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Characterization of Zinc Sulphide Thin Film Prepared by Electrodeposition Method

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Abstract: Zinc sulphide (ZnS) thin films have been successfully deposited on a glass substrate Indium Tin oxide (ITO) by electrodeposition technique. The absorbance was measured using M501 UV-visible spectrophotometer in the wavelength range of 300-900nm. Zinc sulphide (ZnS) Thin films were investigated at room temperature. XRD analysis showed that the Zinc sulphide (ZnS) Thin films, so deposited, exhibit hexagonal (wurtzite) structure with a preferred orientation along (002) plane.
Keywords: ZnS, Thin Films, Electrodeposition, Electrical, Structural and Optical Properties.

Introduction

Zinc sulphide (ZnS) is a II-VI compound semiconductor it is widely applied in the optoelectronic applications consisting of light emitting diodes with short wavelength, electroluminescent devices, and solar cells. For the photovoltaic applications, ZnS thin film is also transparent in all wavelengths of solar spectrum and has high absorption for the wavelength. ZnS has become a promising material in many applications; it is suitable for red, blue and green light, thin film transistors, infrared coating material, photoelectrochemistry, laser screens, n type window layer thin film herterojunction, photodetector, ultrasonic transducers. Many techniques including sputtering [1,2], molecular beam epitaxy [3], pulsed laser deposition [4], chemical vapor deposition [5], successive ionic layer adsorption and reaction [6], spray pyrolysis [7], and chemical bath deposition (CBD) [1, 8] have been proposed to fabricate the ZnS thin films. In electrodeposition method, to prepare thin films substrates are immersed into separately placed cationic and anionic precursors and precipitate formation in the solution, i.e. wastage of the material was thus avoided. Also, electrodeposition can be used to deposit compound materials on a variety of substrates such as insulators, semiconductors and metals. Electrodeposition method and its potential application for large area deposition make it very attractive; Easy control on film thickness by adjusting number of deposition cycles is the beauty of this method. In this study, the electrodeposition method was performed to prepare the ZnS Thin films.

Experimental Procedure

ZnS thin films were prepared on the glass substrates Indium Tin Oxide (ITO) by electrodeposition method. The substrates were cleaned ultrasonically by detergent solution, acetone, and deionized water, respectively, to ensure the complete cleanness. The reaction bath for the deposition of Zinc Sulphide (ZnS) was composed of four electrolyte Zinc Chloride ($ZnCl_2$), hydrated Sodium Sulphide ($Na_2S.H_2O$), Potassium tetraoxosulphate VI (K_2SO_4) and Tetraoxosulphate VI acid (H_2SO_4). The growth of ZnS films were determined with respect to the different bath parameters which includes time of deposition and substrate for the deposition, the concentration and the P^H of the solution were kept constant throughout the experiment. The P^H value was maintained at 2.5 while the concentration of the compounds were maintained as prepared i.e **0.1M** $ZnCl_2$, **0.1M** $Na_2S.H_2O$**, 0.01M** K_2SO_4, and **0.1M** H_2SO_4 with the following reactions;

$$ZnCl_{2(aq)} + Na_2S.H_2O_{(aq)} \rightarrow ZnS_{(s)} + 2NaCl_{(aq)} + H_2O \quad (1)$$

25cm^3 each of $ZnCl_2$ and $Na_2S.H_2O$ was measured into100cm^3 beaker using burette. 5.00cm^3 of K_2SO_4 was measured into the same 100cm^3 beaker containing $ZnCl_2$ and $Na_2S.H_2O$ respectively to serve as the inert electrolyte which helps to dissociate the Zn from the $ZnCl_2$ and S from the $Na_2S.H_2O$ to form the required ZnS film on the substrate and the solutionwas acidified with 5.00cm^3 of dilute H_2SO_4 which serves to adjust the P^H value. The entire mixture was stirred with the glass rod to achieve uniformity.

In each of the reaction baths prepared, a glass substrate and carbon electrode were connected to a DC power supply source and the voltage was maintained at **5V** for different time intervals.

