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Structural and Optical Characterization of Nanostructured Zinc sulfide Thin Films deposited by CBD

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Abstract.

ZnS thin films were grown utilizing CBD method. ZnS films were deposited employing various molar concentrations of (1.0, 1.5 and 2.0) M at a temperature of 90 °C. XRD profile offers an increment in grain size with the increment in molar concentration from 19.74 nm to 24.82 nm. Whilst the strain decreases from 17.55 to 13.96 with increase of molar concentration from (1.0 M and 2 M). AFM images show a fine surface morphology with rms roughness values decrease from 7.57 nm to 6.89 nm with the increment of molar concentration. The average diameter introduced by AFM was seen in the range of 92.74 nm to 86.54 nm with increase of molar content from 1.0 M and 2 M. The optical properties were studied by transmission spectra were found that for ZnS films have high transmittance in visible area is between 95 and 80 %, The absorption coefficient increased with increasing molarity from (1.0 M and 2 M). The bandgap offers a decrement from 3.55 eV to 3.35 eV with the increment in molarity.

Keywords: ZnS thin film, Structural properties, AFM, Optical properties, bandgap.

Introduction

ZnS is II–VI semiconductor , an n-type, whose bandgap was about 3.6 eV [1,2]. It was used as, LED [3], cathode-ray tubes [4], thin film electroluminescence [5], and buffer layers [6]. In general, ZnS occurs in two shape, cubic (zinc blende) and hexagonal (wurtzite) [7]. It is semiconductor with refractive index of (2.35) [8-11]. ZnS is utilized as window layer in solar cells [12-14]. ZnS is also used as a buffer layer [15-17]. Several techniques like sputtering [18], molecular beam epitaxy [19], PLD [20], CVD [21], SILAR [22], spray pyrolysis [23,55-75], and CBD [24-30] CBD can be employed as a large-area growth [31]. In the present work, CBD was employed to study some physical properties of nanostructured ZnS films utilizing various molar concentrations.

Experimental

ZnS thin films are deposited by CBD method on glass substrates (25mm x 50mm x 1mm). Zinc Sulphate of (1.0, 1.5 and 2.0) M concentration in 25 ml of de-ionized water was employed. The glass substrates have been cleaned by first dipping for 30 minutes into HCl and HNO₃, cleaning in acetone with ultrasonic vibration for 20 minutes, inglorious into methanol solution, washed with de-ionized water, cleanly with (HF 5%). ZnS thin films were prepared by mixing 25ml of 0.25M zinc sulphate (ZnSO₄) as Zn^{2+} ion

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source, 25 ml of 3M hydrazine hydrate $(NH_2)_2$ and 25ml of 3M ammonia (NH_4OH) was employed as a complexing agent. The mixture immersed in the heated water bath with a temperature of 90°C, and stirred to guarantee homogeneous solution for 10 minutes. Thereafter, 50ml of 0.4M thiourea $(SC(NH_2)^2)$ as S₂- ion source was added into the mixed solution with Zinc to Sulphur (Zn:S) molar ratio 1.0, 1.5, 2.0. Thereafter, the pre-clean bases were dipped vertically using substrate holder for 60 minutes. After completion film deposition. The films were removed and rinsed with redistilled water to take off soluble impurities and dried with N₂ gas. Thin, uniform and colorless ZnS films were recorded via double beam spectrophotometer (Schimadzu UV-probe 1650 Japan).

Results and Discussion

XRD styles are displayed in Fig. 1 show XRD pattern of ZnS film at 0.05M, can be observed appearing peaks at 2θ = 28.55°,47.51°, 56.28° and 69.52° which matched with (111), (220), (311) and (400) crystalline planes respectively, where the peak refer to the cubic ZnS phase. All the above mention planes refer to the polycrystalline ZnS with cubic phase. The diffraction intensity increases with increasing the molarity due to film thickness increasing and this implies a larger number of Bragg planes. The preferred peak was (111) plane and agree with the standard (ICDD No.05 -0566), it is obvious that, Bragg's peaks became more intense for higher molarity indicating a clear improvement in crystallinity. This behavior appreciably a constant procedure for all films were prepared by CBD as reported in literature [32, 33].

The grain size D of ZnS film was estimated via Scherrer's equation [34-36]:

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \tag{1}$$

Where λ is the wavelength of X-ray, \Box is (FWHM) after making a suitable baseline correction.

