Preparation and Characterization Study of ZnS Thin Films with Different Substrate Temperatures

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ABSTRACT

Zinc sulfide (ZnS) thin films were deposited on a glass and n-type Silicon wafer substrates at temperature range from 50 - 200 C^{o} using pulsed laser deposition (PLD) technique. The structural, morphological, optical and electrical properties of the films have been investigated. The XRD analyses indicate that ZnS films have zinc blende structures with plane (111) preferential orientation, whereas the diffraction patterns sharpen with the increase in substrate temperatures. The Atomic Force Microscopy (AFM) Images shows the particle size and surface roughness of the deposited ZnS thin film at substrate temperature 50 and 150 C^{o} were about 62.90nm, 74.68nm respectively. Also we noticed that the surface roughness is increased at substrate temperature 150 C^{o} compared with temperature 50 C^{o}. At 200 C^{o} the formed films exhibit a good optical property with 80% transmittance in the visible region. The electrical properties confirmed that they depend strongly on the bias voltage and the amount of current produced by a photovoltaic device which is directly related to the number of photons absorbed. *C-V* results demonstrated that the fabricated heterojunction is of abrupt type.

Keywords: ZnS films; pulsed laser deposition; morphological properties; electrical properties.

تحضير وتشخيص دراسة اختلاف درجات حرارة قاعدة الاساس على اغشية كبريتيد الزنك الرقيقة

الخلاصة:

تم ترسيب أغشية مادة كبريتيد الخارصين ZnS الرقيقة على قواعد من الزجاج وشرائح سليكونية من نـوع n-type بإستخدام تقنية الترسيب بالليزر النبضـي (PLD). التغير في درجات الحرارة كـان ضمن المـدى (٥٠-٢٠٠م^{0}) الخواص التركيبية وتركيب السطح والبصرية وكذلك الكهربائية تم دراستها والتحقق منها مع تغير درجات الحرارة. من تحليلات (XRD) تبين ان هذه الاغشية تمتلك تراكيب من خليط الزنك ذات توجه عالي عند المستوى (١١١) وذات انماط حيود حادة تزداد مع زيادة درجة الحرارة. اما صور تركيب السطح (AFM) الموضحة فقد بينت ان حجم الجسيم لأغشية ZnS المرسبة بطريقة (PLD) عند درجة حرارة ٥٠م^{o} و١٥٠م^{o} كانت ٦٢.٩ نانومترو٧٤.٦نانومتر على التوالي. وخشونة السطح كانت اكبر منه عند درجة ٥٠م^{o}. الأغشية المرسبة عند ٢٠٠م^{o} كانت ذات خصائص بصرية جيدة مع نفاذية عالية نسبيا ٨٠% ضمن المنطقة المرئية. لوحظ ان الخواص الكهربائية للأغشية المتكونة تعتمد بشدة على فولتية الانحياز وكمية التيار الناتج الذي يرتبط مباشرة بعدد الفوتونات الممتصة. نتائج (C-V) اثبتت ان الاغشية من النوع الحاد.

INTRODUCTION:

Zinc sulphide (ZnS) is chalcogenide II-VI semiconductor material with wide direct band gap. Among other chalcogenide semiconductors it has the highest band gap of 3.70 eV at 300 K. These semiconductors (PbS, ZnS, CdS, CuS, Bi_2S_3) have attracted the attention of researchers in the recent times due to their special properties and potential uses in photovoltaic and optoelectronic devices [1-3].

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ZnS has a large band gap semiconductor. Consequently, it is a potentially important material to be used as an antireflection coating for heterojunction solar cells. It is an important material used for fabrication detection device, in the region of visible and near ultra violet light [4].

ZnS thin films are promising materials for their use in various device applications. In optoelectronic devices, it can be used as light emitting diode [5] in the blue to ultraviolet spectral region due to large direct band gap [6-7].