Table1. Variation of Parameters ZnS Thin films

Slide No.	Volume of H_2SO_4 (cm^3)	Volume of K_2SO_4 (cm^3)	Volume of $Zn(NO_3)_2.6H_2O$ (cm^3)	Volume of $Na_2S.6H_2O$ (cm^3)	Voltage (V)	Time (minutes)
A	5.00	5.00	25.00	25.00	5.00	5.00
B	5.00	5.00	25.00	25.00	5.00	7.00
C	5.00	5.00	25.00	25.00	5.00	9.00
D	5.00	5.00	25.00	25.00	5.00	11.00

Electrical Properties

ZnS thin films are known to be of n-type conductivity. The resistivity of the films is droped from 2.5 × 10^8 to 1.5 × 10^8 $(\llbracket \Omega m) \rrbracket^{-1}$. The low resistivity for the buffer layers in solar cells helps to improve the conversion efficiency. However, the resistivity should not be too low due to the inevitable defects in solar cells fabricated during the actual production process. Those defects can cause short circuit, furthermore, it can drop the open circuit voltage (V_{oc}) and fill factor (FF). However, the buffer layer with high resistivity can effectively overcome those problems caused by defects. As a result, the ZnS thin film with 1.6 × 10^8 $\llbracket \Omega m) \rrbracket^{\uparrow}(-1)$ resistivity is quit suitable for a buffer layer in solar cell. One method which is based on the capacitance and applied potential measurement is called Mott-Schottky relationship [9] for confirming electrical properties of semiconductor materials. The Mott-Schottky relationship can be described as follows;

$$1/C^2 = B \text{ X } [2/ (\varepsilon\varepsilon_\theta \ell N_D \ell A^2)][E_{FB} - (Kt/\ell)] \quad (2)$$

Where ε is the dielectric constant of the semiconductor, A is the surface area of the semiconductor/electrolyte barrier, N_D is the carrier density of the semiconductor, E_{FB} is the flat band potential of the semiconductor, e is the electric charge and ε_0 is the permittivity of the vacuum. For an n-type semiconductor, B is 1. For a p-type semiconductor, B is −1. Therefore, the conduction type, carrier concentration and flat band potential can be estimated by the Mott- Schottky relationship [9].

Table2. Electrical properties of ZnS films

Slides	Thickness, t (nm)	Resistivity, ℓ $(\llbracket \Omega m) \rrbracket^{\uparrow}(-1)$	Conductivity, σ $(\llbracket \Omega m) \rrbracket^{\uparrow}(-1)$
A	246	$2.5x10^{8}$	$3.6x10^{-4}$
B	256	$2.4x10^{6}$	$3.7x10^{-4}$
C	254	$2.4x10^{6}$	$3.7x10^{-6}$
D	276	$1.6x10^{8}$	$2.0x10^{-7}$

Structural Properties

All the deposited ZnS films were white, homogeneous with a good adherence to the substrate. Generally, ZnS material has the hexagonal, wurtzite type or cubic, zinc blende type structure. X-ray diffraction (XRD) technique is used to determine the crystallite size, orientation, lattice constants, phase of the crystal

and structure of ZnS particles. Figure 1 shows the XRD pattern of the deposited ZnS thin films on ITO conducting glass substrate surface showing crystalline structure with some sharp diffraction peaks.

The peaks corresponding to each plane were identified and indexed to hexagonal (wurtzite) structure. Four sharp peaks were observed in the diffractogram at around 2θ values of 16.04°, 26.92°, 33.53° and 59.00° corresponding to(002), (100), (101) and (004) plane of ZnS and has its highest peak at maximum intensity of 37.9 at around 16.04° corresponding to (002) plane of hexagonal ZnS respectively. From XRD, it is evident that the obtained ZnS has a hexagonal phase. The presence of broad peaks in XRD implies presence of thin films which shows that the preferential orientation of ZnS lies along (002) plane of hexagonal ZnS respectively. The rough structures in the graph showed the presence of noise from the diffractometer. The average crystallite size is calculated using Debye Scherer formula

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (3)$$

The average crystallite size from the calculation was found to be 0.152nm. Details pertaining to the crystallite size calculation is given in table 4.1

The FWHM of the XRD peaks may also contain contributions from lattice strain. Therefore, the average strain of the ZnS thin films is calculated using Stokes-Wilson equation

$$\varepsilon_{str} = \frac{\beta\cot\theta}{4} \quad (4)$$

The average strain from the calculation was found to be 3.147.

