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# Study the Effect of Annealing on Optical and Electrical Properties of ZnS Thin Film Prepared by $CO_2$ Laser Deposition Technique

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**Abstract:** In this work, ZnS thin films have been deposited by developed laser deposition technique on glass substrates at room temperature. After deposition process, the films were annealed at different temperatures (200ºC , 300 ºC and 400ºC ) using thermal furnace.The developed technique was used to obtain homogeneous thin films of ZnS depending on vaporization of this semiconductor material by continuous $CO_2$ laser with a simple fan to ensure obtaining homogeneous films. ZnS thin films were annealed at temperature 200ºC, 300 ºC and 400ºC for (20) minute in vacuum environment. Optical properties of ZnS thin film such as absorbance, transmittance, reflectance, optical band gap, refractive index extinction coefficient and absorption coefficient have been investigated. From this measurements, the bandgaps energies at room temperature, 200ºC , 300 ºC and 400ºC were found to be 3.7eV, 3.6eV, 3.4eV and 3.3eV respectively. The band gap decreased as the annealing temperature increased. The two point probe method was used for the investigation of electrical properties of the ZnS films such as current voltage characteristics and sheet resistance properties. From these measurements it was found that current decreased as the temperature increased, thus, the annealed films were found to be more resistance than the as-grown films.

## Introduction

Zinc Sulphide (ZnS) is an important II–VI semiconductor materials with large direct energy band gap (3.50-3.70) eV in the UV range, direct energy band gap (~3.65 eV) in the bulk ZnS [1, 2]. Due to the large energy band gap of ZnS, it can be used for fabrication of optoelectronic devices such as blue light-emitting diodes, electroluminescent devices, electro optic modulator, optical coating, n-window layers for thin film heterojunction solar cells, photoconductor, cathode-ray tubes and buffer layers in photovoltaic cells [3].

The study of material properties lead to draw attention physicians toward this technique, from the second half of seventeenths centaury, many of researches were taken out in the field [4,5]. In the nineteenth century there has been an improvement in the experimental part of thin film [6,7]. The thin film is one layer or many layers for specific material in the range of tens nanometers thickness in some of micrometers [8].

ZnS thin films have been found useful in various devices. The applications of ZnS thin films which cover a wide area of interest are: antireflection coating for the solar cell, environmental friendly buffer layer as compared to CdS layer in CIGS based thin film solar cell, wide band gap material for electroluminescent and opto-electronic devices, photosynthetic coatings, blue light emitting laser diodes and as$\alpha$ - particle detector [9-12].

The high level of efficiency with $CO_2$ laser, made it the greatest practical importance among different molecular lasers in which laser radiation can be generated in continuous wave (CW) and pulse operation is its most fascinating feature [13].

In the present work ZnS thin films have been prepared by using $CO_2$ laser deposition technique. The optical and electrical properties of the deposited ZnS thin films with different annealing temperature were studied.

## Experimental Work

### Preparation Technique

ZnS thin film was prepared by using $CO_2$ laser deposition technique on glass substrates at normal atmospheric pressure and room temperature. The glass substrates of dimensions (26×76×2) mm were cleaned by distiled water and alcohol respectively. Continuos $CO_2$ laser with maximum output power (10W) and wavelength (10.6 µm) is used to deposited the zinc sulphide on glass substrates. The specification and parameters of $CO_2$ laser can be listed in Table 1.

**Table (1):** $CO_2$ Laser Specification and Parameters

| | |
|---|---|
| Model | ULR10-O-IA-x |
| Manufactured company | Sintec Optronics Technology Pte Ltd |
| Laser mode quality | >95% $TEM_{00}$ Electric Field Purity |
| Maximum peak power | 10W |
| Power stability | ±10% |
| Wavelength | 10.6um |
| Beam size(near field) | 4±1mm |
| Beam divergence(full angle) | 5±1mrad |
| Optical pulse rise or fall time | 120±40µS |
| Optical modulation | 100% up to 5kHz |
| Modulation signal type | TTL compatible |
| Mode of operation | pulsed |

ZnS powder with density 4.09 g/cm$^3$ and molar mass 97.47 g/mol is used as a target material which the laser beam was directed with angle of 45$^0$ on this material [14]. Table 2 shows the properties of ZnS material which is used in this work.

