



## Study the structural and optical properties of nanostructure ZnS thin film prepared by Radio frequency (RF) magnetron sputtering technique

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### ABSTRACT

Zinc sulfide (ZnS) thin films were deposited on glass substrate with different thickness by radiofrequency (RF) magnetron sputtering technique, and deals with effect of thickness on the optical and structural properties. The structure, surface morphology and optical properties are investigated by x-ray diffraction (XRD), atomic forces microscopy (AFM), scanning electron microscopy, and UV-visible spectrophotometer. The result of XRD show that ZnS thin film exhibited cubic structure with strong peaks at (111) as highly preferential orientation. The maximum particle size of films was found to be 14.4 at thickness 868nm. SEM image show that the shape of grain is like spherical. The result of AFM shows that the surface roughness decrease with increasing in film thickness from (6.19 to 1.45)nm. The result of UV-visible suggests that transmittance increasing with increases in film thickness, the value maximum of ZnS transmission was 87.82% at thickness 868nm, can be very much useful in the field of solar cell and optical sensor.

### 1- Introduction

Zinc sulfide (ZnS) is semi conducts material belong to group II-VI, which has broad optical band gap of 3.7eV [1, 2]. The presence of polar surface, good thermal stability, high transmittance in the visible region, high index of refraction and excellent transport [3]. Therefore, ZnS was as a result of growing interest owing to important application in electroluminescent, light emitting diodes, bio sensors and solar cells [4]. The crystal structure of ZnS has two types: cubic zinc blende phase and hexagonal wurtzite phase depending on synthesis condition. Often, the stable structure of ZnS at room temperature is cubic Zinc blende [5]. There are many methods used to prepare of Nano structured ZnS. These are sol - gel synthesis[6], chemical vapor deposition[7], pulse laser deposition[2], RF magnetrons sputtering [8].

A Radio frequency magnetron sputtering sustained only by an external RF source at 13.56MHz having voltage waveform and weak temporal variation of the electron density close to the target material except for the region trapped deeply via magnetic field. RF magnetron sputtering method has some advantages such as high film growth rate, easier controllability of

the deposition parameters and compatibility with sputtering deposition of absorber and window layer [8]. In this paper, the effect of thickness on structural and optical properties of ZnS prepared by RF magnetron sputtering technique has been studied.

### 2 - Experimental

Radio frequency (RF) magnetron sputtering method is used to synthesis ZnS thin film on glass substrate, were approximately 20 g of ZnS (99-9% purity) placed in a mold for compressed by the hydraulic piston with pressure (8-10) tons to prepare target 5cm diameter and thickness 3mm then sintered it for 2 hrs. at temperature 200°C. The target is mounted in the magnetron gun, then close the door of deposition chamber and evacuated to final pressure ( $7.9 \times 10^{-5}$  torr) by Dry scroll pump and then, the pressure up to ( $2.3 \times 10^{-2}$  torr) by introduction high purity Ar gas (99.99% purity) into deposition chamber [8]. The RF power was 100 W. The sputtering time was about (1, 2, and 3) hrs during sputtering process; the substrate temperature was maintained at 100°C.

It is important to wash the glass slides (76mm  $\times$  25mm) with water and cleaning powder to remove any contaminant that might be on the substrate

surface and then the glass slides put in clean beaker containing distilled water and washing for (15) min. Immerse the glass slides in a beaker containing ethanol with purity (99.9%) to removal any contaminant (oil) for 15 min and then put in a beaker containing acetone for (15) min. Finally, the substrate rinsed by deionized water and then dried by heating. The structural characterization of thin film was determined by X-ray diffraction (XRD), using Braker D2 PH ASER X-ray diffractometer with Cu-ka radiation ( $\lambda=1.5406 \text{ \AA}$ ) in  $2\theta$  range from  $20^\circ$ - $80^\circ$ . The surface morphological of film investigation by (AA 3000 scanning probe microscope tib NSC 35/AIBS). The shape and particle size were carried out by scanning electron microscopy (SEM) using Hitachi (S-4160) with magnification 100KX. The optical measurements of the thin films were carried out by using (UV-1650PC Shimadzu software 1800 UV-Visible recording Spectrophotometer) in the wavelength range from 200 to 1100 nm at room temperature. Film thickness was measured by using reflectance method.

