



Preparation and Characterization of ZnS: Mn Nanoparticles with Theoretical Analysis

Abdulhussain K. Elttayef^{1*}, Rajaa K. Mohammad², Rabi N. Hammdi³, Baydaa A.Khudhair⁴

Abstract

Zinc sulfide doped manganese (ZnS: Mn) thin films were deposited on glass substrates at temperature of 100 oC by RF magnetron sputtering technique. The physical properties are analyzed using (AFM, EDX and UV-VIS spectrophotometer). The results show that the values of average diameter of grain size and surface roughness for ZnS: Mn was 73.27 nm and 2.85 nm respectively. The transmittance and optical band gap are found to be 71.38% and 3.26 eV respectively. The calculations of spectrum absorption intensity, IR spectra and energy gap for the ZnS: Mn, which obtained from Density Functional Theory (DFT), gave agreement with the practical results.

Key Words: RF, Magnetron Sputtering, DFT, ZnS, Nanoparticle, EDX.

DOI Number: 10.14704/nq.2020.18.6.NQ20177

NeuroQuantology 2020; 18(6):17-20

Introduction

The Zinc Sulfide (ZnS) is wide band gap semiconductor material belongs to the II-VI group [1] and also the crystal structure is shown in Fig (1). ZnS thin film is a vital semiconductor material because it's low absorbance within the visible range, high index of refraction (2.35) and high dielectric constant. The crystallinity, melting point and structural stability for semiconductor materials are strongly suffering from the reduction within the particle size [2]. The unique properties of zinc sulfide with nanometric composition come from the results of quantum confinement because of the decrease in band structure to separate quantitative levels because the limited size of nanoparticles [2]. ZnS is suitable to be used as host matrix for an oversized style of dopants thanks to its broad energy band gap. Doping ZnS with transitional metal ions like Mn²⁺ is a vital aspect to yield different nanostructures [3]. Also ZnS doped with Mn is favorable phosphor, which supplies best optical properties like small emission band and high luminescent intensity [4].

There are many deposition techniques used for

preparing ZnS thin film, like chemical spray pyrolysis, sol-gel deposition, pulsed laser deposition, thermal evaporation, and RF magnetron sputtering [4]. Among these synthesis techniques, RF magnetron sputtering method has some advantages like high film rate of growth, easier controllability of the deposition parameters and compatibility with sputtering deposition of absorber and window layer [5].

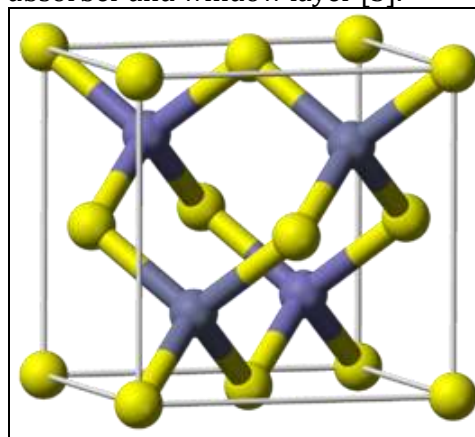


Fig. 1. Structure of ZnS

Corresponding author: Abdulhussain K. Elttayef

Address: ^{1*}Ministry of Science and Technology; ²University of Karbala, College of Science, Physics Department, Karbala, Iraq;

³Al kut University College; ⁴Al kut University College.

Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Received: 02 May 2020 **Accepted:** 30 May 2020



Experimental

Radio frequency (RF) magnetron sputtering method used to synthesis (ZnS: Mn) thin film on glass substrates. The (ZnS: Mn) target of 5cm diameter and thickness 3mm were made by mixing 20 gm of ZnS with 0.4mg of Mn (99.99% purity) placed in a very mold for compressed by the hydraulic piston with pressure 8-10 tons and so sintered it for 2 hours at temperature 200C⁰. The target mounted within the magnetron gun, then close the door of deposition chamber and evacuated to final pressure (7.9×10^{-5} torr) by Dry scroll pump and then, the pressure up to (2.3×10^{-2} torr) by introduction high purity Ar gas (99.99% purity) into deposition chamber [6]. The RF power was 100 watt and therefore the sputtering time was about 2 hour's During the sputtering process; the substrate temperature was maintained at 100C⁰.