**Table (2)** : ZnS Properties

| | |
|---|---|
| Molar Mass | 97.47g/mol |
| Density | 4.09 g/cm$^3$ |
| Solubility in water | negligible |
| Band gap | 3.5-3.7 |

Thickness of the films has been measured by weighting method which used a digital balance with accuracy of (± 0.1 × 10$^{-3}$ gm) for weighting the needed materials and for measured the thickness of the prepared films. From this method the thickness of all prepared films were varied between (350-400) nm with the arrangement uses a fan to get homogeneous films, then the samples were annealed at 200 C$^o$, 300 C$^o$ and 400 C$^o$ to examine the annealing effect on the optical and electrical properties of the films by using thermal furnace.

The resulting vapors passed through the fan with controlled speed of rotation placed above the ZnS target and deposited on the glass

Substrates which covering the top hole of the evaporation system horizontally. The evaporation system can be shown in figure 1, which explains the mechanism of evaporation and precipitation.

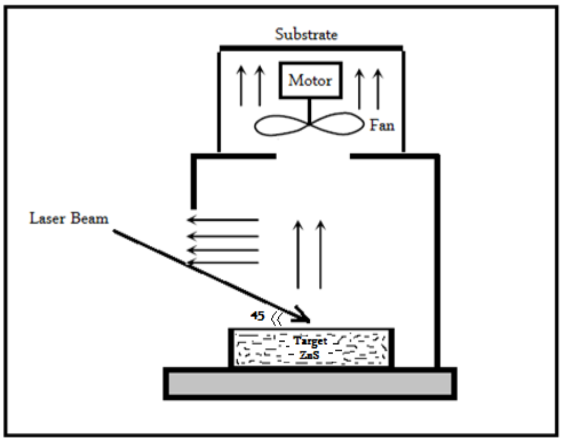


**Fig.(1):** System of Evaporation and Precipitation

Before perform the evaporation process, $CO_2$ laser was calibrated in addition to measure the fan speeds using a flasher process. All evaporation process was done without heating the substrates with normal atmospheric pressure.

The process of preparing the system has been achieved by measuring the distance between the target, substrates and the fan using a simple ruler, from this measurement the most suitable values are:

$Z_1$ = 75 mm (distance between the target and substrates) $Z_2$ = 34 mm (distance between the target and the fan)
The evaporation conditions of the system such as: laser power, evaporation time and the speed of the fan has been assigned.

## Experimental Measurement

The optical transmission spectra of the deposited thin films were measured by UV/VIS spectrophotomitric (Shimadzo, 1650PC, Japan) with (1cm) matched quartz cell, the optical properties where calculated as a function of the wavelength in the range (200-1200) nm from equations (1) to (4).

The electrical properties of the ZnS films such as current voltage characteristics and sheet resistance properties was measured using two point probe method as shown in figure 2.

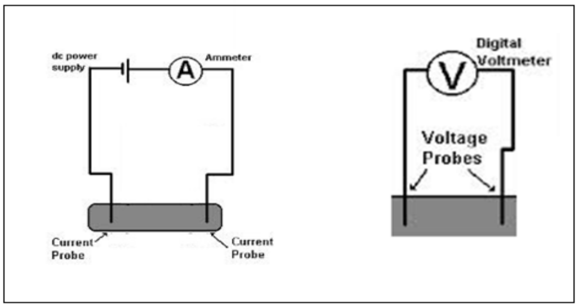


**Fig.(2):** Two Point Probe Method

## Results and Discussion

The optical properties of ZnS thin films which deposited on glass substrates and annealed at different temperature were measured from the transmission and absorption measurements in the range of (200-1200) nm.