### 3- The Results and discussion

#### 3-1 Structural Properties:

The XRD pattern of as deposited ZnS film on glass substrate is illustrated in figure (1). The XRD pattern present that the amorphous structure for as- deposited ZnS film with thickness (400nm) deposited for one hour, then convert to crystalline structure at thickness (733 and 868nm) deposited for (2 and 3) hours. It is noted that thin films deposited at thickness (733 and 868) nm have only one peak at  $28.6^\circ$  with cubic crystal structure, which indicates that the films are distinctly single crystalline with preferred growth direction along (111) plane, these results are in agreement with [8,9]. The diffraction peak is in good agreement with this given in card (JCPDS file No: 80-0020). The increasing in thickness of thin film will enhancement crystal structured by increasing the planes intensity as shown in figure (1), this results is in agreement with behavior the previous results [10]. From full width at half maxima (FWHM) of X-ray diffraction peak is calculated the crystalline size by Debye – sheerer formula [10].

$$D = \frac{k\lambda}{\beta \cos \theta} \dots \dots \dots (1)$$

Where K= is a constant ( $K=0.89$ ),  $\lambda$  is wave length of X-ray ( $1.542 \text{ \AA}$ ), and  $\beta$  is the full width at half maximum in radians of XRD peak. It is observed that the crystalline size of 11.9, and 14.4 nm at thickness (733, and 868nm) respectively, this attributed to increasing of deposition rate, this result agreement [11].

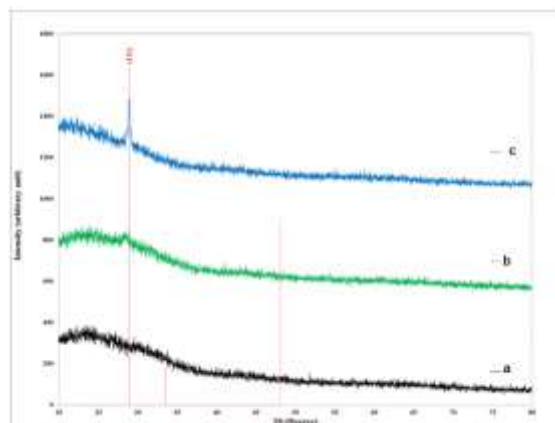


Fig. 1: XRD pattern of ZnS thin films with different thickness (a-400, b-733 and c- 868)

#### 3-2 scanning electronic microscopy

Figure (2) scanning electronic microscopic (SEM) image, with magnification power 100000 X, to allow a review of detail growth mechanism of ZnS thin film, the image clearly exhibit small grains having high uniform, dense and homogenous, furthermore, we can see that thin film without crack, pinholes, and well substrate covered. The surface morphology of thin film has like spherical shape, and seems to be uniform distributed with grain diameter of (22.84 and 31.44, nm) as shown in table (1).

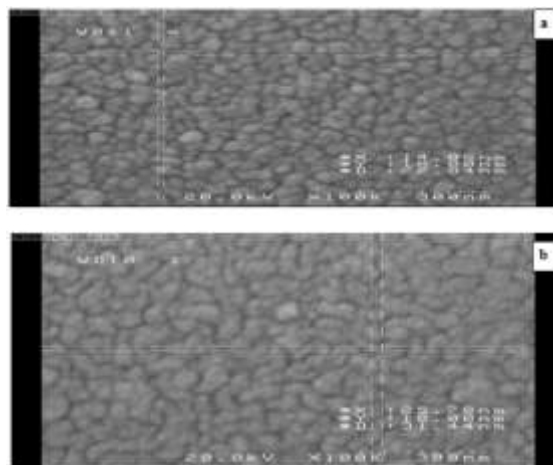


Fig. 2: The SEM image ZnS thin films with different thickness (a-733 and b-868 nm)

#### 3-3 Atomic force microscope

Figure (3) show the 3D –image for surface morphology and the granulite accumulation chart analyzed by atomic forces microscopic (AFM) of ZnS thin film. This image affirms that the film are homogeneity without voids .i.e. that the thin film of ZnS is highly dense structure and is deposited very well. It was observed from table (1) that the average diameter of grain size decrease then increased with increases in film thickness, also observed that surface roughness decrease with increases in film thickness; this is attributed to enhancement in crystallinity.