There are different depositions techniques have been used to prepare ZnS thin films, such as RF sputtering [8], pulsed laser deposition, chemical vapor deposition, electron- beam deposition, thermal evaporation, photochemical and chemical bath deposition [9-10]. In recent years ZnS attracted much attention because the properties in nano form differ significantly from those of their bulk counter parts [11].

In present work, ZnS thin films have been deposited by using pulsed laser deposition. The effects of various substrate temperatures on the structural, electrical, and optical properties of the films have been studied.

Materials and Methods:

Thin films of ZnS are prepared by using the pulsed laser deposition technique (PLD). The chamber was evacuated to a base pressure of (10^{-3} mbar) at different substrate temperature 50, 100, 150, 200 ºC. Q-switched second harmonic generation (SHG), Nd: YAG laser with a wavelength of 532 nm with pule duration (6 ns) and output energy (1000 mJ) with a fixed number of pulses (26 pulses) was used; the focal length for the lens was about 13cm with a repetition rate of 1 Hz. The distance between the target and the substrate was kept at 2.5 cm.
ZnS films were deposited onto a glass and n-tpye silicon wafer substrate by pulsed laser deposition inside evacuated chamber at a pressure of 3.0×10^{-2} Torr. The substrate temperature was varied from 50 C^o to 200 C^o. After deposition, the structural, morphological, optical and electrical properties of ZnS thin films were characterized with X-ray diffraction by XRD, atomic force microscope by AFM, UV-VIS spectrophotometer.

