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Research Paper

STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF CHEMICALLY DEPOSITED ZINC SULPHIDE THIN FILMS

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ABSTRACT

Zinc Sulphide (ZnS) thin films were deposited by dip coating method on a glass substrate. The synthesized thin film was characterized by X-Ray diffraction technique (XRD), Scanning Electron Microscopy (SEM), UV-VISIBLE Spectrophotometer, Four probe method and Hall Effect method. 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 deposited film were characterized by UV-VIS spectrometry and show the presence of direct transition with band gap energy about 3.2 eV. The hot probe and four probe method shows n-type conductivity of the prepared ZnS film. In addition to that the carrier concentration and mobility was in the range of 10^{20} cm^{-3} and 10 to 17 respectively measured using Hall-effect Method.

1. INTRODUCTION

Zinc Sulphide (ZnS) thin film is an important semiconductor material receiving ever increasing attention owing to its potential use in applications like Opto-electronics devices such as Light Emitting Diode in blue to ultraviolet spectral region due to its wide band gap of E_g=3.5-3.84 eV [1,2,5,6,8-13,17,19-22] and n-type conductivity [3,7,18,22], in the area of optics as a reflector because of its high refractive index (2.35) and dielectric filter due to its high refractive index & high transmittance in the visible range respectively [1,2,10,11,13,14,16]. ZnS 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].

There are various techniques used to deposit ZnS thin films, 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 [5,10,11]. 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. Again, due to its simple coating technique involves processing at ambient atmosphere, it is easy to incorporate it into mass production. Also in comparison with CdS, the advantages of ZnS include its non-toxic [4,5,11,12,21] 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]. Zinc Sulphide thin film was synthesized by Dip coating method on a glass substrate. The coated thin film was characterized by X-Ray diffraction technique (XRD), Scanning Electron Microscopy (SEM), UV-VISIBLE Spectrophotometer, Four probe method and Hall Effect method.

2. EXPERIMENTAL DETAILS

Chemicals: Zinc Acetate, Thiourea, Methanol, Acetic Acid, Acetone & Trichloroethylene. ZnS thin films have been deposited 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 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

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S/Zn molar ratio equal to 1.11, indicating film is S-rich and Zn-deficient. This film was characterized using X-Ray diffraction technique (XRD), scanning electron microscopy, Atomic force microscopy and Optical Spectroscopy. The crystalline structure of the films was analyzed 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 mobility of carriers.

3. RESULTS AND DISCUSSIONS

3.1 Structural Properties

Prepared ZnS film was uniform transparent and colorless. The XRD pattern of prepared ZnS film is shown in Figure 1. Diffractogram of the thin film shows sharp peaks at 2θ values of about 28.95˚, which is characteristic of the cubic structure XRD pattern of ZnS (JCPDS card 36-1451), with a preferred orientation along the (111) direction [2].

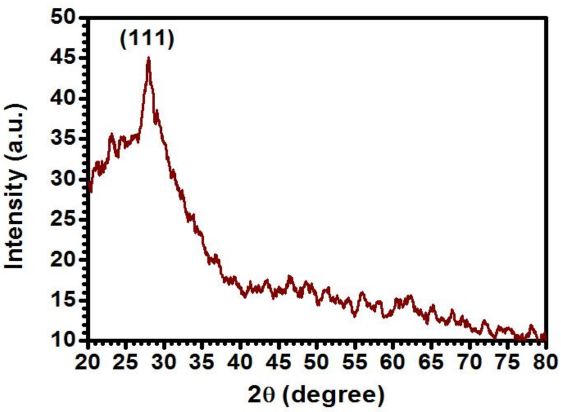

Figure 1 XRD pattern of ZnS thin film obtained by S/Zn molar ratio = 1.11

The average crystallite size of ZnS is estimated by using the well-known Scherrer's formula,

$$D=0.94\lambda/\beta\cos\theta,$$

Where,

λ=1.5404Å for CuKα,

β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians, and

θ is the Bragg's angle [10,19].

The average crystallite size was found to be 7 nm. Further the strain present in the film is 0.021, 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.

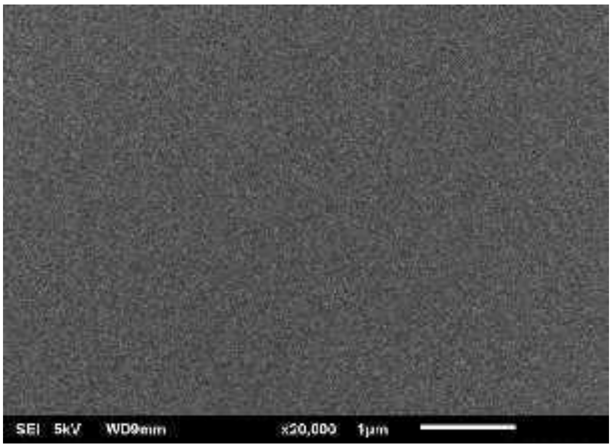

Fig. 2 SEM image of the ZnS thin film

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 the ZnS film is shown in Figure 3.

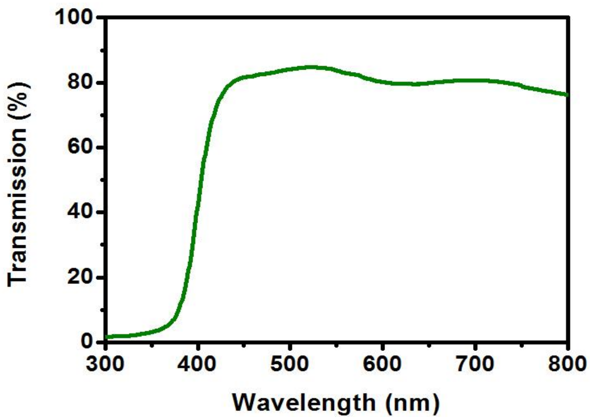

Figure 3 Transmission spectrum of the ZnS films in the wavelength range of 300 – 800 nm

The transmission behavior of the films clearly indicates its high value of transmission (around 80 %) value above 420 nm wavelength. 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 4. 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 3.18 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 optical sensor and solar cell.

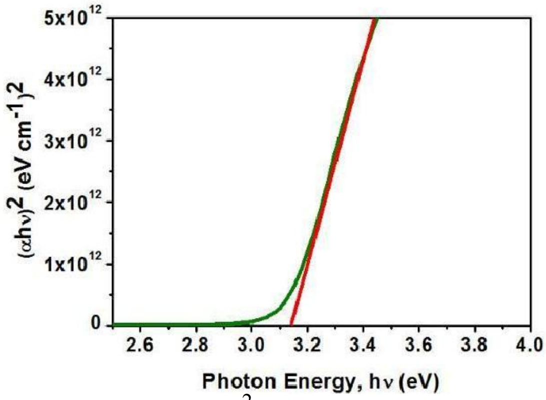

Fig. 4 Plot of $(\alpha h\nu)^2$ as function of energy for ZnS thin film

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. In addition to that the carrier concentration and mobility was in the range of 10^{20} cm^{-3} and 10 to 17 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 3.18 eV. N-type conductivity, carrier concentration of 10^{20} cm^{-3} and mobility in the range of and 10 to 17 cm^2/Vs, shows its future use as a top transparent n-type layer in many optoelectronics devices.

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