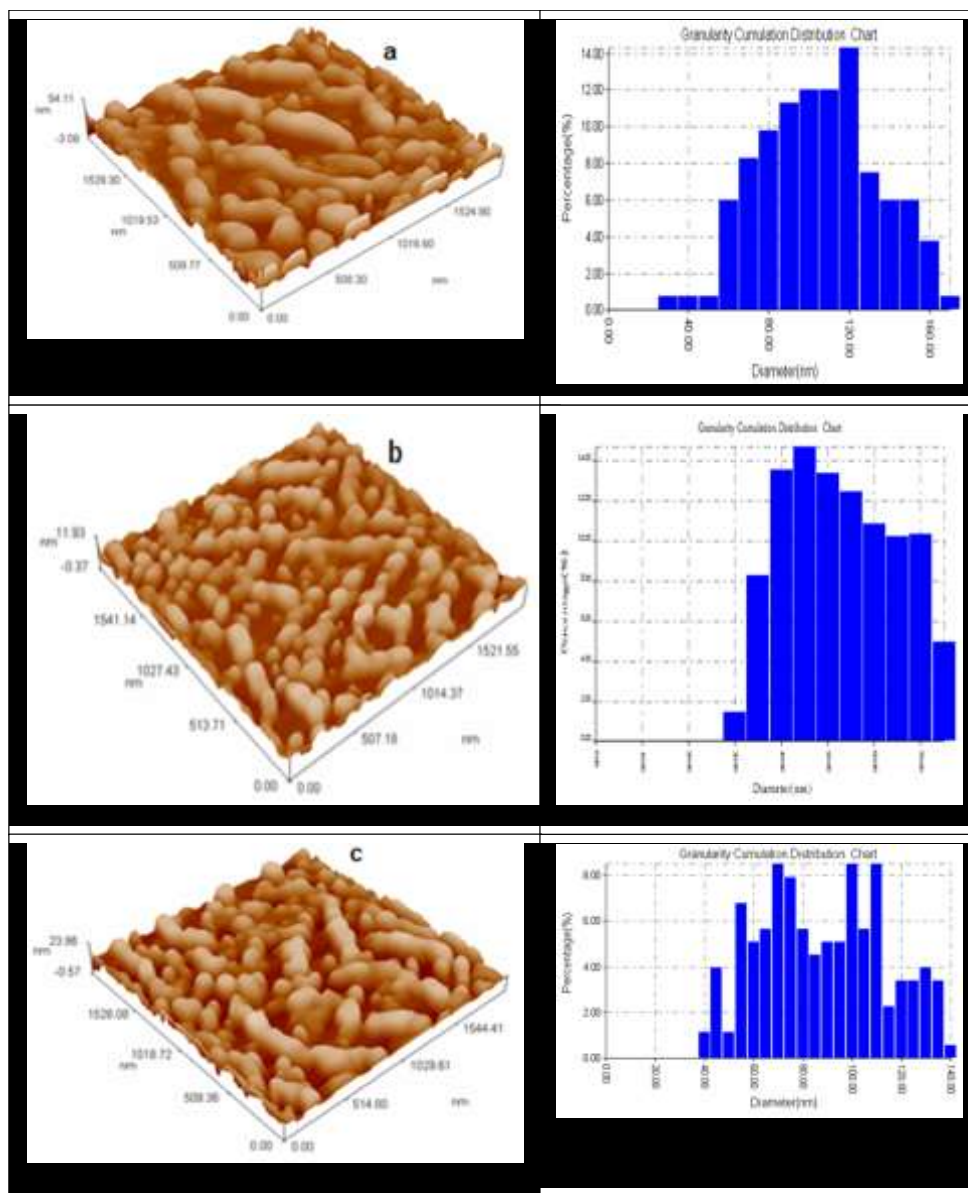


Fig. 3: Three dimensional AFM image and granularity accumulation distribution chart of ZnS thin films with different thickness (a-400, b-733 and c-868).

Table 1: Variation of grain size of ZnS from XRD, SEM, AFM at different thickness.

Deposited time (hrs)	Thickness (nm)	Crystallite size (nm) XRD	Grain size (nm) SEM	Grain size (nm) AFM	Roughness (nm)
1h	400	-	-	100.72	6.19
2h	733	11.9	22.84	50.48	2.85
3h	868	14.4	31.44	85.48	1.45

### 3-4 UV- Visible spectroscopy:

Optical transmittance for ZnS thin film is measured in the range incident light wave length (200-1100) nm. Figure (4) transmittance spectra of the deposited film on glass substrate. It can be seen that transmittance of the deposited ZnS films at thickness of 400, 733, and 868 nm are 64.43, 78.81, 87.82% in visible region respectively. These results are in agreement with the results published by [12].

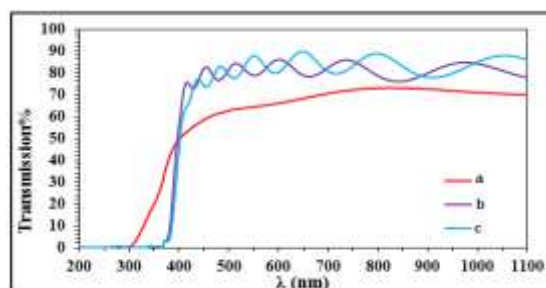


Fig. 4 : Variation of transmittance with wavelength of ZnS thin film with different thickness (a-400, b-733 and c-868 nm)



The absorption coefficient ( $\alpha$ ) defines the penetrate of wave length inside the thin film before it have been absorbed, it depends on semiconductor properties and on incident photon energy ( $h\nu$ ). It can be observed from figure (5) and table (2) that the absorption coefficient decreases with increase in film thickness from (21982 to 6494) $\text{cm}^{-1}$ . From figure (5) it is clear that the absorption edge for all films is observed to shift towards higher values of photon energy (shorter wavelengths) with decreases in film thickness.

