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Influence of Chromium Doping on the Structural and Optical Properties of Zinc Sulfide Thin Films Prepared via Spray Pyrolysis

Asmaa Mohammed Raoof
Department of Physics, College of Education, Mustansiriyah University, Baghdad, Iraq

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ABSTRACT

In this study, doping impact of Chromium (Cr) on the actual properties of Zinc Sulphide (ZnS) at different content of (0, 2, and 4 wt % Cr) was discussed. The considered examples were readied utilizing Spraying Technique. Other published papers matched structural, topographical, and optical characterization in similar writings. X-ray diffraction reveals the high peak matched (008) plane; grain size is set to increase from 12.23 to 13.44 nm with Chromium doping. In contrast, the dislocation density decreases from 66.85 to 55.36, while strain decreases from 28.33 to 25.79. AFM images indicate that average particle size was 63.3 nm to 31.89 nm with Undoped ZnS and ZnS: Cr with 0% and 4% concentrations, respectively. Transmittance offers good transparency, in the visible area between 68 and 63, for undoped ZnS and 4% Cr content. The absorption coefficient indices increased via increasing Chromium doping. The optical bandgap of undoped ZnS and ZnS:Cr films decreases from 3.47 eV to 3.37 eV as the chromium concentration increases from 0% to 4%. The extinction coefficient and refractive index decrease via increasing Chromium doping.

Keywords: ZnS thin film, Cr, structural, topography, Optical Properties, bandgap.

INTRODUCTION

In recent years, ZnS with a wide band gap became a potential semiconductor for electroluminescent devices (ELD) and solar systems [1]. Researchers focused on zinc sulphide (ZnS) and studied it theoretically and experimentally due to its novel properties [2, 3]. ZnS is found to be n-type semiconductor with a bandgap of 3.6 eV [4-6]. Therefore, ZnS is utilized in heterojunction solar cells as an anti-reflective coating layer [8-10]. ZnS is widely used in industrial applications like LED [12], ELD and PV cells [15], sensors and lasers [16], There are several methods to deposit ZnS, like sol-gel [17], thermal evaporation [18], sputtering [19], chemical bath deposition, SILAR [20] and chemical methods like MOCVD [21], PLD [22], electrodeposition [23], SPT [24], etc. In this study, Undoped ZnS and ZnS: Cr films were deposited via SPT to study their physical characterization.

METHODS AND MATERIAL

Zinc sulphide thin films were prepared by SPT, using $ZnCl_2$ (purity: 99.99%) from Sigma-Aldrich UK. The solution molarity was 0.1 M. Redistilled water and methanol were mixed with ratio of 1:1, then $ZnCl_2$ is dissolved in it. In addition, the thiourea was dissolved in deionized water. The solubility of $ZnCl_2$ is enhanced by adding few drops of HCl. Chromium trichloride ($CrCl_3$) (provided by PubChem India) is used as a doping agent that is dissolved in deionized water. With compressed air maintained at 10^5 Nm^{-2} at a flow rate of 5ml/min and a deposition period of 8 seconds, the solutions obtained were pulverized on glass substrates before being allowed to cool for 1.5 minutes in immediately to protect over-cooling. The temperature of the substrate is held constant at 400 degrees Celsius. The distance between the heater and the spray spout was 28 centimeters .The resultant thin films were adherent and uniform to the substrates. XRD was used to obtain Structural parameters of the intended films by X-ray diffractometer. AFM are used to explore surface of grown films. The transmittance was recorded by double beam spectrophotometer.

RESULTS AND DISCUSSION

Figure (1) represents X-ray styles of the intended films by spraying technique and notes from the figure that all the membranes are polycrystalline and recorded with preferred diffraction pattern (008) at 2θ= 28.52°. Increased Chromium dopant weight ratio increased the intensity of the dominant reflection. It reduced the intensity of FWHM, which increased the crystalline size from 12.23 nm to 13.44 nm. A number of secondary reflections in (10), (008), (110) and (118) is also observed associated with 2θ = 26.93°, 28.52°, 47.62° and 56.53 °. It is noted that all secondary reflections were consistent with ICDD card No (05 - 0566). The figures (2- a, b, c and d) represent the half maximum (FWHM), Grain size, dislocation density and strain versus the doping weight ratios. Note from Figure (2- a), which shows a decrease in FWHM with increasing dopant ratio, from Figure (2- b), which shows the increase in grain size to 13.44 nm is due to increasing the doping to 4 % that calculated from the equation of Scherrer (1), leadjng to improved crystallization [25].

The crystallite size D is calculated via Scherrer's formula [26]:

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

Where β and λ are FWHM and X-ray wavelength (1.54056Å), respectively, the strain Ɛ for preferential reflection (008) and dislocation density δ were obtained by Eq. (2) and (3) [27]:

$$\varepsilon = \frac{\beta\, cos\theta}{4} \qquad (2)$$

$$\delta = \frac{1}{D^2} \qquad (3)$$

The calculated structural parameters S_p are shown in Table 1.