The Transmission spectra of ZnS thin films that prepared at different annealing temperature are shown in figure 3; this figure shows that the tranmittance of the ZnS thin films increased as annealing temperature increased.

All ZnS thin films show that a high transmittance in the visible and near- infrared region and low transmittance in the ultraviolet region, because of the high optical transmission of ZnS thin films in the visible and near-infrared region , These results obtained compare favourably with high transmittance (60 – 99%) in the visible and near infrared region obtained by [15] and 96% obtained by [16] so ZnS have a significant role in photovoltaic and optoelectronic devices as a window layer.

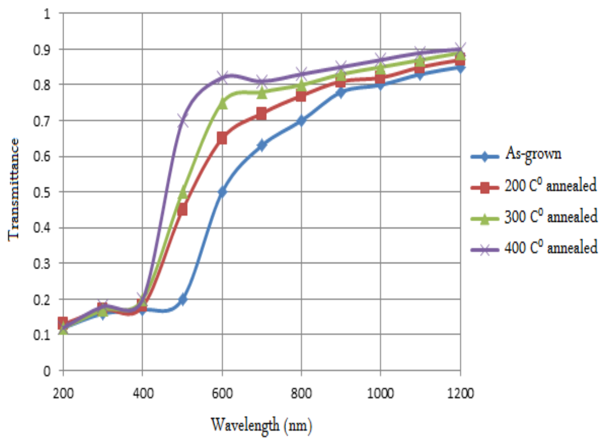


**Fig.(3):** Transmittance of ZnS thin films as a function of wavelength for different annealing temperatures

Figure 4 shows the absorbance of ZnS thin films at different temperatures. This figure shows that all samples have good absorbance in the ultraviolet regions and low absorbance in near-infrared regions. While in the visible regions, it absorbed slightly .This make the material to be useful in several coating process. This figure also shows that the absorbance of the ZnS thin films will decreased when the temperature of annealing will be increased. The result obtained by [15] and [17] on the optical absorbance of ZnS thin films for wavelength in the infrared region showed that ZnS is practically non-absorbing in these regions which compares favorably with the result obtained in this present work. Similar behavior was observed by [18].

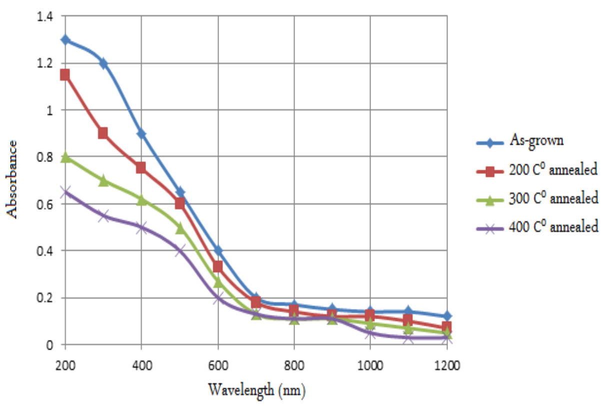


**Fig.(4):** Absorbance of ZnS thin films as a function of wavelength for different annealing temperatures

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

$$R + T + A = 1 \qquad (1)$$

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. This figure shows that there is a rapid reduction will appear in the range of (310-500) nm that mean the absorption of the film will be very little amount at the photon energy less than the value of the energy gap ( hυ< Eg) ,while there is a small change in the values of reflectance for all samples in the range of ( 450-1000 )nm ,this results is compare favorably with [19].

