	22.4334	22.435	3.9606	3.96299	0.0984	44.83
550	23.9014	23.8443	3.7280	3.7311	0.0832	53.15
600	25.005	25.0272	3.5552	3.55813	0.0689	64.33

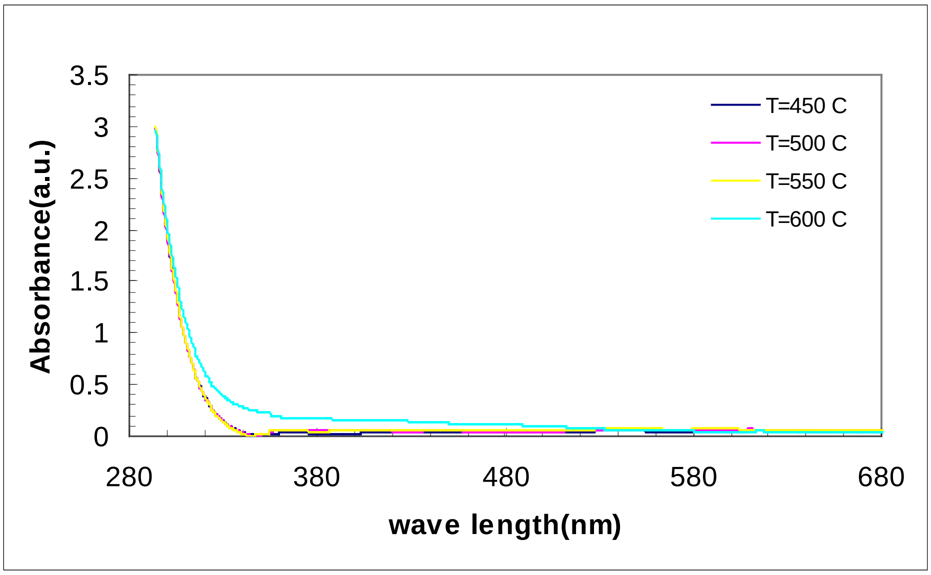

Fig.(2):Absorption spectra of different annealing temperature (450,500,550, and 600 °C) of ZnS.

Where, A is constant, E_g is the band gap of the material and exponent depends on the type of transition [23]. Here transitions are direct because α is more than (10^4 cm^{-1}) ,the transition called "direct transition " ,where electron moves from valence band(V.B) to conduction band (C.B) with the same wave vector (k') ,then the energy and momentum stay conserved[24] .

The values of optical band gap are calculated by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs hν graphs at different temperature (450,500,550,and 600 °C) as shown in (Figure 3-A,B,C and D) respectively . The obtained band gap values for different temperature are nearly (4.05, 4.07, 4.09,and 4.07eV) respectively.

The thickness of the thin film can be calculated by knowing the equation following (3)[25].The thickness was(283nm).

$$d= \{\lambda_1\lambda_2 / 2(n_2\lambda_1 - n_1\lambda_2)\} \qquad (3)$$

where 'd' is the thickness of the film, and n_1 and n_2 is the refractive index at two adjacent maxima or minima corresponding to their wavelengths λ_1 and λ_2.

The variation of optical transmission spectrum with wavelength for ZnS thin films at different temperatures (450, 500, 550,and 600 ^{o}C is shown in Fig. (4).

5. Conclusions

ZnS is prepared by chemical method, the thin films are prepared at (350 ^{o}C). The optical properties of films were investigated at different temperatures (450,500, 550, 600 ^{o}C). The band gap of ZnS films are calculated; their values are nearly of (4 eV) for all samples. ZnS sintered film may be suitable for solar cells, Wide band gap window material and other photovoltaic devices. The experimental diffraction angle θ and d- spacing values are in a good agreement with the standard ASTM data at all annealing temperature used (450,500,550,600 ^{o}C) of ZnS thin films. The grain size (D) increases with increasing temperature. The increase of the temperature of annealing leads to lower peaks of x- ray diffraction pattern for structural analysis.

