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Research Paper

STUDY OF ZINC SULPHIDE THIN FILMS OBTAINED BY DIP COATING METHOD

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ABSTRACT

Thin films of Zinc Sulphide (ZnS) were prepared by dip coating method. These films were investigated as a function of [S]/[Zn] ratio in the solution. ZnS thin film was characterized by X-Ray diffraction technique (XRD), Scanning Electron Microscopy (SEM), Automatic force microscopy (AFM), UV-VISIBLE Spectrophotometer, Hot probe, Four probe and Hall Effect technique. The XRD Patterns of the synthesized film show the preferred orientation of (111) planes, confirming the Cubic structure of ZnS. Surface morphology of thin film were studied using Scanning Electron Microscopy. The optical properties of the prepared film were characterized by UV-VIS spectrometry and show the presence of direct transition with band gap energy about 3.03 eV. The hot probe and four probe method shows n-type conductivity of the prepared ZnS film. Here the carrier concentration and mobility were measured.

1. INTRODUCTION

Zinc Sulphide (ZnS) is an inorganic compound prototypical II-VI semiconductor with an ability to adopt structures related to many of the other semiconductors, such as gallium arsenide. ZnS in cubic form has a band gap of about 3.54 eV and in the hexagonal form has a band gap of about 3.91eV [1-24]. ZnS can be doped as either an n-type semiconductor or a p-type semiconductor. Zinc Sulphide (ZnS) thin film is receiving ever increasing attention owing to its potential use in applications like Opto-electronics devices such as LED in blue to ultraviolet spectral region due to its wide band gap and n-type conductivity [3,7 and 18-24], in the area of optics as a reflector due to its high refractive index 2.35 and dielectric filter due to its high refractive index & high transmittance in the visible range respectively [1,2 and10-16]. Zinc Sulphide thin film is highly suitable as a window layer in heterojunction photovoltaic solar cells, because the wide band gap decreases the window absorption loses and improves the short circuit current of the cell [2,5,10,12,19,21 & 22]. Zinc sulphide, with addition of few ppm of suitable activator, is used as phosphor in many applications, from cathode ray tubes through X-ray screens to glow in the dark products. It also exhibits phosphorescence due to impurities on illumination with blue or ultraviolet light. Zinc Sulphide is also used as an infrared optical material, transmitting from visible wavelengths to just over 12 micrometers.

ZnS thin films can be prepared using various techniques including spray pyrolysis [1,2,16], Chemical Bath Deposition (CBD) [3,6-9,15,17-20], RF magnetron sputtering [4], sol-gel deposition [10,11], cathodic electro deposition [12] and dip coating [5,10 and 11]. However, dip coating technique for preparing ZnS thin films [5] is major concerned in regarding the cost of deposition process and waste management. This technique appears as an interesting technique because it is inexpensive, simple and capable of deposition of optically smooth, uniform and homogeneous layers. Due to its simple coating technique involves processing at ambient atmosphere, it is easy to incorporate it into mass production. Again in comparison with CdS, the advantages of ZnS include its non-toxic [4,5,11,12 and 21] and environmentally safe handling as well as its ability to provide better lattice matching to CIGS absorbers having energy band gaps in the range of 1.3 to 1.5 eV compared with CdS, which transmits even higher energy photons and increases the light absorption in the absorber layer [4]. In the present work ZnS thin film was obtained by Dip coating method on a glass substrate. The deposited thin films were characterized using X-Ray diffraction technique (XRD), Scanning Electron Microscopy (SEM), Automatic Force Microscope (AFM), UV-VISIBLE Spectrophotometer, Hot probe, Four probe and Hall Effect method.

2. EXPERIMENTAL DETAILS

ZnS thin films were prepared using the dip coating method. Prior to the deposition of ZnS, glass substrate was cleaned with Methanol, Acetone, Trichloroethylene and Deionized (DI) water. The precursor solution for the dip-coating was prepared by dissolving Zinc Acetate and Thiourea in methanol. The glass substrate was dipped into this solution and then kept at 473°K for 5 minutes to promote thermolysis. In heat treatment

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process, the metal salt and thiourea decomposes and gives raise to formation of ZnS phase on the substrate. This process was repeated five times. The sample was prepared with this method by keeping S/Zn molar ratio equal to 0.7, indicating film is Zn-rich and S-deficient. This film was characterized using X-Ray diffraction technique (XRD), scanning electron microscopy (SEM), Atomic force microscopy (AFM) and Optical Spectroscopy. The crystalline structure of the films was analysed using a D2 PHASER – The Second Generation Bench top X-Ray Diffractometer using CuKα radiation *lambda=1.54056 angstroms.* The surface topography and composition was studied using JSM-6010LA high performance SEM. PerkinElmer UV-VIS double beam spectrophotometer (LAMBDA-35) was used. Four point probe, hot probe, and Hall effect measurement were used to measure Electrical properties of the ZnS films such as type of conductivity, carrier concentration and the mobility of carriers.