Results and discussions

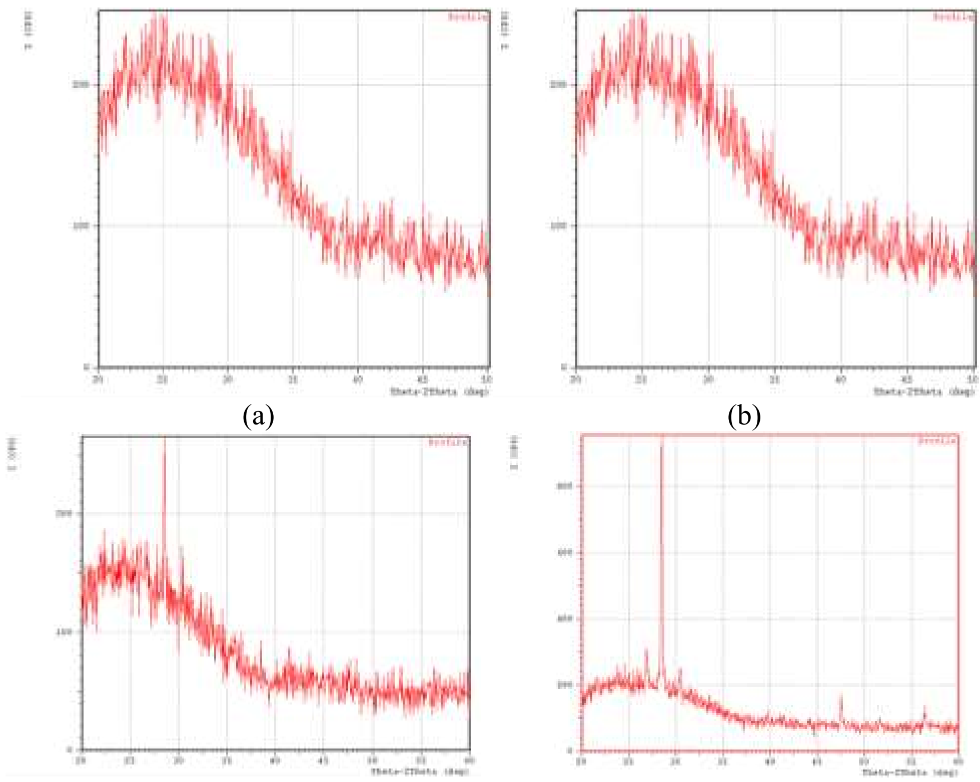
Structure properties

Fig. (1) Shows XRD patterns of the prepared thin films at a substrate temperatures range from 50 to 200 C^o. From Fig. (1a,b), it has been noticed that the amorphous structure of the thin film which did not exhibit any peak (i.e. at substrate temperature 50, 100 ºC respectively). As the substrate temperature increased to 150 C^o a crystalline phase (zinc blende structure) was appeared with a preferred orientation had (111) plane as shown in Fig. (1c). At substrate temperature 200 ºC the XRD exhibit a sharpened pattern with three distinguished peaks corresponding to diffraction of (111), (220), and (311) planes of the cubic phase and the growth rate was increased too as shown in Fig. (1d).It was to be depending on substrate temperature [12-13].
The average nanocrystalline size was calculated using the Debye – Scherrer Formula. [14].

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad \text{….. (1)}$$

Where
λ is the X-ray wavelength. (Cu Kα radiation = 1.54056 A°), θ is the diffraction angle; β is the FWHM at the XRD peak at the diffraction angle θ.

The average crystalline size is calculated from x-ray line using (111) peak and eq. (1) to be about (22.8nm).



(a) (b)

(c) (d)

Figure (1) : XRD patterns of ZnS films grown at substrate temperatures (a) 50, (b) 100 (c) 150 and (d) 200C^{o}.

Morphological properties

The AFM analysis revealed that the estimated grain size of PLD deposited ZnS at substrate temperature 50 C^{o} and 150 C^{o} were about 62.90 nm and 74.68 nm, respectively. The surface roughness of the deposited thin film on substrate heated at 150 C^{o} greater than its value at 50 C^{o}. From Fig. (2), it has been noticed that the films formed at temperature 150 C^{o} become more uniform and dense with the increasing in substrate temperature.

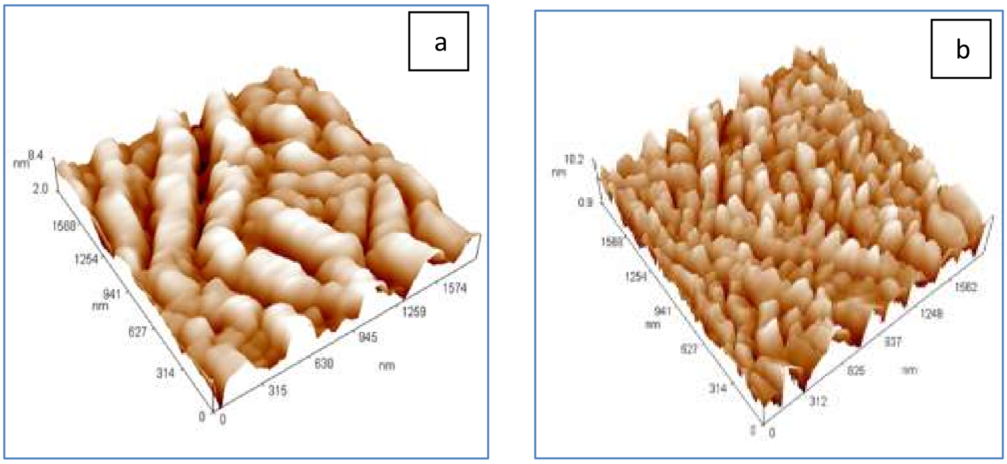


Figure (2) : AFM images of ZnS films deposited on glass substrate at substrate temperatures (a) 50 and (b)150 C^{o}.

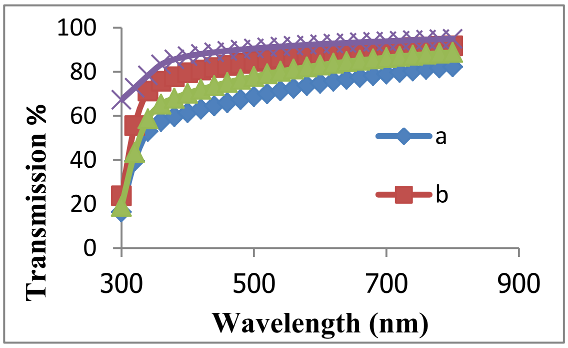
Consequently, it can be thought that an increase in substrate temperature implies an increase in film density and also, increase in grain size [15].