The dislocation density (δ) which represents the amount of defects in the sample is calculated using the relation

$$\delta = \frac{1}{D2} \quad (5)$$

The inter-planar spacing known as d-spacing is calculated using the relation d_{hkl} by calculating θ values from the peaks of the X-ray spectrum using Bragg's relation

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \quad (6)$$

The lattice parameter is calculated according to the relation

$$a = d(\sqrt{h^2+k^2+l^2}) \quad (7)$$

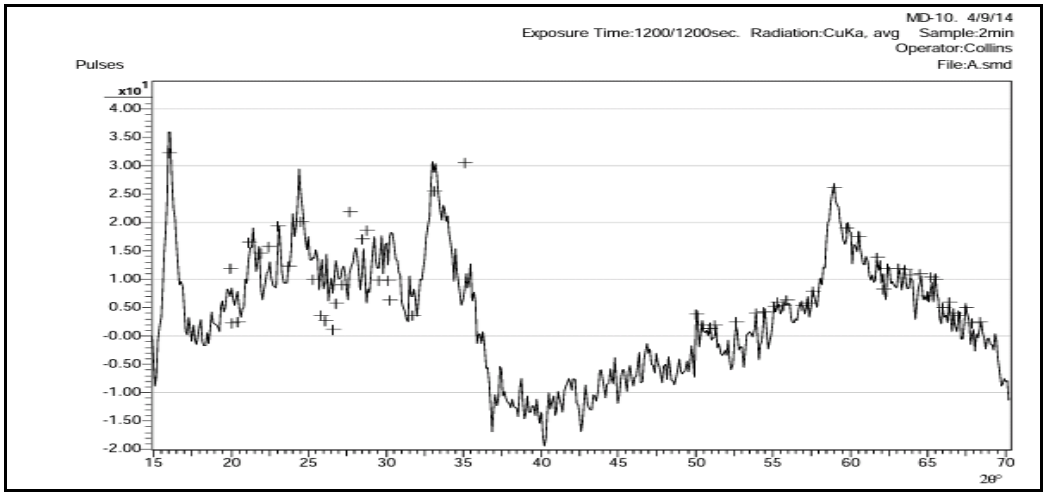

Figure 1: X-ray Diffraction pattern of ZnS

Table3. Structural parameters of ZnS films

Sample	Hkl	θ 2 (degree)	d(°A) measured	d(°A) standard	Lattice constant	FWHM	Grain size d(°A)	Dislocation density×1	Micro strain
A	002	16.04°	5.52	5.53	3.82	0.78	1.77	0.319	1.401
	100	19.97°	4.44	4.45		7.82	0.18	0.860	1.109
	101	20.06°	4.42	4.43		1.00	1.40	0.510	1.420
	103	20.43°	4.34	4.37		0.66	2.11	0.225	0.927
	004	21.18°	4.19	4.20		0.65	2.14	0.218	0.880

Absorbance Of The Deposited ZnS Films

The optical absorption spectral of ZnS nanoparticles is shown in figure 2. These spectral reveal that the films grown under the same parametric conditions at room temperature and at varying deposition time of 5mins, 7mins, 9mins and 11mins for slides A, B, C and D have low absorbance in the visible and near infrared region. However, absorbance of the films was found to be high in the ultraviolet region with peak around 360nm which is in accordance with the result obtained in [10] reported that the enhanced absorption is observed in the neighborhood of λ = 360nm. From the graph, it was observed that slide A and slide B are relatively constant, slide C has low absorbance in the visible and near infrared region of about 1.3% and high absorbance of about 1.5% in the ultraviolet region while slide D has a different trend to the other slides having a low absorbance in the ultraviolet region of about 1.1% and a high absorbance in the infrared region of about 1.5%. The overall observation shows that the absorbance is high and increases with deposition time. This high absorbance in the UV region makes ZnS useful in p-n junction formation of solar cells with other suitable thin film materials for photovoltaic applications, while the low absorption of ZnS in the infrared makes it useful for window coatings in cold temperate regions of the world.