3. RESULTS AND DISCUSSIONS

3.1 Structural Properties

X-ray diffraction patterns of the thin film prepared at S/Zn molar ratio equal to 0.7 is shown in Figure 1. The sample is almost amorphous but exhibit three rough peaks corresponding to diffraction of the (111), (220) and (311) planes of the cubic phase [9,16] are as per standard JCPDS-ICDD (card no. 77-2100, 80-0020) [19]. The average nano-crystalline size (D) was calculated using Debye-Scherrer equation formula [9]. Three peaks at the angles 28.6°, 47.7°, and 56.5° reveal a cubic lattice structure and can be assigned to the (111), (220), and (311) planes respectively. Films prepared from a solution containing Zinc acetate as a Zn precursor gave a S/Zn ratio below 0.85, a rough surface, and an amorphous structure justifies as per M.C. Lopez et al [2] and Li et al [3]

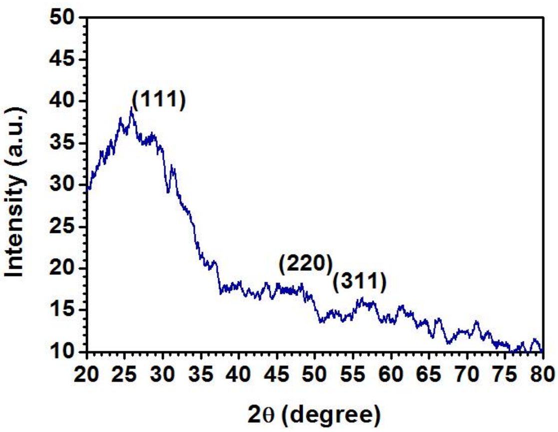

Figure 1 XRD pattern of ZnS obtained with S/Cd molar ratio 0.7

The d-spacing for all samples can be evaluated from the position of the major peak at about 28.6° and by the Bragg condition,

$$n\lambda = 2d\sin\theta \qquad (1)$$

Where, n is the order of diffraction, λ the wavelength of the incident X-ray, θ the diffraction angle, d the distance between the planes parallel to the axis of incident beam.

In addition, the average grain size of the crystallites has been calculated using Scherrer's equation,

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (2)$$

Where,

constant k is a shape factor usually = 0.94,

β is full-width at half maximum (FWHM) of the peak

Using the size of crystallites, the dislocation density can be found,

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

The lattice strain in the film can be found by,

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

The average crystallite size was found to be 14 nm. The dislocation density was found to be 0.005 and the strain present in the film is 0.0103 which indicates the stability of the crystal structure in the prepared film.

3.2 Surface Morphology

The surface morphology of the thin film plays a crucial role in any optoelectronic devices. In the present study the surface morphology of the prepared ZnS film is observed by SEM as shown in Figure 2. Surface of the film appears like smooth, uncolored, reflecting and well adhered to the glass substrate. As discussed in the XRD section the film contains the nano-sized crystalline structure of the atoms, which is verified by the SEM [1-4,7,8,12,17-23].

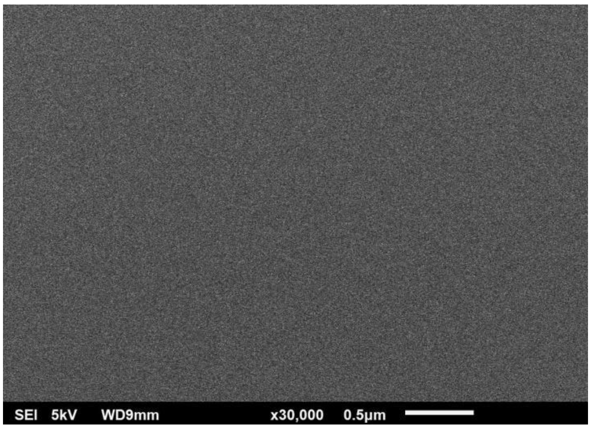

Figure 2 SEM micrograph of the ZnS thin film

Atomic force microscopy (AFM) is also called as Scanning Force microscopy (SFM), is a basic technique and inevitable for all nanoscopic research [12]. The AFM image of ZnS is shown in Figure 3. Surface topological features of ZnS thin film are observed under AFM 3D pattern. The micrograph at 5µm*5µm exhibit an uniform surface with cone like grains covering the ZnS surface can be seen for this sample.

Sa Average Roughness, Sq Root Mean Square Roughness, Sp Maximum Peak Height, Sv Maximum Valley Depth, Sz the Maximum Height of the Surface were measured by Automatic Force Microscope. Sp, Sv, and Sz are parameters evaluated from the absolute highest and lowest points found on the surface. Sp, the Maximum Peak Height, is the height of the highest point, Sv, the Maximum Valley Depth, is the depth of the lowest point (expressed as a negative number) and Sz the Maximum Height of the Surface), is found from,

Sz = Sp – Sv. Here it is -8.6 nm.

The surface roughness, RMS average value and heights were determined by AFM analysis. The average roughness was found 1.5 nm and Root mean square roughness was found 2225 pm. AFM observation showed rough distribution of ZnS over the thin film.

