Growth of Nanopartical Zinc Sulfide Films by Chemical Spray Pyrolysis Technique

Ali A. Yousif[*] Aseel A. Jasib[*]

[*]Department of Physics, College of Education, University of Al-Mustansiriyah, Baghdad, Iraq/ Email:

Abstract

In this study, nanopartical ZnS films have been successfully deposited on glass substrates by chemical spray pyrolysis (CSP) technique at substrate temperature of (400 ± 5^{O}C) and different thickness (75, 150, 225, 300, 375, 450 and 525 nm). The structural and surface morphological properties of these films have been investigated using XRD and AFM.

The XRD results showed that all films are polycrystalline in nature with cubic structure and preferred orientation along (111) plane. The crystallite size was calculated using Scherrer formula. The crystallite size of the samples was maximum (10.6nm) at thickness 375 nm, and it was minimum (8.4nm) at thickness 75 nm, prepared at the same films. AFM results showed homogenous and smooth Zinc Sulfide thin films. The average grain size, average roughness and root mean square (RMS) roughness for nanopartical ZnS films were estimated from AFM.

Key words: *Nanopartical, Zinc Sulfide (ZnS),* Surface Morphological, *Chemical Spray Pyrolysis.*

Introduction

Zinc sulfide (ZnS) is found in nature as zinc-blende (also called sphalerite or β-ZnS and with a cubic structure) and wurtzite (α-ZnS, which is a hexagonal structure). The names of these minerals are used to designate the corresponding crystal structures. It is a II–VI compound semiconductor material and is commercially used in solar cells [1], infrared windows [2], and phosphor materials by doping with transition or rare-earth metals [3,4]. There has been growing interest in developing techniques to prepare semiconductor ZnS thin films. ZnS thin films are produced using various techniques, including radio frequency (RF) magnetron sputtering [5], chemical vapor deposition (CVD) [6], solvothermal [7], chemical bath deposition [8] and chemical spray pyrolysis technique [9].

ZnS was found that zinc blend changed to wurtizt phase at or before sublimation temperature, which affirm that the last phase is the most stable structure at high temperature [10]. Both wurtzite and zinc blend are intrinsic, wide band gap semiconductors .The hexagonal form of ZnS has a band gap of about 3.91 eV but the cubic form has a band gap of about 3.54 eV at 300 Kelvin [11]. ZnS can be doped as either an n-type or a p-type semiconductor.

ZnS is a potentially important to be used for application in a wide range of optoelectronic devices such as antireflection coating for heterojunction solar cells. It is an important device material for the detection, emission, and modulation of visible and ultraviolet light [12]. In particular, ZnS is believed to be one of the most promising materials for blue light emitting laser diodes [13]. In this work nanopartical zinc sulfide thin films are prepared by chemical spray pyrolysis technique. The aim of this work is to preparing ZnS films and studying the effect of different thickness on the structure, and morphology properties.

Experiment

System used for fabricating thin films

Chemical spray pyrolysis method was employed in the present work, where in this method, thin films were prepared by spraying the solution on a hot glass substrate to a certain temperature, and the film could be then obtained by the chemical reaction on the hot substrate. However, in some application these thin films could have good properties, for example. It might be used in solar and sensor applications.

Preparing of the Spray Solution

The spraying solution which contains the materials necessary for fabrication of the ZnS film can be prepared by mixing zinc chloride $ZnCL_2$ and thiourea $CS(NH_2)_2$ as starting materials. The molar concentration of the solution should be equal to 0.1 mole/liter.

In order to prepare the solution of 0.1 molar concentrations from these two materials, 0.6814 grams weight of $ZnCL_2$ and 0.3806 grams weight of $CS(NH_2)_2$ are needed from each of them, melted in 100 ml of distilled water, according to the following equation:

Weight of the material (gm) =Volume (ml) × Molecular concentration (mol/l) × Molecular weight (gm/mol)…………… (1)

Finally, the two weights materials melted in (100ml) of distilled water to get the wanted solution (The spray solution).The solution then sprayed and deposited on a cleaned glass (400 ºC) substrate to get the finally ZnS thin films.

It is necessary to leave the glass substrate on the electrical heater for one hour at least after finishing the operation of spraying to complete its oxidation and crystalline growth process.

Thickness Measurements

In this work the experimental method of thickness measurement was used:

Optical interferometer method by (He – Ne) laser:

There are a many optical methods to measure the film thickness, these methods are based on the interference of the light within thin film. The film thickness measurements by optical interferometer method have been obtained. This method is based on interference of the light beam reflection from thin film surface and substrate bottom. He-Ne laser (0.632 µm) is used and the thickness is determined using the following formula: [14]

$$d = \frac{\Delta x}{x} \times \frac{\lambda}{2} \quad \text{..} (2)$$

Where x is the fringe width, Δx is the distance between two fringes and λ wavelengths of laser light. The film thickness from applying equation (2) is (75, 150, 225, 300, 375, 450 and 525 nm). The interference mode is formed as a result of the phase difference between the rays reflected from the back surface and the rays reflected from the front surface.

Structure and morphological measurements

X-Ray Diffraction

The structure of nanopartical ZnS thin films grown on glass substrates by Chemical spray pyrolysis method at T=(400)ºC were examined by X-ray diffractions using a(XR-DIFRACTOMETER/6000) type Shimadzu X-ray diffractometer system.