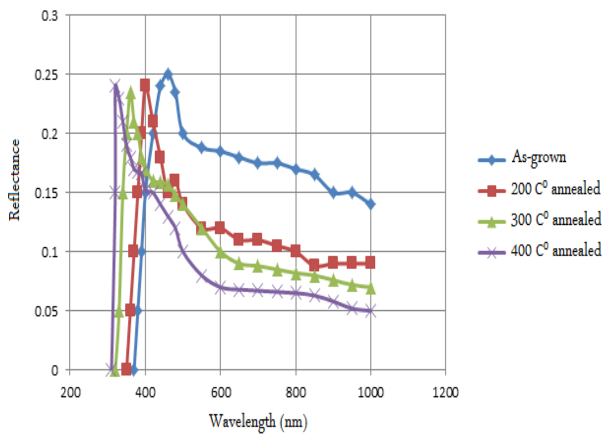


**Fig.(5):** Reflectance of ZnS thin films as a function of wavelength for different annealing temperatures

The energy bandgaps, Eg, were determined from the linear part of the optical absorption spectral. To determine the energy bandgap, $(\alpha h\upsilon)^2$ will be plotted against hυ and from the intercept of the straight-line portion of $(\alpha h\upsilon)^2$ against hυ energy gap was determined as shown in figure 6. From this figure the values of the energy bandgap of ZnS thin films has a value of 3.7 (eV) of the as-grown thin film at room temperature, while the films were annealed at 200C°, 300 C° and 400C° showed that the energy bandgaps have a values of 3.6 (eV) , 3.4 (eV) and 3.3 (eV) respectively. The energy band gaps ranging from (3.3-3.7) eV obtained in this work compare favorably with (3.73-3.57) eV obtained by [20], (3.51-3.84) eV obtained by [15], 3.68eV obtained by [21] and 3.5eV by [22]. It could be observed that for each annealing temperature, the optical band gap was decreasing with increasing annealing temperature as shown in figure 7.

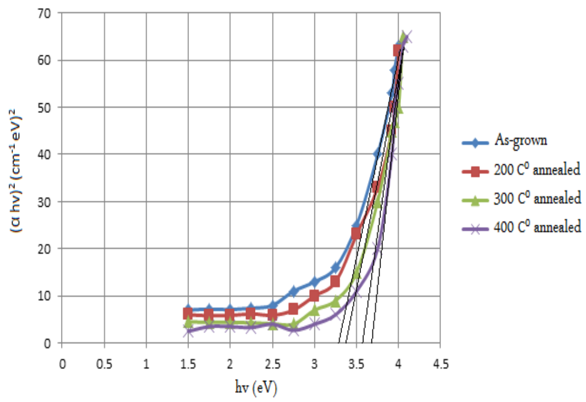


**Fig.(6):** Optical Spectral of ZnS thin Films for different annealing temperature

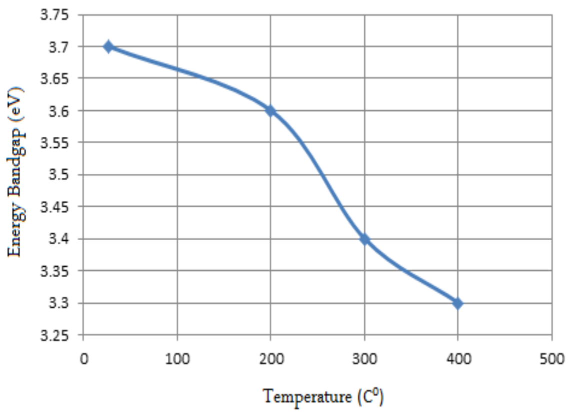


**Fig.(7):** Energy bandgap of ZnS thin film as a function of temperature.

The absorption coefficient α of ZnS film was determined from the absorbance measurements and calculated using the following relation;

$$\alpha = 2.303A/t \qquad (2)$$

where (t) is the thickness of the film.

Figure 8 shows the absorption coefficient as a function of the photon energy for the annealed ZnS films; the absorption coefficient (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 different annealing temperatures. This figure also shows that the absorption coefficient of the ZnS thin films will decreased when the temperature of annealing will be increased, this results is compare favorably with [19].