The surface morphological of film investigation was measured using Atomic Force Microscopy (AFM). While, the form and particle size of the thin films were administrated by scanning electron microscopy (SEM) using Hitachi (S-4160) with magnification 100KX.

Structural Properties Results

Atomic Force Microscope

Figure (2) shows 3D -images for surface morphology and granulite accumulation analyzed by AFM of Mn doped ZnS at doping concentration of 2% with 770nm thickness and deposited on glass substrate. This figure exhibited that thin film uniformly distributed over the film are high dense structure and is deposited very well .The values of average diameter of grain size and surface roughness for ZnS :Mn was 73.27 nm and 2.85 nm respectively.

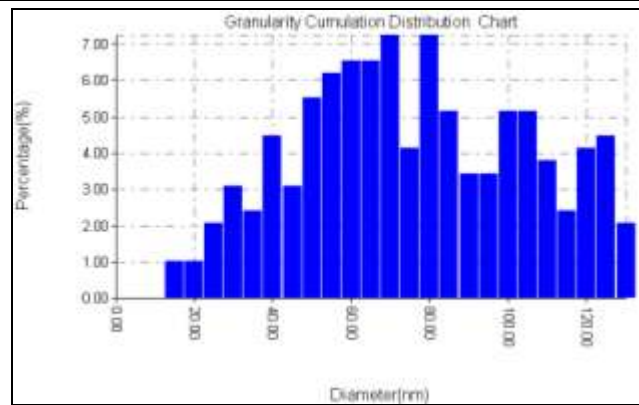
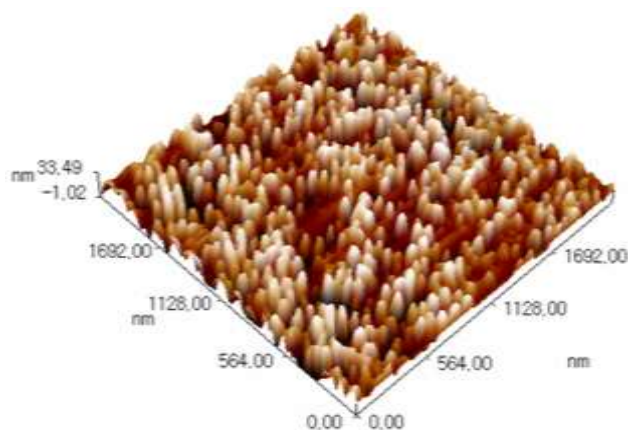


Figure 2. Three Dimensional AFM Image and Granularity Accumulation Distribution Chart of ZnS Thin Films

Scanning Electronic Microscopy

Figure (3) shows the SEM image (magnification power 100kX) of Mn doped ZnS at doping concentration of 2% with thickness (770) nm. The image clearly exhibit tightly packed grain, furthermore, we will see that the grain having uniform, dense and homogenous distribution. It is found from this figure that the average diameter was 24.45nm.

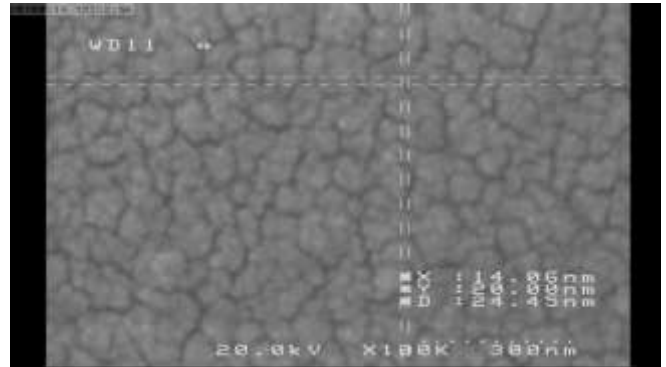


Figure 3. The SEM image ZnS thin film

The composition of ZnS: Mn deposited on glass substrate is analyzed using the Energy Dispersive X-ray analysis (EDX), which besides allows knowing the presence of any impurities as shown figure (4). The EDX analysis demonstrate the presence of Zinc (Zn), sulphur (S), and manganese (Mn) are deposited on glass substrate.