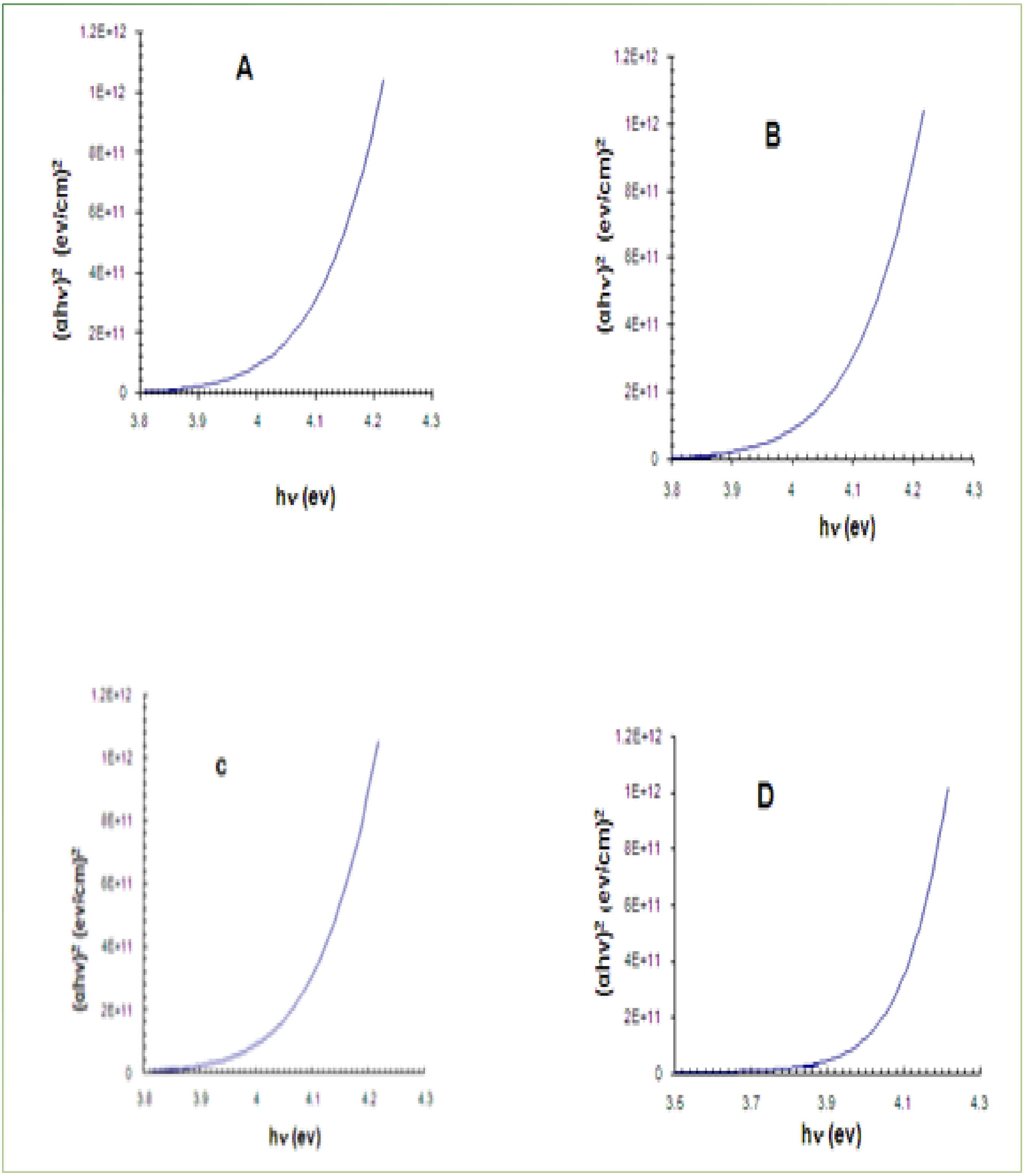

Fig. (3): Band gap determination of ZnS (A) T=450 ^{o}C, (B) T=500 ^{o}C, (C) T= 550 ^{o}C (D) T= 600 ^{o}C.