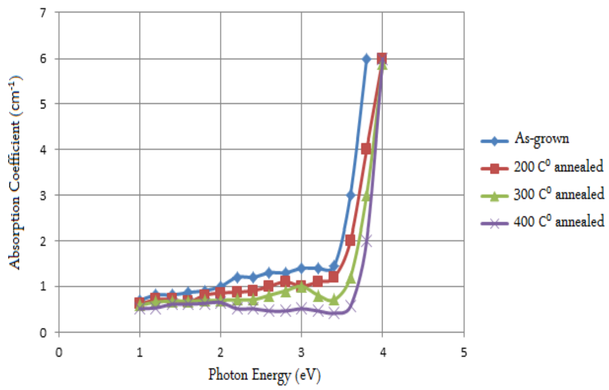


**Fig.(8):** Absorption coefficient of ZnS thin films as a function of photon energy for different annealing temperature.

The extinction coefficient (k) can be determined from the absorbance measurements as a function of photon energy as shown in figure 9. It can be calculated by using the following equation:

$$k = \alpha \lambda / 4\pi \quad (3)$$

where $\lambda$ is the wavelength.

Figure 9 shows there is a little increased in the extinction coefficient in the range (200-800) nm**,** then the rapid increase appeared within the range (800-1000) nm, and it was decreases with increasing the annealing temperature. The increased values of extinction coefficient in the ultraviolet and visible region is due to the high absorbance of ZnS thin films in that regions.

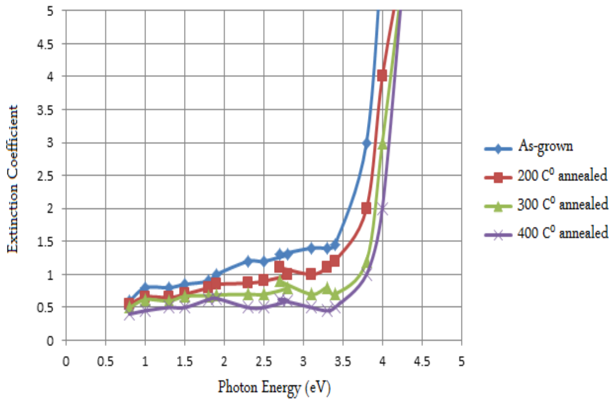


**Fig.(9):** Extinction coefficient of ZnS thin films as a function of photon energy for different annealing temperature

The refractive indices of the ZnS thin films at various temperatures were determined using Moss rule:

$$n^4 \, Eg = 77 \quad (4)$$

where n is the refractive index, Eg is the energy band gap. Figure 10 shows that the ZnS films has a refractive index of 2.19 for film grown at room temperature, 2.18 for film annealed at 200C°, 2.15 for film annealed at 300C° and 2.13 for film annealed at 400C°, respectively. The reported value of the refractive index in the visible region is 2.35 obtained by [23, 24]. The I-V characteristics for as-grown and annealed ZnS thin films at 200 C°, 300 C° and 400 C° were shown in Figures (11 to 14). Current of (4.2 x $10^{-9}$ A) was recorded for as-grown film, (3 x $10^{-9}$ A) for 200C° annealed ZnS film, (4 x $10^{-10}$ A) for 300C° annealed film and (2.1 x $10^{-10}$ A) for 400C° annealed ZnS film. It was found that the current values decreased with increase the annealing temperature. Therefore the annealed films were more resistance than as-grown films. These values of current compares favorably with the result obtained by [25]. Current of 3.1x $10^{-9}$A was recorded for as-grown film, 1.7x$10^{9}$A for 373K annealed ZnS film, 3.02x$10^{-10}$A for 423K annealed film, 2.26x$10^{-10}$A for 473K annealed ZnS film and 4.71x$10^{-11}$A for 523K annealed ZnS film. This could be explaining by the presence of elemental Zn in the as-grown film. The as-grown film was more conductive than the annealed films due to high current value possessed by the sample. The average voltage measured for all samples are (8V).