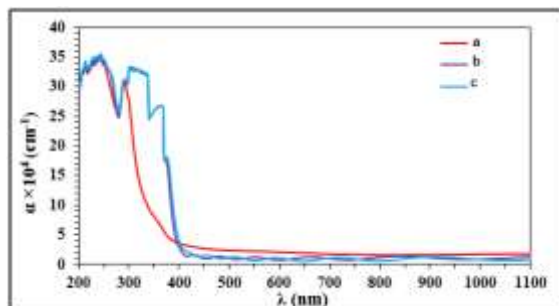


Fig. 5: absorption coefficient ( $\alpha$ ) versus. wavelength for ZnS thin film

The optical band gap is calculated by using the equation [13].

$$\alpha h\nu = B(h\nu - E_g^{\text{opt}})^r \dots \dots \dots 3$$

Where B is constant,  $E_g$  is band gap energy and  $r=1/2$  for direct allowed transition. The band gap value was determined from extrapolating straight of the plot  $(\alpha h\nu)^2$  versus the  $h\nu$  graph on the  $h\nu$ - axis. The linear part indicates that transition mode in this film is of direct nature. It can be seen that band gap values of the deposited ZnS films decreased from (3.9 to 3.18) eV with increases in film thickness from (400, to 868) nm as shown in figure (6) and table (2). These

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results are in agreement with previous behavior result [12].

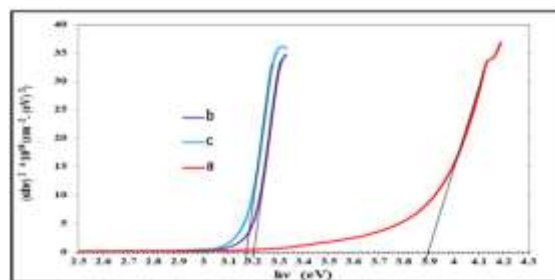


Fig. 6: Band gap of ZnS with different thickness (a-400, b-733 and c-868 nm)

Table 2: Variation of transmittance, absorption coefficient, and Band gap of ZnS with different thickness.

Time (hrs)	Thickness (nm)	T% ( $\lambda=550\text{nm}$ )	$\alpha$ (cm-1) ( $\lambda=550\text{nm}$ )	$E_g$ (eV)
1	400	64.43	21982	3.90
2	733	78.81	11907	3.20
3	868	87.82	6494	3.18

## Conclusions

ZnS thin film of thickness (400, 733, and 868)nm are deposited on glass substrate at temperature 100°C have been synthesis successfully by RF magnetron sputtering. Structural analysis by XRD pattern indicates that the ZnS Nano particles crystalline with cubic structure and were aligned perpendicular to the (111) plane. The AFM reveals that the surface roughness decreases with increasing film thickness. The ZnS film exhibited good optical properties, the percentage optical transmittance was observed to increases with increasing in film thickness, also band gap decreases with increases in film thickness, may be used in solar cell.

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## دراسة الخصائص التركيبية والبصرية لأغشية ZnS ذات التركيب النانوي والمحضرة بتقنية التريز

### الماكنتروني ذي التردد الراديوي

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### الملخص

تم ترسيب أغشية كبريتيد الخارصين على قواعد زجاجية بسماك مختلفة بواسطة تقنية التريز الماكنتروني ذي التردد الراديوي RF، ودراسة تأثير السمك على الخصائص التركيبية والبصرية. تم تشخيص التركيب البلوري وطبوغرافية سطح الغشاء والخواص البصرية، بواسطة حيود الأشعة السينية، ومجهر القوة الذرية، والمجهر الكتروني الماسح ومطياف UV-vis. بينت نتائج حيود الأشعة السينية أن الغشاء يمتلك تركيب مكعب وهناك قمة واضحة بالاتجاه (111). أعلى حجم للجسيمات كان مساويا إلى 14.4nm عند السمك 868nm. بينت صور SEM بأن الجسيمات شب كروية. نتائج AFM بينت بأن خشونة السطح تناقصت مع زيادة سمك الغشاء من (6.19 إلى 1.45) نانو متر. أوضحت نتائج UV-vis أن النفاذية تزداد مع زيادة السمك، أعلى قيمة للنفاذية كانت 87.82% عند السمك 868nm، مفيدة جدا في الخلايا الشمسية والمتحسسات البصرية.