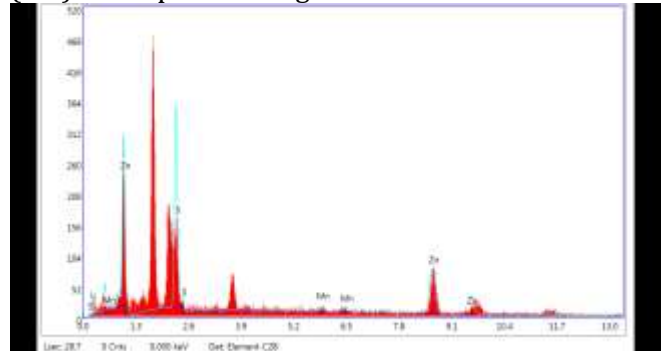


Figure 4. The EDX pattern ZnS thin film

UV- Visible Spectroscopy

Optical transmittance for ZnS: Mn film as measured within the range of incident light wave length (200-1100) nm. Figure (5) shows transmittance spectra of the deposited film on glass substrate. This plot indicates that the film at thickness (770 nm) possess good optical transparency in visible region with transmittance of 70% this result agreement with [4].

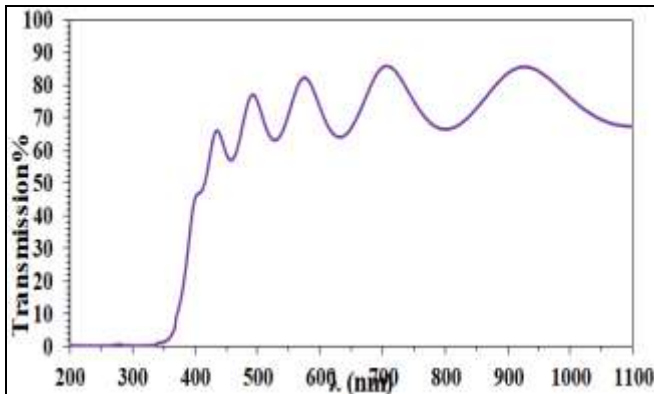


Figure 5. Variation of transmittance with wavelength of Zn thin Films

Figure (6) shows that the absorptance coefficient as function of wavelength for ZnS: Mn at thickness 770nm. It is often observed from this figure that the absorptance is possess high values at short wave length, then decrease sharply to reach constant value at long wave length above 405nm.

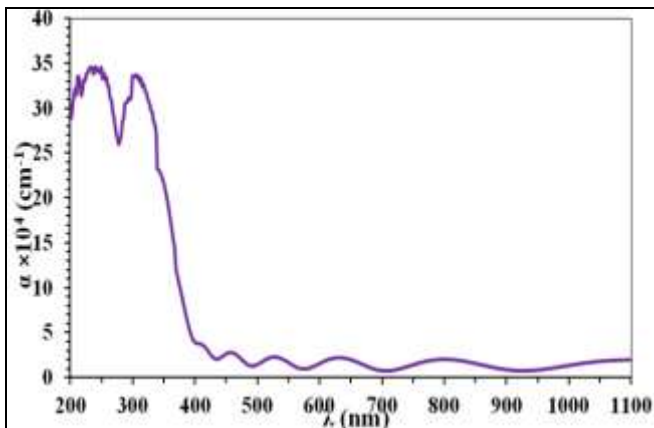


Figure 6. Absorption Coefficient (α) versus Wavelength for ZnS Thin Film

From the value of transmission spectra, optical band gap was calculated by using tauc relation [10, 11].

$$\alpha h\nu = B(h\nu - E_g^{opt})^r \quad (2)$$

Where, E_g is that the energy band gap, B is constant and $r=1/2$ for allowed electron transition. The band gap value was calculated by drawing a straight line that intersects the x-axis as shown within the figure (7). The linear part indicate that the transition mode during this film is of direct nature. It is found from figures (8 & 9) that the band gap value of ZnS

thin film was 3.26 eV and for ZnS: Mn was 1.75 eV.