Table 1: morphological characterization of ZnS films

Substrate temperature (C°)	Roughness Average (nm)	Diameter Average (nm)
50	1.19	62.90
150	1.52	74.68

Optical properties

Fig. (3) Shows the transmission spectra of deposited ZnS thin films with different substrate temperature. It can be seen that at 200 C° the transmittance of the formed film is higher than the transmittance of the other films which was prepared at another temperature. This is due to the high degree of crystallinity, as shown in XRD result. Also this Figure indicates that the optical transmittance was increased as the substrate temperature increased.



Figure(3) : Transmission spectra of ZnS films on glass substrates with substrate temperature (a) 50 C°, (b)100 C°, (c)150 C°, (d) 200 C°.

Table (2) shows the measured energy band gap values. It is seen that the band gap was increased from 3.5 to 3.92 eV as the substrate temperature increased from 50 to 200C° which has a larger value than the typical value of the bulk ZnS (~3.6 eV) according to the quantum confinement effect [16].

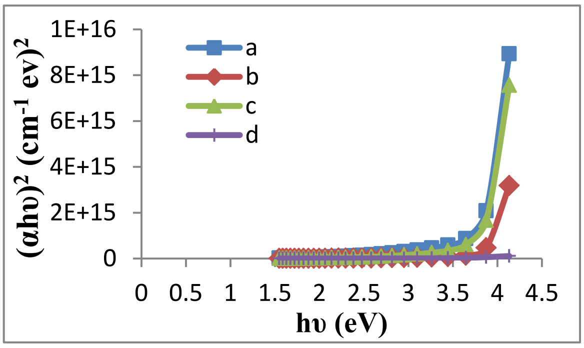


Figure (4) : Optical energy band gap for ZnS films at different substrate temperature of (a) 50 °C, (b) 100 °C, (c) 150 °C, (d) 200 °C.

Table (2): Measured energy gap of the ZnS thin films at various substrate temperature

substrate Temperature (°C)	Energy Gap (eV)
50	3.5
100	3.90
150	3.90
200	3.92

Electrical properties

Fig. (5). shows I_d-V characteristics for ZnS heterojunction prepared at various substrates temperatures (50, 100, 150 and 200°C) at forward and reverse bias voltages. In general, the forward dark current is generated due to the flow of majority of carriers and the applied voltage injects majority of carriers which lead to a decrease in the built - in potential, as well as the width of the depletion layer. Also we can observe from this figure that the value of the current increases with the increase in substrate temperature of ZnS films which is attributed to eliminating of defects and dislocations that have an effect on the mobility of charge carriers which act as active recombination centers consequently, current flow across the junction will be increased.

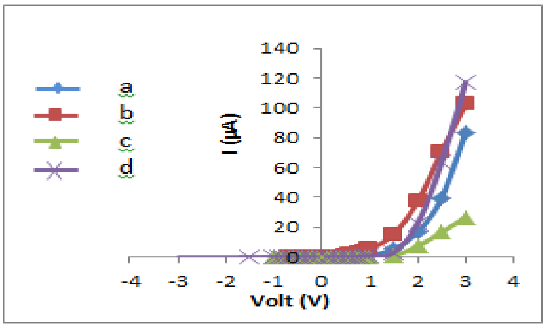


Figure (5): I-V characteristics for ZnS heterojunction prepared at various substrate temperatures (a) 50, (b) 100, (c) 150 (d) 200C°

Fig. (6) shows that the photocurrent density increases with increasing of substrate temperature, and this is attributed to the increasing in the grain size, reducing the grain boundaries and improvement of structure, which leads to an increase in the mobility, increase the photocurrent density as well as the depletion width which leads to an increase in the creation of electron-hole pairs [17].