This system recorded the intensity as a function of Bragg's angle. The measurement conditions are as follows:

Target: CuK_α
Wavelength = 1.5406Å
Voltage = 40 kV
Current = 30mA
Scanning angle: (20- 60°)
Scanning Speed = 5 (degree/min)

While, the average crystallite size of the films can be estimated by the Scherrer formula using the full width at half-maximum (FWHM) value of the XRD diffraction peaks.

Atomic Force Microscopy (AFM)

The surface morphology, particle size distribution and root mean square of roughness of ZnS films prepared under various condition were analyzed using atomic force microscope (AFM), (ateliess .MAITRE), made by PLARST. The AFM is capable of measuring nanometer scale images of insulating surfaces with little or no sample preparation as well as measuring three dimensional images of surfaces and studying the topography [15,16].

Results and Discussion

Structural Properties (X-ray Diffraction)

XRD pattern of nanopartical ZnS films with different thickness (75, 150, 225, 300, 375, 450 and 525 nm) prepared by chemical spray pyrolysis technique at substrate temperature of ($400\,^{0}C$) has been shown figure (1),the peaks of the XRD are observed between 20^{0} and 60^{0} .

The presence of diffraction peaks indicates that the film is polycrystalline with cubic structure and no amorphous phase is detected. It is revealed that the films have peaks corresponding to (111), (220) and (311). When comparing these results with the card JCPDS (Joint Committee on Powder Diffraction Standards) cards number (96-900-0108) for ZnS material, the results were compatible to some extent.

From measurements of X-ray diffraction We will conduct a full analysis of the X-ray diffraction and represents every form and the changes in them, as well as to find out the nature of the crystal growth and compositional for crystallization and phase formed by the material prepared, and is influenced by x-ray spectrum greatly depending on the circumstances preparations, particularly substrate temperature and films thickness. Figure (1) represents the X-ray diffraction of (ZnS) films at deposited temperature (400˚C) and it can be inferred that the films gelling for the existence of more than one summit, as well as the results showed that the ZnS thin films was cubic structure, and we note that one of the peaks are prominent more than its peers, and the reason is due to the Influence of deposition temperature on the growth of these levels, the emergence of multi-gelling composition is normal because the material deposited on the flat bases and amorphous.

In all cases the intensity of (311) peak is extremely low in comparison with (220) and (111) ,this indicates that a dominant peak corresponding to (111) plane .Also one can observe that when thickness increases ,the locations of peaks do not change significantly as seen in table (2). These results are in good agreement with (JCPDS) card [17].