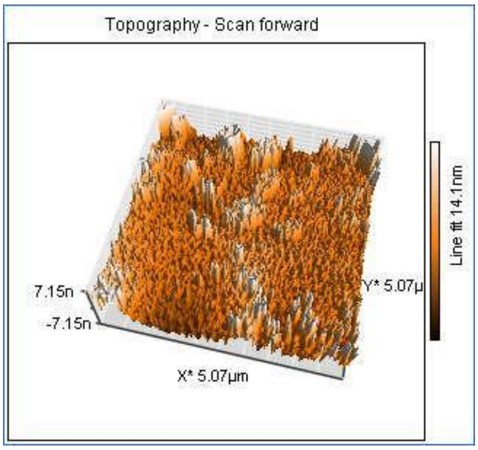

Figure 3 AFM 3D image of the ZnS thin film

3.3 *Optical Properties*

The optical properties of ZnS film were observed using the Transmission spectra of the film, which is measured using UV-VIS spectrophotometer. The transmission spectrum of ZnS film as a function of wavelength is shown in Figure 4.

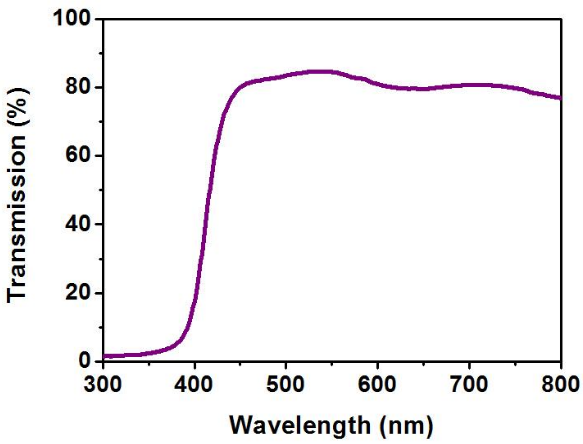

Figure 4 Optical Transmission spectrum of the ZnS film as a function of wavelength

The transmission behaviour of the film clearly indicates its high value of transmission around 80% value above 450 nm wavelength. Films prepared from a solution containing Zinc acetate as a Zn precursor gave a S/Zn ratio below 0.85, a transmission lower than 80% in the visible region justifies as per M.C. Lopez et al [2] and Li et al [3]. The observed value closely matches with the reported value of ZnS thin films prepared by different method [1,3,4,7,20,21]. From the values of transmission spectra, optical band gap was determined using Tauc relation,

$(\alpha h\nu)^2 = B(h\nu - E_g)^m$

where, E_g is the energy band gap and B is constant.

Here, considering direct band gap nature of the material, the value of m is taken to be 0.5. The Tauc plot drawn using the above mentioned equation is shown in Figure 5. The extrapolation of Linear portion of the $(\alpha h\nu)^2$ to zero indicates the band gap of the film.

As per the extrapolation of the linear part of the curves to the intercept on horizontal axis, the band gap of sample is about 3.03 eV, which is in good agreement with the bulk value ZnS [1,2,4,21]. This high value of transmission and the ~ 3 eV band gap can be very much useful in the field of solar cell and optical sensor.

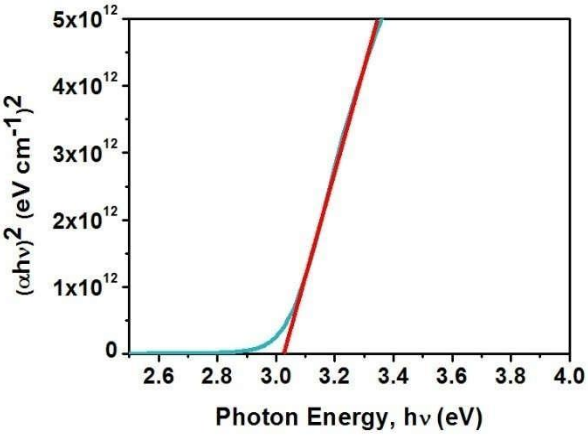

Figure 5 Variation of $(\alpha h\nu)^2$ vs hν for ZnS thin film

3.4 *Electrical Properties*

The Hot probe, Four point probe method and Hall Effect measurement were used to find the electrical properties of the prepared ZnS films at room temperature. The hot probe and four probe method shows n-type conductivity of the prepared ZnS film. It was found that the carrier concentration and mobility was about 9.5×10^{20} and 10 cm^2/Vs respectively measured using Hall-effect Method. This observed value closely matches with the reported values of chemically deposited ZnS thin films [6].

4. CONCLUSION

Cubic uniform ZnS thin films were prepared using Dip Coating method and the characterized using different analytical techniques. The grown ZnS films are crystallized in the cubic structure and were aligned perpendicular to the (111) plane. The SEM shows the uniform film over the glass substrate. The ZnS film exhibited good optical properties with a relatively high transmittance of 80% in visible region, and the optical band gap is about 3.03 eV. Films prepared from a solution containing Zinc acetate as a Zn precursor gave a S/Zn ratio below 0.85, a rough surface, a transmission lower than 80% in the visible region and an amorphous structure. N-type conductivity, carrier concentration of 9.5×10^{20} cm^{-3} and mobility of 10 cm^2/Vs, shows its future use as a top transparent n-type layer in many optoelectronics devices.

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