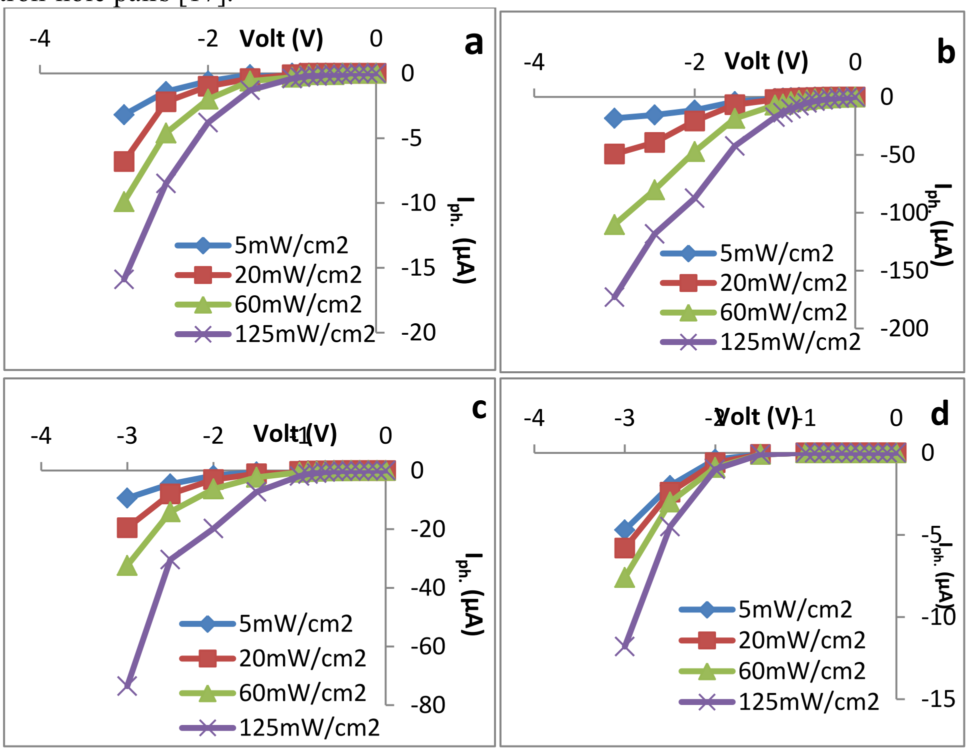
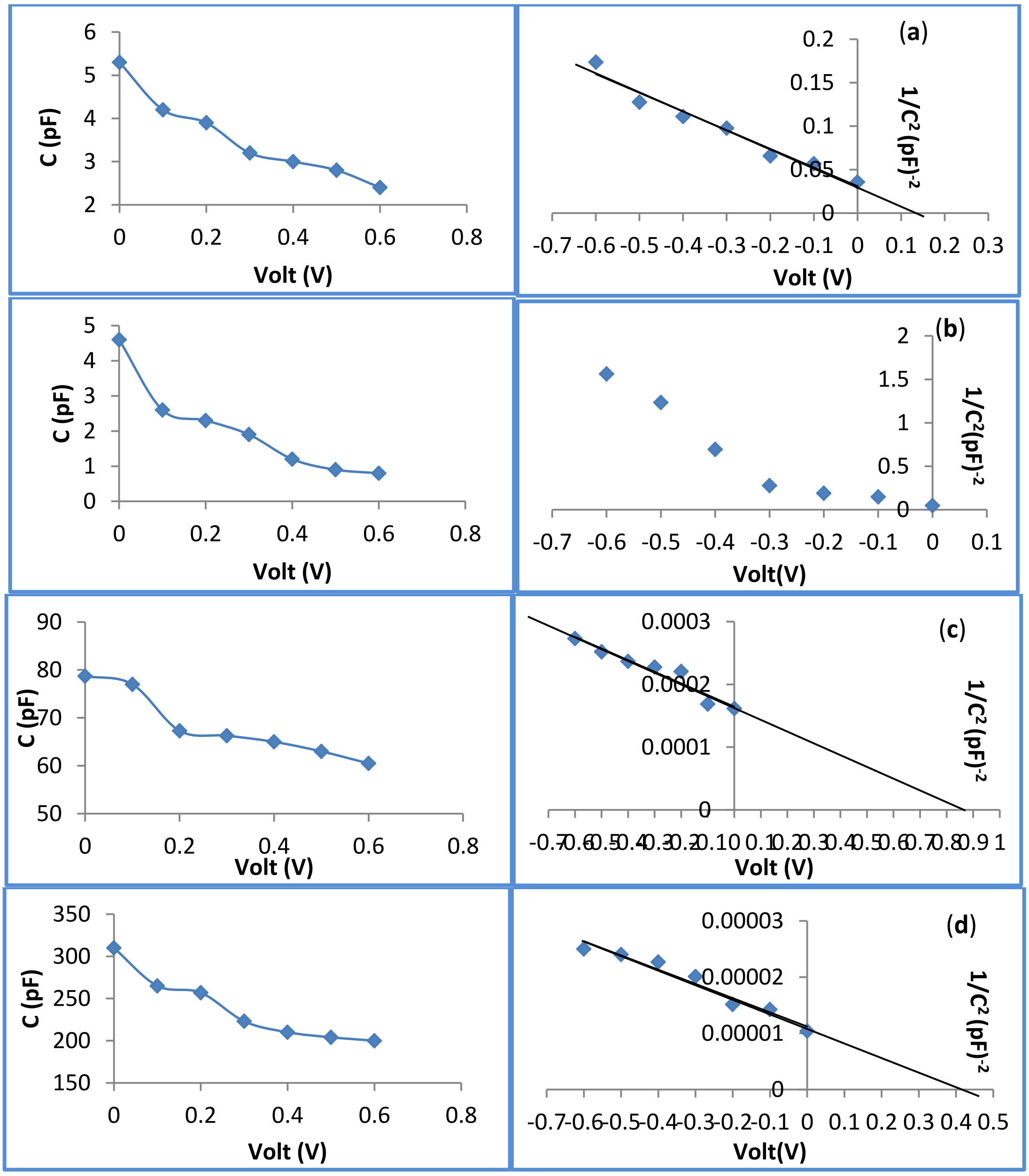