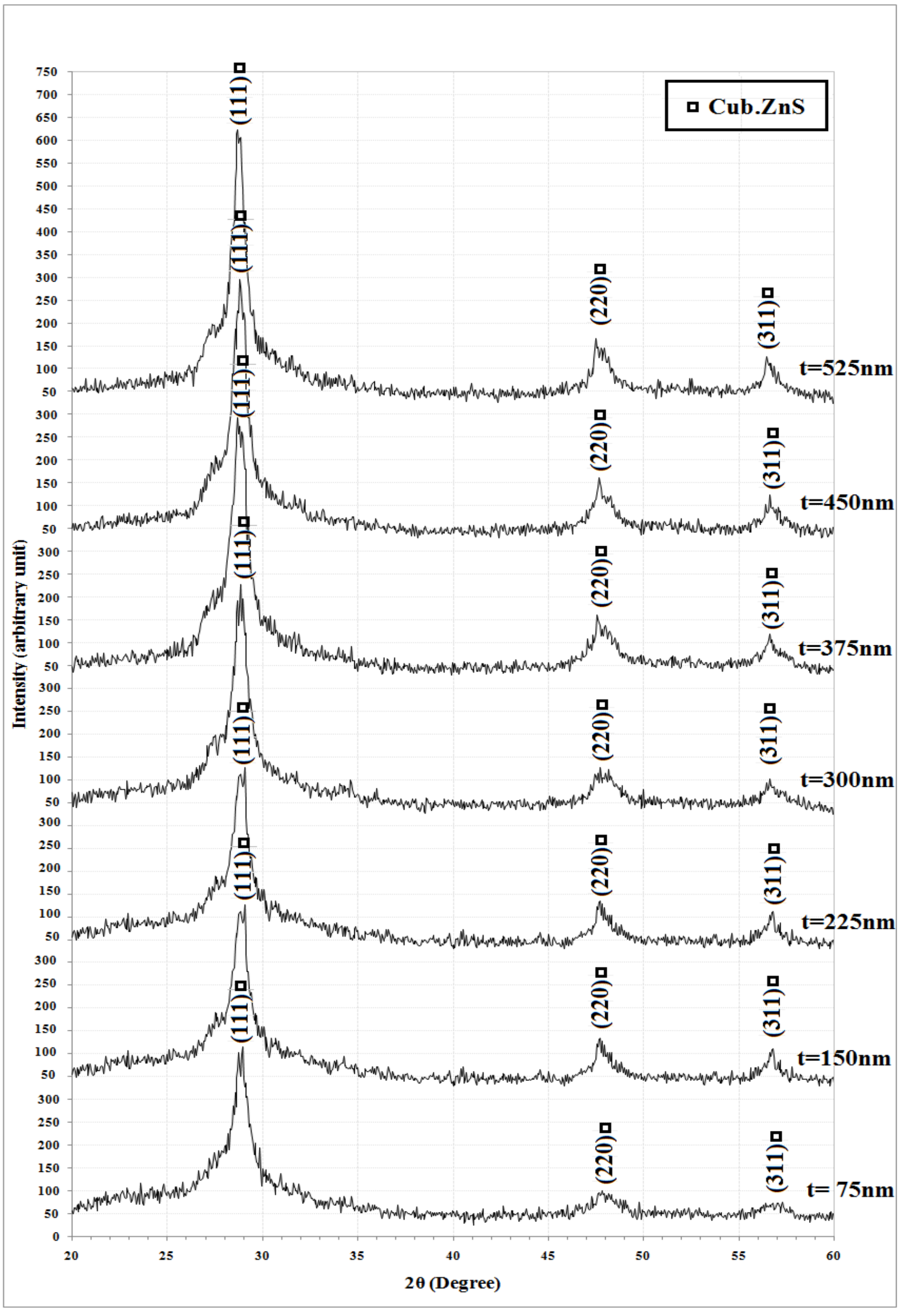


Fig (1): represents the X-ray diffraction of (ZnS) films at deposited temperature (400˚C).

The lattice constant a for the prepared ZnS thin film are shown in table (1), from the figure (2). We can see the lattice constant (a) slight increase with increase the thickness of ZnS thin films.

Table (1): the lattice constant value (a) for ZnS films with different thickness.

Thickness (nm)	75	150	225	300	375	450	525
a (Å)	5.3409	5.3497	5.3497	5.3563	5.3575	5.3674	5.3852

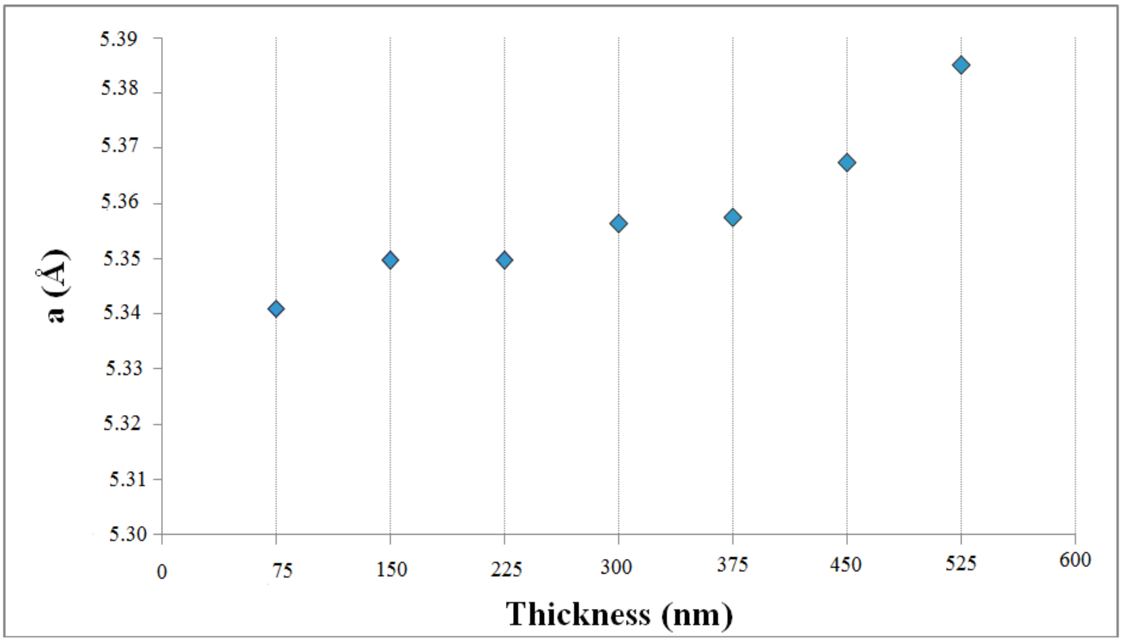


Fig (2): represents lattic constant variation with thickness.

The (d) value, that in inter planar spacing of (111) plane of the films was evaluated from the position of (111) peak from the XRD date, the observed (d) value which is in excellent agreement with the standard (d) value taken from the (JCPDS). The scherrer formula equation (1), [14] is used to determine the grain size and it is increased with increases thickness as shown in the figure (3) and table (2).

$$g.s = \frac{(0.94\lambda)}{[\Delta_{(2\theta)} \cos\theta]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where:
λ: is the x-ray wavelength (Å) .
$\Delta_{(2\theta)}$: FWHM (radian).
θ: Bragg diffraction angle of the XRD peak (degree) .