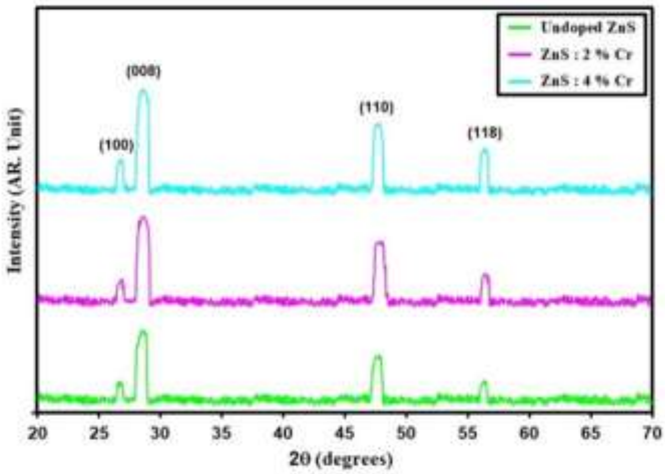

Fig.1. XRD patterns of the deposited films

Table 1. Crystallite size (D), optical bandgap, and Sp of the deposited films

Sample	2θ (°)	(hkl) Plane	FWHM (°)	E_g(eV)	D(nm)	δ (× 10^{14}) (lines/m²)	ε(× 10^{-4})
Undoped ZnS	28.52	008	0.67	3.47	12.23	66.85	28.33
ZnS: 2% Cr	28.49	008	0.65	3.42	12.67	62.29	27.48
ZnS: 4% Cr	28.47	008	0.61	3.37	13.44	55.36	25.79

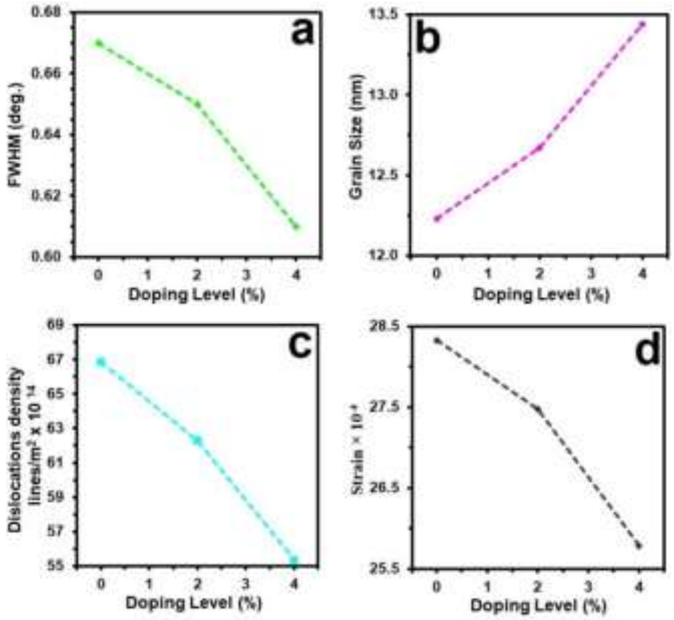

Fig.2. S_p of the intended films

Figure 2 a, b and c depicts the three-dimensional AFM images. As obtained from AFM images, the distribution of spherical shape grains in films demonstrates that they are uniform. The average particle size P_{av} was in the range of 63.3 nm to 31.89 nm for ZnS and ZnS: Cr with 0% and 4% concentrations respectively, AFM examines uncovered a smooth surface with root-mean-square harshness esteems decline from 9.68 nm to 4.36 nm from the film undoped ZnS and ZnS:4% Cr. Table (2) shows that the average roughness and average particle size P_{av} increases of the intended films.

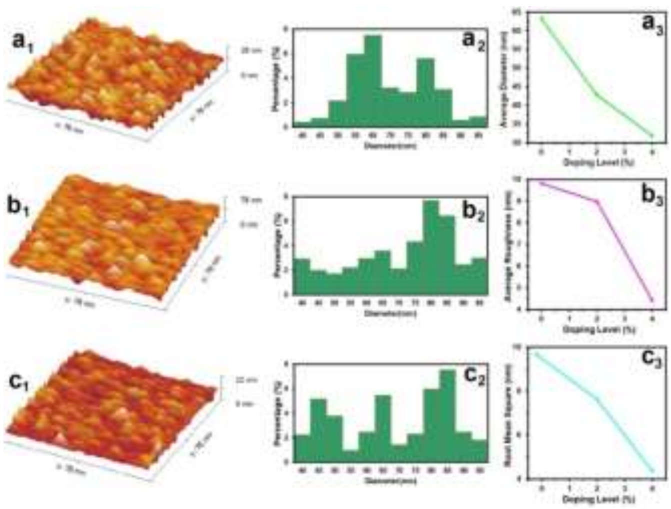

Fig.3. AFM results of the prepared films

Table 2. AFM parameters of the prepared films

Samples	**P_{av} nm**	**R_a (nm)**	**R. M. S. (nm)**
Undoped ZnS	63.30	9.82	9.68
ZnS: 2% Cr	42.86	8.98	7.63
ZnS: 4% Cr	31.89	4.42	4.36