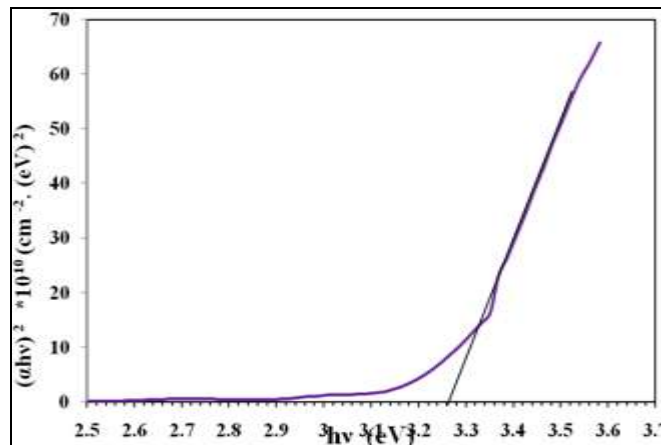


Figure 7. Band gap of ZnS

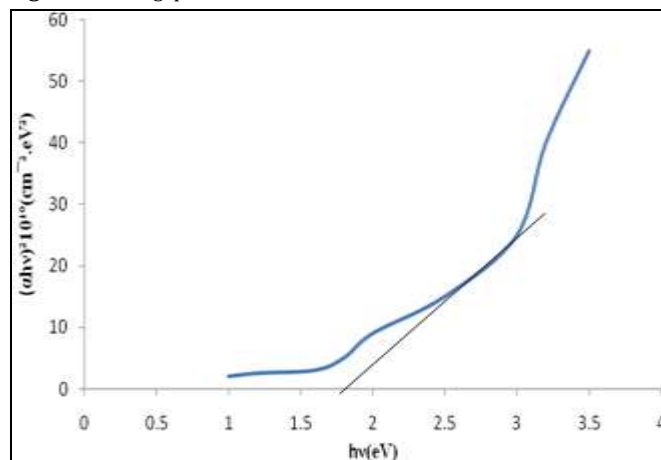


Figure 8. Band gap of ZnS: Mn

Computational Methods

The calculations are performed using DFT/B3LYP; the geometric structures were optimized using Gaussian 09 program. The Gaussian perspective 5.08 system is looking on (DFT) technique with premise set B3LYP/3-21G, while UV-VIS spectrum is computed by TD-DFT method [12]. It involves the probability density functions of the electrons during a molecule to see other properties of the molecule [13].

The results of calculation gave energy gap of ZnS was $E_g=3.3$ eV, while ZnS+Mn equal 1.6 eV, which gave agreement with the practical results. In this investigation, it is seen that the absorption of ZnS at the wavelength 368.5nm as shown in Figure (9). Figure (10) shows the computed IR spectra for (ZnS), the harmonic vibrational frequencies were calculated for the studied molecules by using B3LYP level with a 3-21G basis set. The (Zn=S) symmetric stretching has been studied at band (447.935) cm^{-1} .