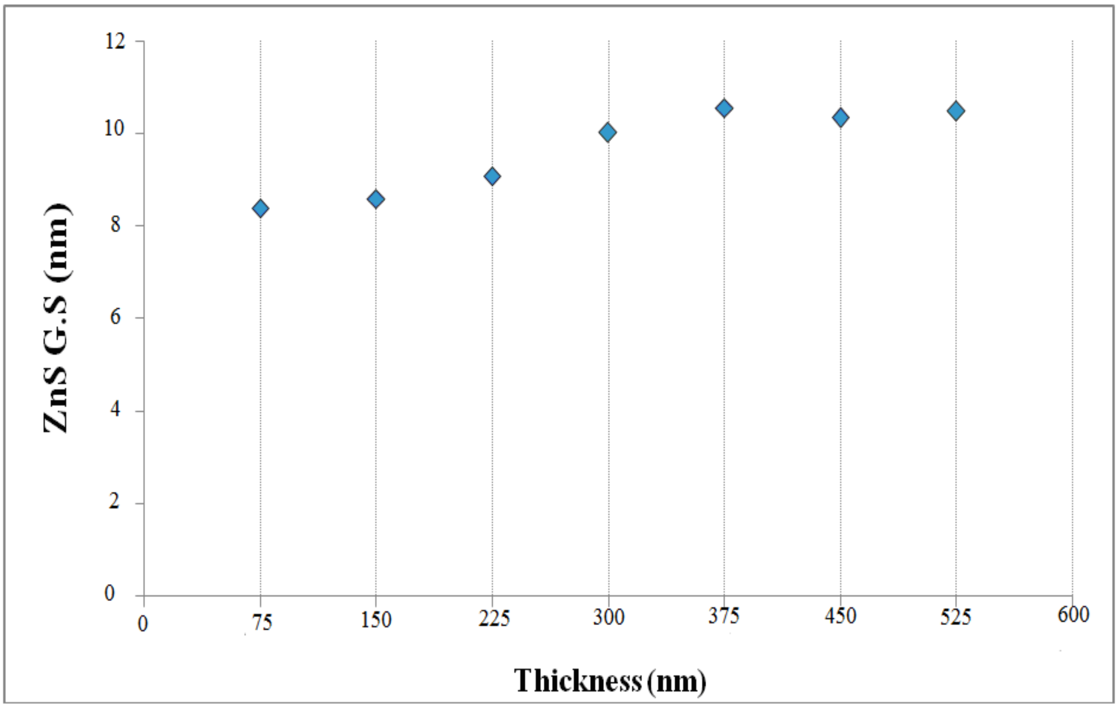


Figure (3): represents grain size variation with thickness

The grain size increases from (8.4 – 10.5) nm as the thickness increased from (75 nm – 525 nm). Similar results are reported by [17].

The intensity of (111) cubic plane has been increased with increases thickness, indicating that the degree of preferential orientation toward this direction increased as shown in figure (1) the FWHM of the peak decreased as in table (2), such crystalline is provements with increasing the thickness have observed by [17].

The increasing of intensity with increasing the thickness may be permitting better grain growth by maintaining the preference for the (111) plane.

Table (2), Results of X-rays diffraction of ZnS thin films with different thickness.

t (nm)	2θ (Deg.)	FWHM (Deg.)	G.S (nm)	d_{hkl} Exp.(Å)	d_{hkl} Std.	hkl	phase	card No.
75	28.9320	0.9773	8.4	3.0836	3.1231	(111)	Cub.ZnS	96-900-0108
	47.8155	1.3786	6.3	1.9007	1.9125	(220)	Cub.ZnS	96-900-0108
	56.7961	1.1814	7.6	1.6197	1.6310	(311)	Cub.ZnS	96-900-0108
150	28.8835	0.9518	8.6	3.0887	3.1231	(111)	Cub.ZnS	96-900-0108
	47.7184	1.5405	5.6	1.9044	1.9125	(220)	Cub.ZnS	96-900-0108
	56.6019	1.7413	5.2	1.6248	1.6310	(311)	Cub.ZnS	96-900-0108
225	28.8835	0.9021	9.1	3.0887	3.1231	(111)	Cub.ZnS	96-900-0108
	47.7184	0.8385	10.4	1.9044	1.9125	(220)	Cub.ZnS	96-900-0108
	56.7476	0.4543	19.9	1.6209	1.6310	(311)	Cub.ZnS	96-900-0108
300	28.8474	0.8172	10.0	3.0925	3.1231	(111)	Cub.ZnS	96-900-0108
	47.6636	1.4065	6.2	1.9064	1.9125	(220)	Cub.ZnS	96-900-0108
	56.6355	0.8105	11.1	1.6239	1.6310	(311)	Cub.ZnS	96-900-0108
375	28.8408	0.7765	10.6	3.0931	3.1231	(111)	Cub.ZnS	96-900-0108
	47.6214	1.4530	6.0	1.9080	1.9125	(220)	Cub.ZnS	96-900-0108
	56.6019	1.1265	8.0	1.6248	1.6310	(311)	Cub.ZnS	96-900-0108
450	28.7864	0.7926	10.3	3.0989	3.1231	(111)	Cub.ZnS	96-900-0108
	47.6214	1.0409	8.3	1.9080	1.9125	(220)	Cub.ZnS	96-900-0108
	56.5534	0.6375	14.2	1.6260	1.6310	(311)	Cub.ZnS	96-900-0108
525	28.6893	0.7813	10.5	3.1091	3.1231	(111)	Cub.ZnS	96-900-0108
	47.5243	1.1272	7.7	1.9117	1.9125	(220)	Cub.ZnS	96-900-0108
	56.4563	0.6251	14.4	1.6286	1.6310	(311)	Cub.ZnS	96-900-0108

Texture coefficient (TC)