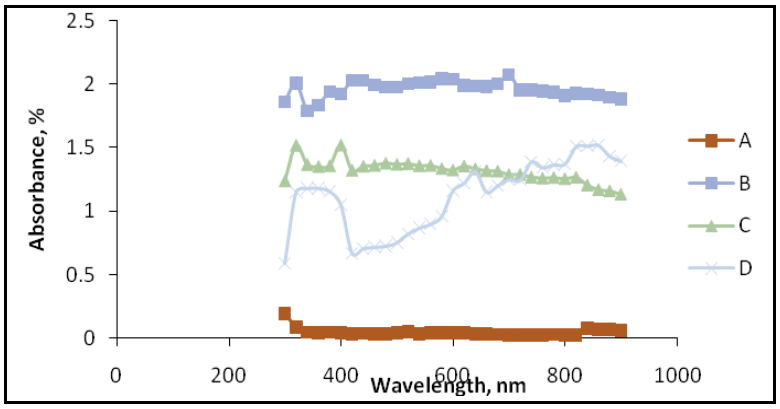

Figure2. Plot of absorbance as a function of wavelength of incident radiation

Transmittance Of The Deposited ZnS Films

The transmittance spectral (%) of the ZnS film is shown in figure 3 the transmittance spectral reveals transmission of above 0.95% in the infrared region and transmission of about 0.63% in the ultraviolet region for slide B. It was observed that slide A and slide C are relatively constant while slide D has a low transmittance in the near infrared and visible region of about 0.03% and a high transmittance in the ultraviolet region of about 0.26%. The general observation show that the overall films demonstrate more than 60% transmittance at wavelength longer than 400nm which is comparable with the values for the ZnS thin films deposited in [11] using SILAR method. Below 400nm, there is a sharp fall in the transmittance spectral of the films, which is due to the strong absorbance of the films. Films of low transmittance in the infrared region is used in window coatings in hotter regions of the world like Nigeria while films with high transmittance in the ultraviolet region is useful in photosynthetic coatings because they exhibit selective transmittance of photosynthetic active radiation (PAR) and also used as reflector and dielectric filter.

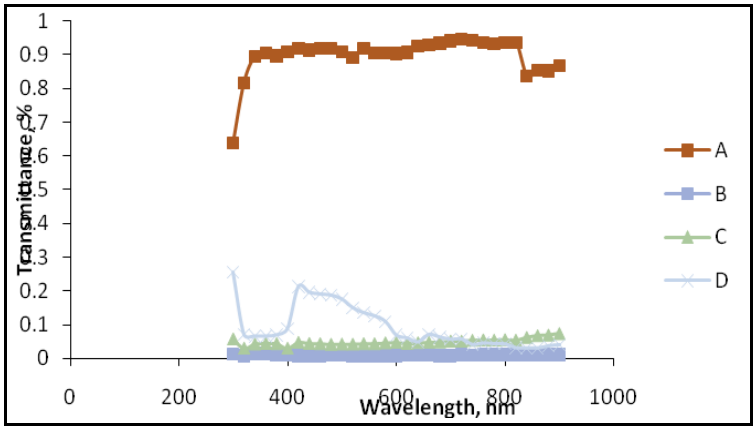

Figure 3 Plot of transmittance as a function of wavelength of incident radiation

Conclusion

It has been illustrated in this work that electrodeposition (ED) method was used to deposit semiconductor ZnS films. The X-ray diffraction (XRD) confirmed the hexagonal crystalline structure of ZnS with an average crystallite size of 0.152nm as calculated using the Debye Scherrer's equation. The deposited film showed polycrystalline structure. The effect of substrate on the deposited film show the presence of broad peaks indicating the presence of Thin films. The film has its highest peak around 16.04° at a maximum intensity of 37.9 which gave the preferential orientation of (002) hexagonal phase respectively using the scattering selection rules.

The electrodeposition technique is one of the fastest, easiest and simplest method of growing adherent thin films as the thickness of the coating may berelatively controlled. The disadvantage associated with the electrodeposition ethod is that it is very expensive as the cost of purchasing the required apparatus is relatively high and not found everywhere except in special places.

Another disadvantage is that the electrodeposition method requires constant supply of power and in the case of power failure as part of what we experience today in our country would need the back up of an alternative energy resource (for instance, fuel) to supply power for the deposition process which requires cost.

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