Figure (6): I_{ph}-V characteristics for ZnS/Si heterojunction at reverse bias voltage at various substrate temperatures (a) 50C° (b) 100C° (c) 150C° (d) 200 C°

Fig (7) gives capacitance -voltage characteristics and square of inverse capacitance which is plotted against applied reverse bias voltage ($1/C^2$-V) for ZnS heterojunction prepared at different substrate temperature.



Figure(7): The variation of $1/C^2$ versus reverse bias voltage for ZnS/Si heterojunction at different treatment temperatures (a) 50 C° (b) 100C° (c) 150C° (d) 200 C°

Table (3) shows the obtained results from the measurement of ZnS films. Results show that the device is "abrupt" which is confirmed by the relation between $1/C^2$ and reverse bias voltage, which seemed to be linear.

Table (3): Values of W, V_{bi} and N_e for ZnS/Si heterojunction with different substrate temperatures.

Substrate Temperature (°C)	V_{bi} $(Volt)$	N_e (cm^{-3})	W (μm)
50	0.15	1.45×10^{8}	0.78
100	-	-	-
150	0.9	1.66×10^{13}	3.5
200	0.46	1.15×10^{14}	1.35

CONCLUSION

ZnS film properties are influenced most strongly by substrate temperature. It affects not only sample morphology but structural, optical and electrical properties.

At 200°C the formed films exhibit good optical properties with a relatively high transmittance reach up to 80% in the visible region.

The effect of substrate temperature on ZnS films preparation is very promising for photovoltaic application.

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