The values of texture coefficient of nanoparticle ZnS films are listed in table (3). The texture coefficient is calculated for crystal plane (111) for all films, the value of texture coefficient increase with increasing thickness. The value of the texture coefficient indicates the maximum preferred orientation of the films along the diffraction plane, meaning that the increase in preferred orientation is associated with increase in the number of grains along that plane, as the relation. [14]

$$TC(hkl) = \frac{[(I(hkl)/I_o(hkl)]}{[Nr - 1\sum I(hkl)/I_o(hkl)]} \ldots\ldots\ldots\ldots\ (4)$$

Where:

I : is the measured intensity .
Io : the ASTM standard intensity .
Nr : the reflection number .
(hkl) : Miller indices

Number of layers (N_L)

The number of layers evaluated from film thickness is listed in table (3). The variation of layer number varies with different thickness in random way. It is thought that the substrate temperature varies and quantities of drop play a great role in this random change, as the relation [18]:

$$N_L = \frac{t}{g.s} \qquad (5)$$

Dislocation density (δ)

The dislocation density is the measure of amount of defects in a crystal. The values of dislocation density obtained in the present work confirmed good crystallinity of the nanoparticals ZnS films fabricated by employing spray pyrolysis technique as shown in table (3), can be calculated using the following relation [19]:

$$\delta = \frac{1}{g.s^2} \qquad (6)$$

The number of crystallites per unit area (N)

By using the films thickness and grain size of the films prepared on glass substrate by spray pyrolysis technique at the substrate temperature (400 ˚C) the number of crystallites per unit area was calculated and listed in table (3), can be calculated using the following relation [20]

$$N = \frac{t}{g.s^3} \qquad (7)$$

Table (3): some synthetic parameters that have been obtained from XRD diffraction with different thickness.

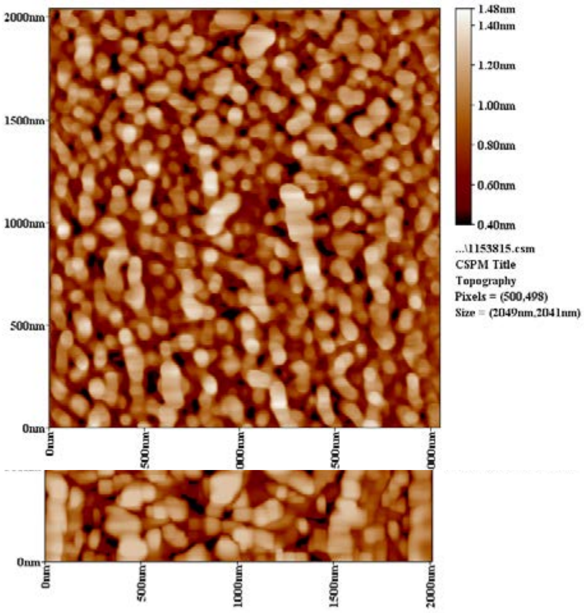
t (nm)	**(hkl)**	**Texture Coefficient T_C (h k l)**	**Number of Layers (N_L) (nm)**	**Dislocation Density (δ) x 10^{14} (m^2)**	**Number of Crystallines per unit area(N) x 10^{14} (m^2)**
75	**(111)**	**2.179**	**8.92**	**141.7**	**16.8**
150	**(111)**	**2.238**	**26.78**	**318.8**	**56.9**
225	**(111)**	**2.332**	**24.72**	**92.4**	**8.89**
300	**(111)**	**2.38**	**30**	**100**	**10**
375	**(111)**	**2.344**	**35.37**	**88.9**	**8.3**
450	**(111)**	**2.359**	**43.68**	**94.2**	**9.1**
525	**(111)**	**2.343**	**50**	**90.7**	**8.6**

Atomic Force Microscopy (AFM)

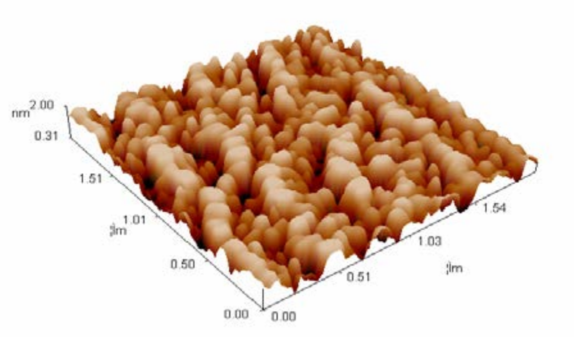
Atomic force microscopy (AFM) technique is a useful method analysis of the surface topography of the thin films. Figures (4) shows two and three dimensional AFM images for the ZnS thin films with different thickness(*t*= 75, 150, 225, 300, 375, 450, and 525 nm) deposited on glass substrate temperature 400 °C with scanning area (2 × 2 μm^2) that showed the variation of surface roughness with variation in the layers thickness. As can be noticed from this figures, the nanoparticals ZnS thin films have high degree of homogeneity and the small grains have uniform distribution on the substrate. Root mean square (RMS) values are (0.233, 0.38, 0.557, 0.733, 1.61, 1.66 and 2.17 nm) with (75, 150, 225,300,375,450 and 525) respectively. It is found from the AFM studies that the Root Mean Square (RMS) and Surface Roughness (RS) average and maximum height of the films increase with increasing thickness of thin films are shown in the table (4).