The optical transmittance of undoped and Chromium doped ZnS films for various doping ratios (0, 2 and 4) %. Figure (4) represents the transmittance spectrums of ZnS: Ni films. The undoped ZnS film exhibited transmittance 68 % in the Visible and near IR range, then a remarkable decrease in the transmittance from its maximum value of 63 % as the doping ratio increased to 4 %, due to the increases in the Crystallite size [28].

The absorption coefficient (α) can be estimated by the relation [29]:

$$\alpha = (2.303 \times A)/t \quad (4)$$

Where (t) is the thickness of the film. Figure (4) shows α versus photon energy (hν) (From figure 5 we can conclude that absorption coefficient relays on Chromium content and E_g increase as Chromium increase.

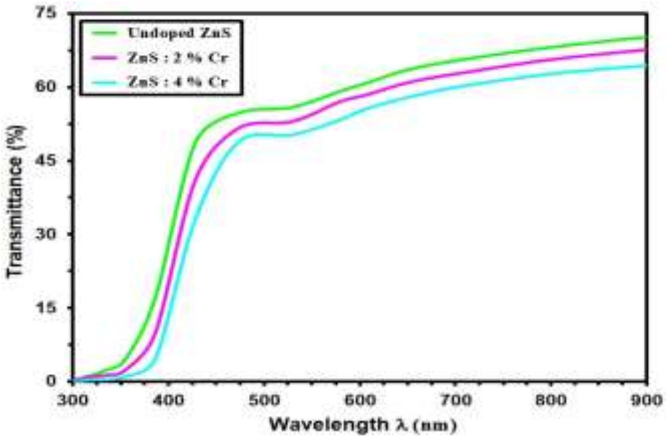

Fig. 4: Transmittance as a function of wavelength for the deposited films

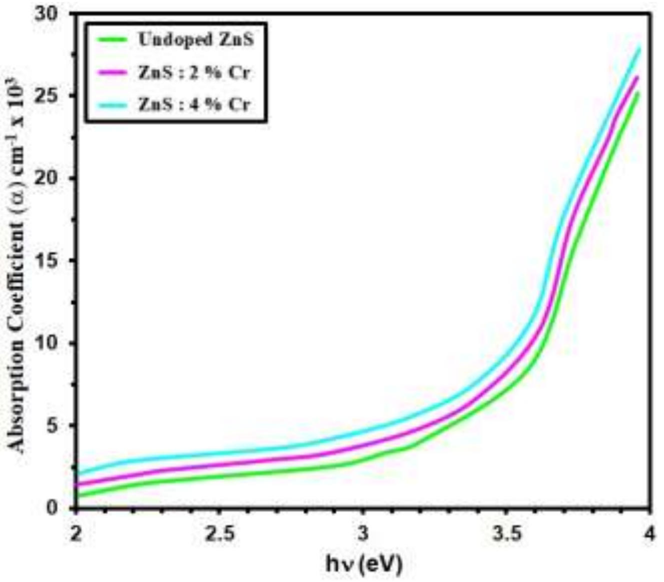

Fig. 5: Plot of α versus hν for the prepared films..

The direct energy gap of undoped and Ni doped ZnS and is calculated from equation (4) [30]:

$$(\alpha h\nu) = \boldsymbol{A}(h\nu - E_g)^{\frac{1}{2}} \qquad (5)$$

where, **A** is a constant, by plotting of $(\alpha h\nu)^2$ via the energy of incident radiation see figure (6). The calculated energy band gap value of the undoped ZnS films is decreased from 3.47 eV to 3.42 eV as the film doping ratio decreased from 0 wt. % to 2 %, the energy bandgap decreases to 3.37 eV as the doping increases to 4 % due to improvement in the film crystallinity [31].