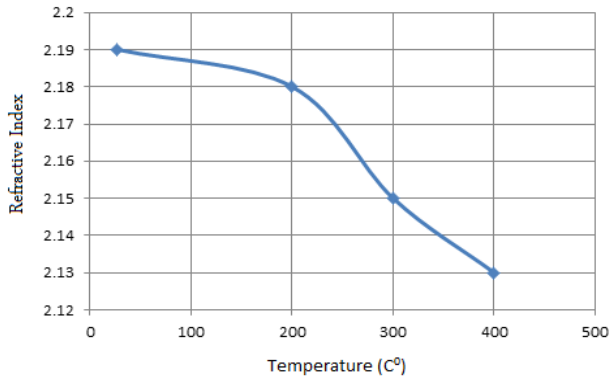


**Fig.(10):** Refractive index of ZnS thin film as a function of temperature

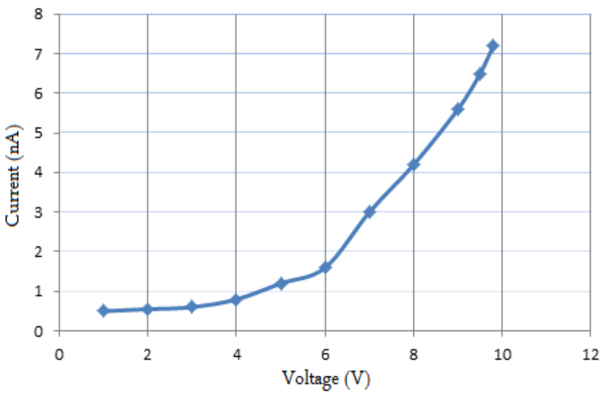


**Fig.(11):** The I-V characteristics for as-grown ZnS thin films

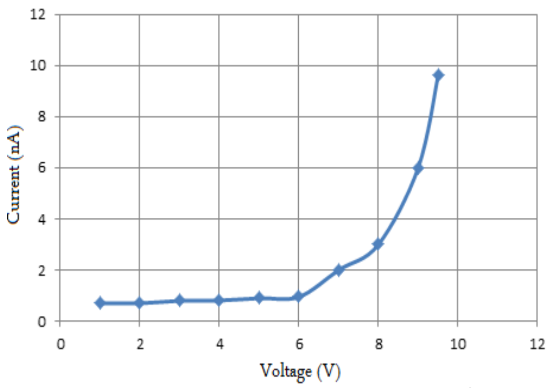


**Fig.(12):** The I-V characteristics of 200C° annealed ZnS thin films

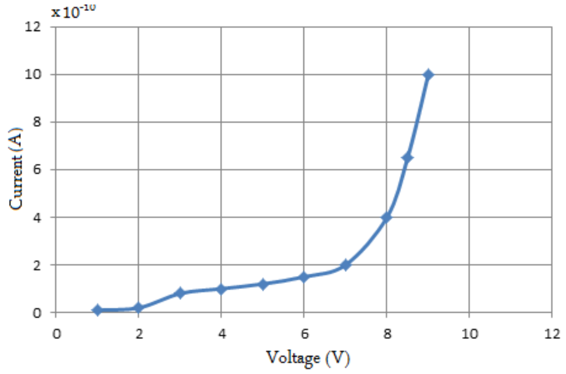


**Fig.(13):** The I-V characteristics of 300C° annealed ZnS thin films

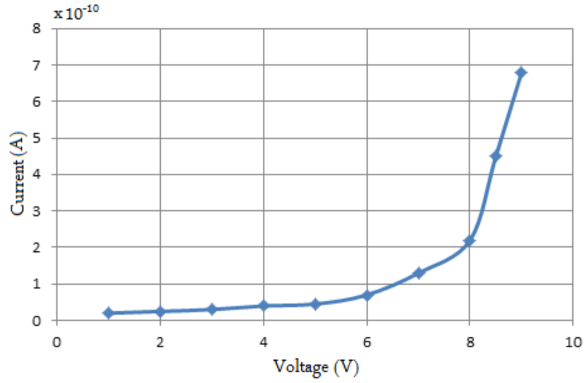


**Fig.(14):** The I-V characteristics of 400C° annealed ZnS thin films

The sheet resistance was determined using the following equation:

$$R_s = \frac{\pi}{\ln 2}\,\frac{V}{I} \qquad (5)$$

Where Rs is the sheet resistance, V is the voltage and I is the current.