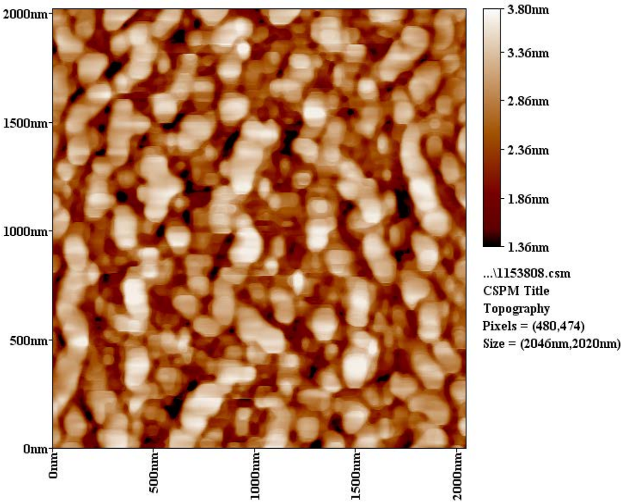
It can be seen that films are uniform, densely packed and pinhole free, and it shows that the morphology of these films are homogeneously distributed, which indicates the crystalline nature of the films. Initial visual in vestigations of the deposited film have shown that they are compact and have good adherence to the substrate. No evidence of cracking observed the grains are made of different size varying from (8.4 – 10.5 nm) for grain size (XRD), as show in table (2). However, the grain density reduced indicating the smaller grains agglomerate together to form larger grains of nanopartical ZnS films. On the other hand, the surface roughness and Root Mean Square (RMS) of the films were measured using AFM technique, as in table (4). The surface roughness defined as the standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness [17]. The surface roughness is unavoidable since the grains are grown with different size. It can be seen that the surface roughness and RMS values increase with increasing thickness indicating an increase in the grain size as in table (2) and (4) and figure (4), and this is agreement with other [21].