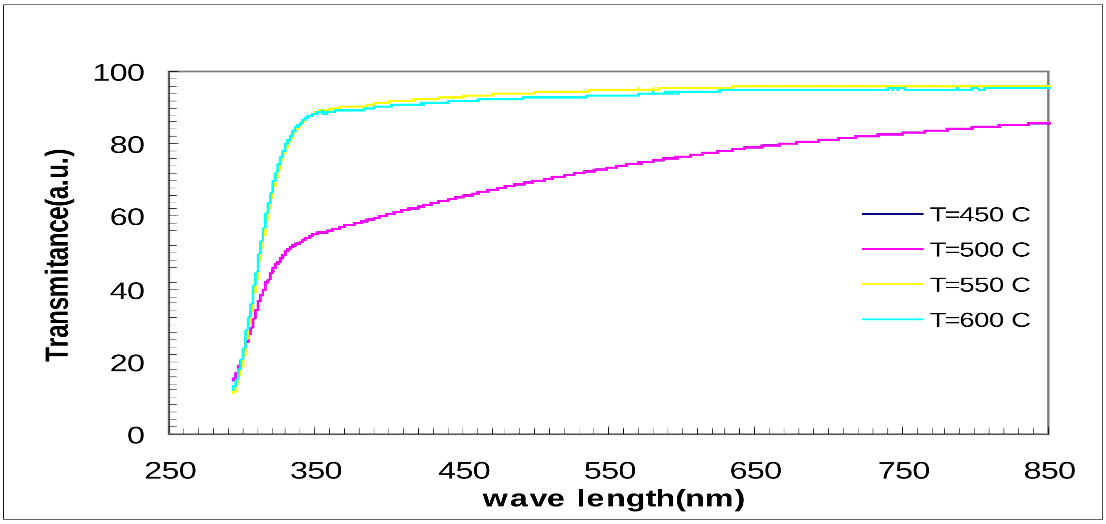

Fig. (4): Variation of transmittance (T) with wavelength (λ) for ZnS at different temperatures (450, 500, 550 and 600°C) thin films.

5. Conclusions

ZnS is prepared by chemical method, the thin films are prepared at (350 °C). The optical properties of films were investigated at different temperatures (450,500, 550, 600 °C). The band gap of ZnS films are calculated their values are nearly of (4 eV) for all samples. ZnS sintered film may be suitable for solar cells, Wide band gap window material and other photovoltaic devices. The experimental diffraction angle θ and d- spacing values are in a well agreement with the standard ASTM data at all annealing temperature used (450,500,550,600 °C) of ZnS thin films. The grain size (D) increases with increasing temperature. Increase the temperature of annealing leads to lower peaks of x- ray diffraction pattern for structural analysis.

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تحضير ودراسة الشفافية البصرية لأفلام كبريتيد الخارصين ZnSالمحضرة بطريقة الرش الكيميائي ولدرجات حرارة تلدين مختلفة

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المستخلص:

قمنا بتحضير كبريتيد الخارصين بالطريقة الكيميائية. كما تم حساب فجوة الطاقة لأغشية كبريتيد الخارصين وكانت بحدود

(4 الكترون فولت) لجميع العينات. وقد وجدنا عمليا ان قيم زاوية الانعكاس θ وقيم المسافة بين مستويات البلورة d تتفق مع القيم القياسية ASMT عند جميع درجات حرارة التلدين المستخدمة لأغشية ZnSالرقيقة . لاحظنا زيادة حجم الحبيبة D بزيادة درجة الحرارة. كما ان زيادة درجة المعالجة الحرارية يؤدي الى انخفاض قمم الاشعة السينية المنعكسة عند تشخيص المركب. (283 nm)سمك الافلام المحضرة كان بحدود