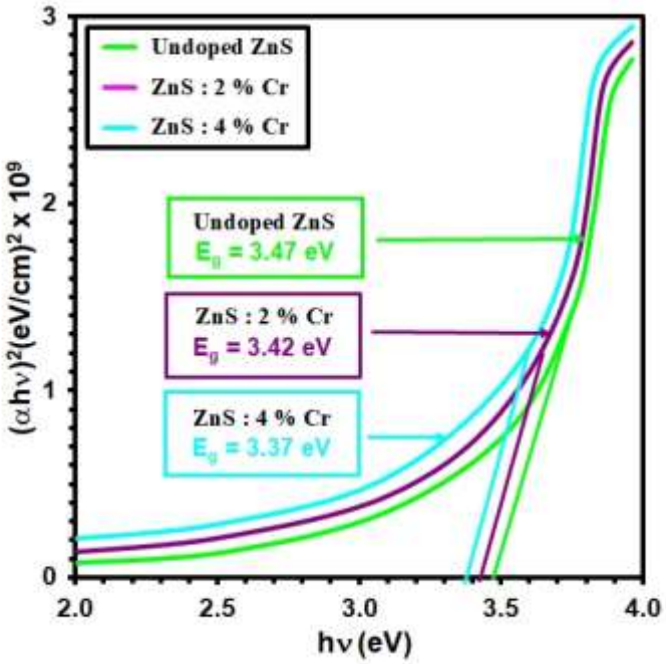

Fig. 6: $(\alpha h\nu)^2$ of the intended films.

Extinction coefficient (k) has been calculated by the formula [32]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (6)$$

Fig.7 represents k via wavelength. An increase in Extinction coefficient with increasing Chromium doping.

The refractive index (n) was obtained by eq. 7 [33]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (7)$$

The difference of refractive index versus wavelength is illustrated in figure (8). refractive index decreases with the increase in Chromium concentration.

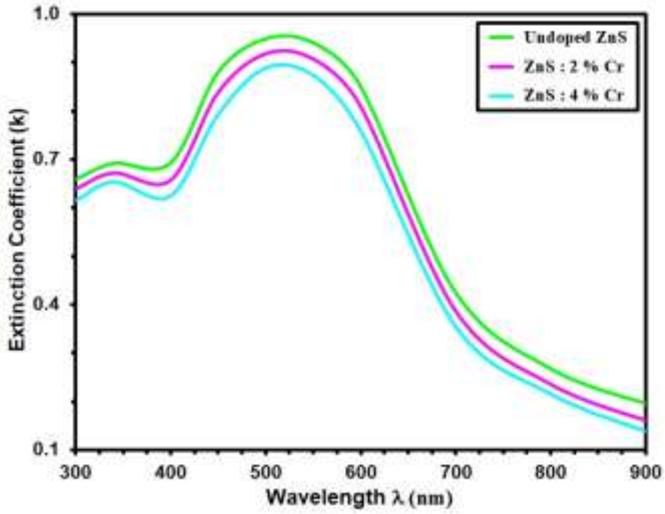

Fig. 7: k of grown films

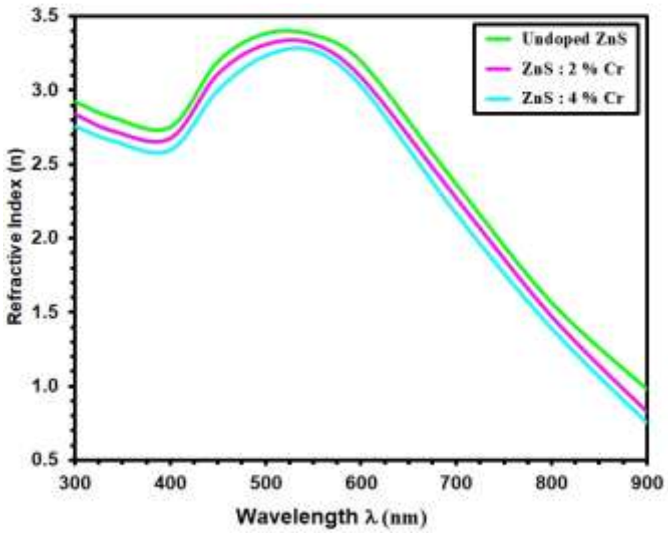

Fig. 8. n of grown films

CONCLUSION

ZnS and ZnS:Cr thin films were deposited using a simple and costless Spraying technique. The data obtained by XRD detect that deposited thin films were polycrystalline and a preferred orientation along (008) direction. The Grain size for unadulterated undoped ZnS molecule is about (12.23 – 13.44) nm with ZnS:4% Cr, though the strain (%) boundary expanded from 28.33 to 25.79, AFM picture demonstrated that average particle size of the saw in the scope of 63.30 nm to 31.89 nm with undoped ZnS and ZnS:4% Cr separately. AFM examines uncovered a smooth surface with root-mean-square harshness esteems decline from 9.68 nm to 4.36 nm from the film undoped ZnS and ZnS:4% Cr. The transmittance is decreased with increasing Chromium doping. It is found that absorption coefficient indices increase Chromium doping, the optical Eg of undoped ZnS is 3.47 eV, and expanding Chromium dopant from 0 to 4 % has been diminished from (3.47 to 3.37) eV. Whereas n and k decreases with Chromium concentration.

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