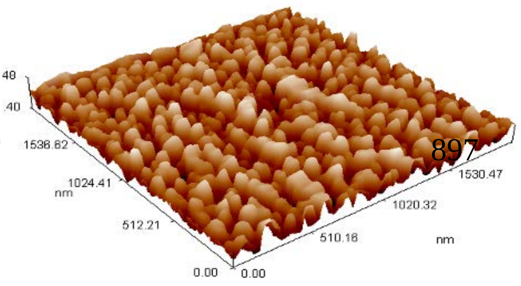
t=75nm



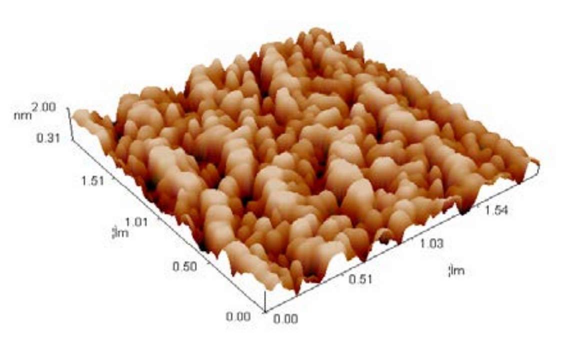
t=150nm

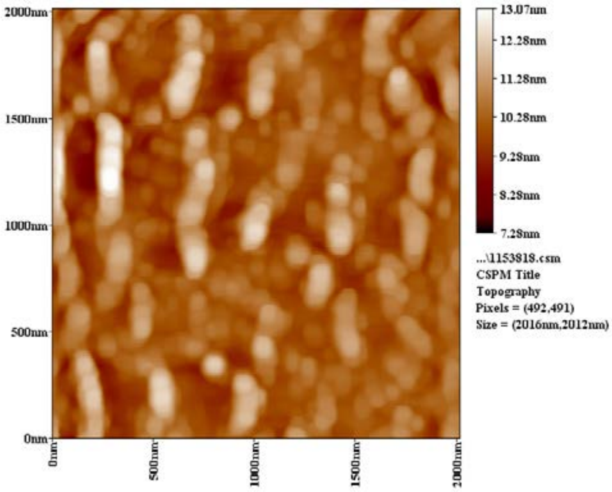






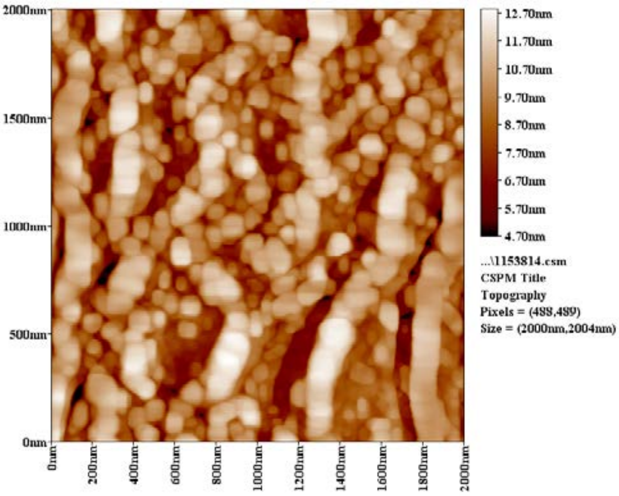
t=225nm

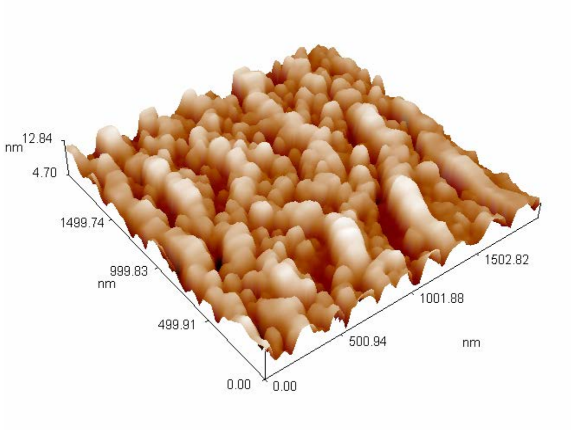


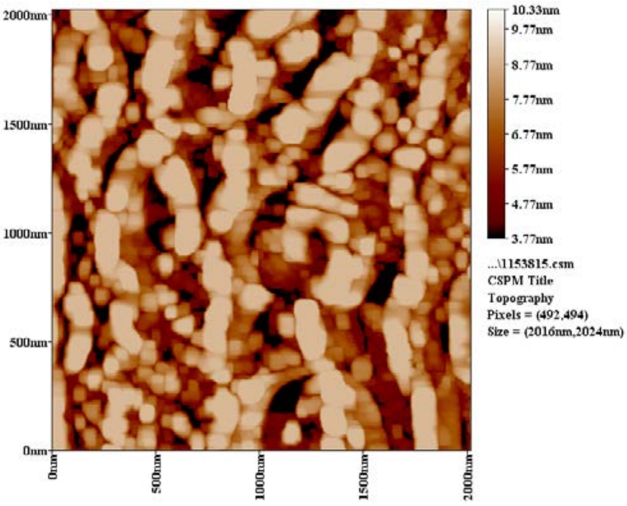


t=300nm

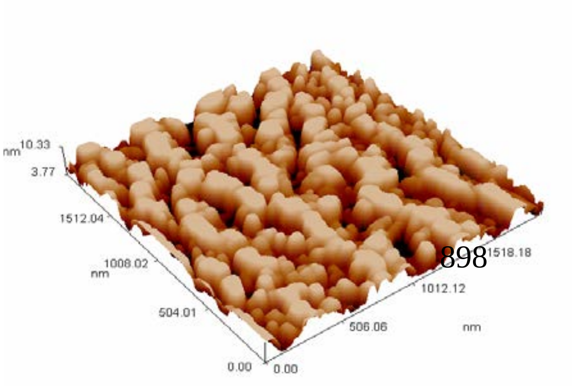
t=375nm







t=450nm



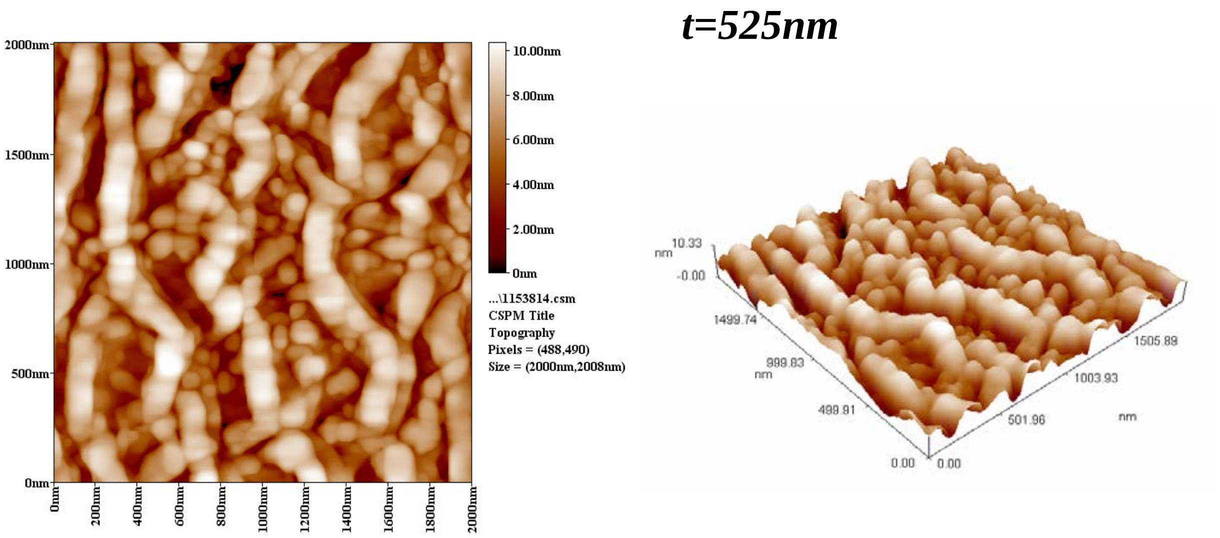


Fig (4): 2D and 3D AFM images of ZnS films deposited at 400 °C temperature with different thickness.

Table (4):Morphological characteristics from image for ZnS thin film with different thickness.

ZnS-Thickness [nm]	Root Mean Square (RMS) [nm] taken from (2×2 µm^2)	Surface Roughness (RS) [nm]	Ten Point Height [nm]
75	0.233	0.197	1.03
150	0.38	0.318	0.825
225	0.557	0.467	2.33
300	0.733	0.572	5.05
375	1.61	1.32	4.7
450	1.66	1.43	3.35
525	2.17	1.81	6.13

Conclusion

Nanopartical zinc sulfide films were prepared by chemical spray pyrolysis (CSP) technique at substrate temperature of (400±5 ^{o}C) on glass substrate and different thickness (75, 150, 225, 300, 375, 450 and 525 nm). The XRD results showed that all films are polycrystalline in nature with a cubic structure and the preferred orientation was along the (111) plane for all films. The average grain size for ZnS, estimated from XRD analysis. The thickness (375 nm) has highest grain size of about 10.6nm, and the thickness (75 nm) has minimum grain size of about 8.4nm, and was shown and have well identical with standard card (JCPDS) for cubic ZnS crystal.