$K = \frac{\pi}{\ln 2} = 4.53$ , where k is a geometric factor.

The values of the sheet resistance as a function of temperature can be shown in figure 15. It shows that the sheet resistance increases when the annealing temperature increases, this results is compare favorably with [25].

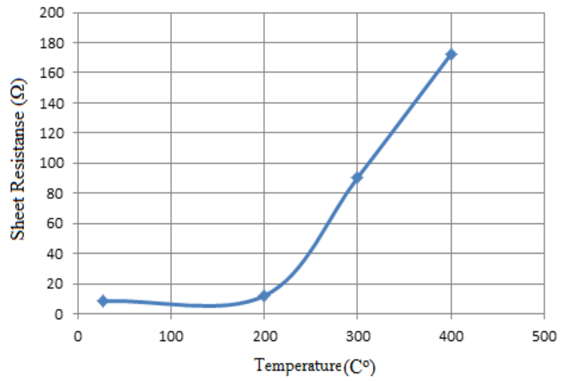


**Fig.(15):** Sheet resistance of ZnS thin film as a function of temperature

## Conclusion

Zinc sulfide thin films were successfully deposited onto glass substrates by using a developed laser deposition technique. From the results of the prepared films and measurements, it was observed that the prepared films have wide direct energy gap, the estimated value of the energy gap is in good agreement with the recent reported value. The wide band gap makes these films good material for optoelectronic devices. Increasing the value of annealing temperature will increase the value of transmittance and sheet resistance of prepared films and decrease the value of absorption coefficient, refractive index and current. The results obtained were in agreement with the literature.

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## دراسة تأثير التلدين على الخواص البصرية والكهربائية لأغشية كبريتيد الزنك المحضرة باستخدام تقنية الترسيب بليزر ثنائي اوكسيد الكاربون

**ليث مخلص عبدالجبار**

كلية دجلة الجامعة ، بغداد ، العراق

**الخلاصة :** في هذا البحث تم ترسيب اغشية رقيقة من مادة كبريتيد الزنك بأستخدام تقنية الترسيب بالليزر المطورة على ركائز من الزجاج بدرجات حرارة مختلفة. تم استخدام هذه التقنية المطورة للحصول على اغشية رقيقة ومتجانسة من مادة كبريتيد الزنك وذلك بتبخير هذه المادة التي تعتبر من اشباه الموصلات المهمة باستخدام ليزر ثنائي اوكسيد الكاربون المستمر مع مروحة بسيطة لضمان الحصول على اغشية متجانسة.تم تلدين الاغشية الرقيقة من مادة كبريتيد الزنك في الفراغ بدرجات حرارة مختلفة (200 ,300 ,400) درجة سيليزية ولمدة 20 دقيقة . وقد تم دراسة الخواص البصرية للاغشية المحضرة مثل الامتصاصية , والنفاذية , الانعكاسية ,فجوة الطاقة , معامل الامتصاص والانكسار والخمود. من هذه القياسات تم حساب فجوة الطاقة لمادة كبريتيد الزنك الغير ملدن والملدن بدرجات حرارة (200 ,300 ,400) درجة سيليزية وقد وجد قيمتها (3.7 ,3.6 , 3.4 , 3.3)الكترون فولت على التوالي , حيث وجد نقصان بقيمة فجوة الطاقة مع زيادة درجة حرارة التلدين.تم استخدام طريقة المجسات لقياس ودراسة الخواص الكهربائية لاغشية كبريتيد الزنك مثل خصائص التيار- الفولتية وخواص المقاومة .وجد من هذه القياسات نقصان بقيمة التيار مع زيادة درجة حرارة التلدين لذلك الاغشية الملدنة تمتلك مقاومة اعلى من الغشاء الغير ملدن.