The grain size was increased from 19. 74 nm to 24.82 nm with molarity increasing from 1.0 M to 2.0 M [35-38]. and the diffraction peaks become more strong and acute which marked that the grains be larger and the crystal fineness was enhanced. The variation in grain size could be attributed to cluster by cluster deposition and ion by ion deposition[7]. Table 1 shows that the strain(%) parameter decreases are (17.55 nm) to (13.96 nm) with molarity increasing from 1.0 M to 2.0 M thin films respectively, The dislocation density (δ) was evaluated utilizing the equation below [37-40]:

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

E =

The lattice strain (ε) is evaluated using the equation below [41-43]:

$$= \frac{\beta cos\theta}{4}$$
(3)

It can be seen that the value of ε (Table 1) increases With increasing with molarity increasing from 1.0 M to 2.0 M thin films respectively, Values of structural parameters are shown in Table. 1

Figure (2) displays FWHM, *D*, Dislocation density and Strain as a function of the prepared films, It notes the inverse relationship between Crystallite size and other parameters.



Fig.1. XR	D styles of t	he prepared films
	2	1 1

Table 1. D , E_g and structural coefficient of the grown films.								
Molar Observed	(hkl)	2 🗆	FWHM	<i>D</i> (nm)	E _g (eV)	$\delta \ (\times \ 10^{14}) (lines/m^2)$	3	
	Plane	(°)	(°)				(x10 ⁻⁴)	
1.0	111	28.55	0.39	19.74	3.55	25.66	17.55	
1.5	111	28.37	0.37	21.15	3.45	22.35	15.65	
2.0	111	28.05	0.33	24.82	3.35	16.23	13.96	



Fig. 2. FWHM (a) D (b) δ (c) ε (d) of the grown films.

Fig3. Shows AFM images to get surface features like root mean square (rms) or average roughness R Shown in Table 2. When taking two images with dimensions, Figure 3 $(a_1, b_2 \text{ and } c_1)$ 3D. Films are dole out orderly in the form of small granules. Figure 3 $(a_2, b_2 \text{ and } c_2)$ Shows curved volumetric distribution for crystalline granules where difference with molarity from 1.0 M ,1.5 M 2.0 M thin films respectively, From Figure 3 $(a_3, b_3 \text{ and } c_3)$. R and rms values of (7.57, 6.89 and 5.14) nm and (8.96, 8.09 and 6.00) nm, respectively, were determined for the surface roughness with molarity. The above analysis assure that R and rms are increase with molarity increased .

Table (2) offers AFM parameters A_P.



Fig.3. AFM images (a₁, b₁ and c₁), granularly distributed (a₂, b₂ and c₂) and A_P versus doping (a₃, b₃ and c₃). **Table 2.** A_P of the grown films.

Molar Observed	Average Particle size	R	rms	
	nm	(nm)	(nm)	
1.0	92.74	7.57	8.96	
1.5	91.97	6.89	8.09	
2.0	86.54	5.14	6.00	

Fig. 4. shows the transmittance T spectra. The maximum T was monitored at 95%, 85% and 80% for 1.0M, 1.5M and 2M respectively

The absorption coefficient (α) is specified by [44--46]:

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

Where (t) is film thickness, A is absorbance. Fig. 5. displays α versus energy photon (hv), films have ($\alpha > 10^4 \text{cm}^{-1}$) refereed to direct electronic transitions.

The bandgap energy E_g was determined by Tauc's relation [47-50]:

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

where, **A** is a constant, A plot of $(\alpha hv)^2$ versus (hv) was displayed in Fig. 6. E_g of the intended films were 3.55 eV, 3.45 eV and 3.35 eV. These results agree with references [51-54].

Table (1) represent the values of E_g .

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Fig. 6. $(\alpha hv)^2$ against hv of grown films.

Conclusion

ZnS thin film was grown utilizing CBD method. The XRD styles of the synthesized films offer a preferred orientation of (111) plane, *D* was increased from 19. 74 nm to 24.82 nm with molarity increasing from 1.0 M to 2.0 M, the strain parameter decreases are (17.55 nm) to (13.96 nm) with molarity increasing from 1.0 M to 2.0 M thin films respectively, AFM image offered that The grain size was noticed in the region of 92.74 nm to 86.54 nm for ZnS with increase of molar concentration from (1.0 M and 2 M). transmittance decreased by increasing from 1.0 M to 2.0 M thin films respectively. Transmissions was observed at 95%, 85% and 80% for 1.0 M, 1.5 M and 2 M respectively, α increased with increasing of molarity, The optical gap offer a decrement with the increment of molar concentration ratio from (3.55 -3.35 eV).

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