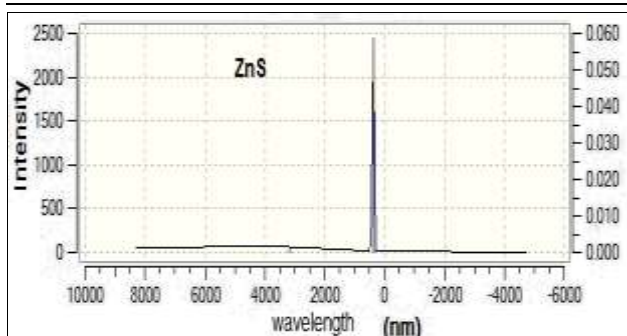


Figure 9. UV-VIS Spectra of ZnS Using DFT- B3LYB /3-21G Method

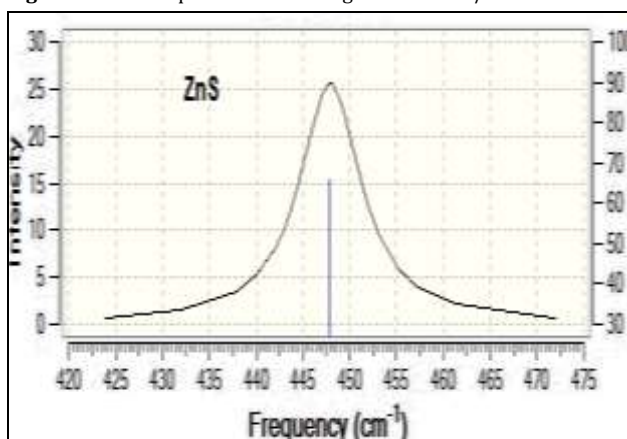


Figure 10. IR spectra of ZnS using DFT-B3LYB /3-21G Method

Conclusion

ZnS: Mn thin films successfully deposited by R.F. magnetron sputtering technique on glass substrates at 100 °C. SEM image show the surface of the film is uniform and no pinhole might be observed. EDX analysis exhibits the presence of Zinc, sulphur and manganese. AFM reveals that homegeinty distribution of grain size with average diameter was found to be 73.27 nm. The energy band gap for the ZnS: Mn, which obtained from Density Functional Theory (DFT), gave agreement with the sensible results.

Acknowledgments

This research was supported by the Ministry of science and technology .We thanks our colleagues who provided insight an expertise that greatly assisted the research.

References

- Ikhioya IL. Characterization of zinc sulphide thin film prepared by electrodeposition method. *Inter. J. Chem. Res.*, 2015; 8(2): 655-660.
- Ozautok F, Eriturk K, Bilgin V. Electrical and Optical Study of ZnS-Mn Thin Films . *Act. Phys. Polo.*, 2012; 121(1): 221-223.
- Nabiyouni G, Sahaei R, Toghiany M, Majles MH, Hedayati K. Preparation and characterization of nano structured Zns

thin films grown on glass and N- type Si substrates. *Rev.Adv. Mater. Sci.*, 2011; 27: 52-57.

Bodo B, Prakash D, Kalita PK. Synthesis and characterization of ZnS:Mn nanoparticales. *Inter. J. Appl. Phys. Math.*, 2012; 2(3).

Devi LS, Devi N, Sharma BS, Sarma HN. Effect of Mn⁺² doping on structural morphological and optical properties of ZnSnanoparticales by chemical Co-precipitation method.J. *Appl. Phys.*, 2014; 6: 6-14.

Kong L, Deng J, Chen L. Structural and optical characterization of magnetron sputtered Zns thin films annealed in different atomshere. *Chalc. Lett.*, 2017; 14(3): 37-96.

Bioki HA, Zarandi MB. Effects of annealing and thickness on the structural and optical properties of crystalline ZnSthin films prepared by PVD method . *Inter. J. opt.* 2011: 5(2).

Vishwakarma R. Thickness - dependent structural, electrical, and optical properties of ZnS thin film deposited by thermal evaporation. *Ukr.J. Phys.*, 2017: 62(5).

Zaware RV, Borse RY, Wagh BG. Properties of thin film ZnS:Mn sprayed by improved method : the rol of Mn⁺² ion concentration. *Mater. Scie. Polo.*, 2017; 35(2): 291-302.

Borah JP, Sarma KC. Optical and optoelectronic properties of ZnSnanostructural thin film. *Act. Phys. Polo.*, 2008; 111(4): 713-719.

Shinde MS, Ahirro PB, Patil IJ, Patil RS. Studies on nanocrystalline ZnS thin films prepared by modified chmical bath deposition method. *J. Pu. Appl. Phys.*, 2011; 499: 765-768.

Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Fox DJ. Gaussian 09,revision A. 02 Gaussian, Inc., Wallingford CT. 2009.

Santos JC, Andres J, Aizman A, Fuentealba P. An aromaticity scale based on the topological analysis of the electron localization function including σ and π contributions. *Journal of chemical theory and computation*, 2005; 1(1): 83-86.