AFM results showed homogenous and smooth ZnS thin films, the average roughness (RS) and root mean square (RMS) roughness for ZnS thin films, estimated from AFM. The thickness (525 nm) has highest average roughness and RMS roughness, and the thickness (75 nm) has minimum average roughness and RMS roughness of the ZnS thin films.

References

[1]. R.Maity and K.K.Chattopadhyay, Synthesis and optical characterization of ZnS and ZnS:Mn nanocrystalline thin films by chemical route, Nanotechnology, 15(7), 2004, 812 - 816.

[2]. Y.T.Nien, I.G.Chen, C.S.Hwang and S.Y.Chu, Copper concentration dependence odf structure, morphology and optical properties of ZnS:Cu,Cl phosphor powder, J.Phys.Chem.Solids, 69 (2-3), 2008, 366.- 371

[3]. F.Gӧde and C.Gumus, Influences of copper and manganese concentrations on the properties of polycrystalline ZnS:Cu and ZnS:Mn thin films, Optoelectron. Adv. Mat.11 (3), 2009, 429 - 436.

[4]. A.Klausch, H.Althues, C.Schrage,P.Simon,.A.Szatkowski,, M. Bredol, D.Adam and S.Kaskel, Preparation of luminescent ZnS:Cu nanoparticles for the functionalisztion of transoarent acrylate polymers, J.Lumin.130 (4),2010, 692 -697.

[5]. X.J.Zheng, Y.Q.Chen, T.Zhang, B.Yang, C.B.Jiang, B.Yuan and Z.Zhu, Photoconductive semiconductor switch based on ZnS nanobelt film, Sens. Actuators B147 (2), 2010, 442 - 446.

[6]. J.Hu, G.Wang, C.Guo, .D.Li, L.Zhang and J. Zhao, Au catalyst growth and photoluminescence of zinc blende and wurtzite ZnS nanobelts via chemical vapour deposition, J.Lumin,122–123,2007, 172 - 175.

[7]. C.Wang, Y.Ao., P.Wang, S. Zhang, J.Qian and J. Hou, A simple method for large scale preparation of ZnS nanoribbon films and its photocatalytic activity for dye degradation, Appl.Surf.Sci, 256 (13), 2010, 4125 - 4128.

[8]. F.Gӧde, C.Gumus and M.Zor, Infiuence of the thickness on physical properties of chemical bath deposited hexagonal ZnS thin films, Optoelectron.Adv.Mater, 9 (7), 2007, 2186 - 2191.

[9] K. R. Murali, Optical properties of pulse electrodeposited ZnS films, Journal of Applied Physics, Volume 6, Issue 3 Ver. II (May-Jun. 2014), PP 09-14.

[10] L. I. Berger, B. P. pamplin, “properties of semiconductors”, in R. C. Weast (ed.) Handbook of Chemistry and physics, &3rd edn., CRC press, Boca Raton, FL, p. 12-78 to 12-85, (1993).

[11] Y. NicolaM. Dupuy, and M. Brunel, J. Electrochem. Soc.,1990, 137, 2915.

[12] M.A. Hasse, J. Qiu, J.M. Depuydt, H. Cheng, Appl. Physic let.,1991, 59, 1272.

[13] Mahdi Hasan Suhail and Raoof Ali Ahmed, Structural, optical and electrical properties of doped copper ZnS thin films prepared by chemical spray pyrolysis technique, Advances in Applied Science Research, 2014, 5(5):139-147.

[14] Ali A. Yousif, "Preparation and Construction of Efficient Nanostructures Dopant ZnO Thin Films Prepared by Pulsed Laser Deposition for Gas Sensor", Ph.D. Thesis, Dept. of phys., University of Al-Mustansiriya, (2010).

[15] Yao , N. and Z. L. Wang ,“ Handbook of Microscopy for Nanotechnology” ,(2005).

[16] Garcia, R. and R. Perez ,“ Dynamic atomic force microscopy methods ”, Surface science reports , Vol. 47, (2002), pp. 197-301,.

[17] Nadeem and Ahmed, "Studied the optical properties of ZnS thin films", (1999).

[18] A. Ivashchenko, and I. Kerner," Physical approaches to improvement of semiconductor gas sensors based on SnO_2 thin films "Moldavian J. Phys. Sci., vol. 2, (2003).

[19] A.Moses Ezhil Raj,L.C.Nehru, M.Jayachandran, and C.Sanjeeviraja, “ Cryst. Res. Technol ” ,vol. 42,No 9, (2007) p.867.

[20] M. Dhanam, R.R. Prabhu and P. K. Manoj, Materials Chemistry and Physics,”Investgations on chemical bath deposited cadmium selenid thin films”, Vol.107, (2008) PP. 289-296.

[21] M. Y. Nadeem and Waqas Ahmed, "Optical properties of ZnS thin films using resistive heating technique", Turkish Journal of Physics , Vol 24, 2000, p. 651.