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Structural and Optical Properties of Zinc Sulfide Thin film prepared by sol-gel Spin Coating method

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Abstract : Metal Sulfide nanoparticles have attracted considerable interest because of their unique semiconducting and electronic properties. ZnS thin films have been deposited on glass substrates by spin coating method with Zinc Nitrate as starting material. The samples were synthesized by mixing Zinc Nitrate and Thiourea in Isoproponal. The crystal structure, orientation and surface morphology were investigated by X-Ray diffractometer (XRD) and Scanning Electron Microscopy (SEM). XRD pattern reveals the hexagonal structure of ZnS thin films. Optical properties were studied using UV-visible spectroscopy. The film shows good optical properties with high absorption and energy band gap value. These prepared films can be used for solar cell applications.
Keywords : Zinc Sulfide thin films; Spin coating method; structual and optical properties

I. Introduction

In recent years, most researches in material sciences have been focusing on semiconductor materials with wide band gap. One of them is Zinc sulfide (ZnS) and it is a promising material for its uses in various application devices. In optoelectronics, it can be used as a Light emitting diode in the blue to ultraviolet spectral region owing to its wide band gap 3.6eV at room temperature [1]. Zinc Sulfide has found wide use as a thin film coating in optical and microelectronics industries. Accordingly the synthesis and characterization of zinc sulfide via different techniques have attracted considerable attention. In providing ZnS, various techniques used including sputtering [2], evaporation [3], chemical bath deposition (CBD) [4], SILAR [5], sulfur oxidation method and many others. ZnS thin films have also been proposed as potential replacement for the window layer in chalcopyrite based solar cells [6–8] currently, the preferred choice of window layer material for chalcopyrite-based solar cells is cadmium sulfide (CdS), due to its superior electrical performances and simple set-up [9]. However, cadmium is highly toxic and would present significant environmental obstacles towards large scale-integration and general public acceptance of chalcopyrite based solar cell. In contrast, ZnS is deposited using non-toxic, abundant elements that posse's higher band gap than CdS, which eliminate absorption loss and improve overall solar cell power conversion efficiency. In the present work, ZnS thin film was synthesized on glass substrate by spin coating techniques. The coated film was characterized to examine their physical properties.

Experimental

The sol–gel technique for preparing zinc sulfide nanoparticles has become very attractive due to its simplicity and ease of scale-up. The deposition of film was carried out by using commercially available glass slides as substrates which were initially boiled in concentrated chromic acid for 30 minutes rinsed in acetone and again in sodium hydroxide for another 30 minutes rinsed in acetone, double deionised water and finally ultrasonically cleaned. All analytical grade (A.R) reagents were used as it's without further purification for the deposition of ZnS thin films. Spin coating method was employed to deposit ZnS thin film onto glass substrates using Zinc Nitrate as Zinc ion source and Thiourea as sulfur ion source. For the preparation of ZnS thin film samples were synthesized by mixing 0.3 m Zinc Nitrate and 0.6 m Thiourea with Isoproponal 80% and 20 % Deionsied water. The prepared solution was dropped on the cleaned glass substrates and the substrates were rotated at 3000 rpm for 80s (Apex Instruments Co SCU – 2008C) and the ZnS films were prepared by repeated coating. After each coating the films were heated at 200^{o} for 10 min to evaporate the solvent and the organic residuals (Pre – heat treatment) and were allowed to cool to room temperature before applying a new coating. The spin coating and pre – heating process was repeated for five times.

II. Result and Discussion

X-ray Diffraction

It has been reported that ZnS may have either cubic or hexagonal structure, depending on the synthesis conditions such as deposition temperature and precursor concentration [10]. The phase purity and crystal structure of these samples were analyzed by using CuKα radiations source in the range of 20^{o} to 60^{o} with 0.050 step size using XPERT – PRO diffractometer. Figure 1 shows the XRD Pattern of the synthesized ZnS film. The diffraction data were in agreement with the JCPDS data for ZnS (JCPDS 72-0163). Three main peaks at (004), (008) and (1011) suggest Hexagonal wurtzite structure with lattice parameter α = 3.820 A˚.[11]

From the X-ray diffraction peaks in Figure 1 the particle size are determined from at the full-width at half-maximum [FHWM] of the XRD peaks. Using the Debye – Scherrer formula:

$$D = 0.89 \lambda / \beta \cos \theta \qquad (1)$$

Where D, λ, β and θ are the average particle size, wavelength of the CuKα radiation, full width at half maximum of the diffraction plane and diffraction angle respectively. The average calculated particle size of the synthesized ZnS nanopracticles is about 99nm.

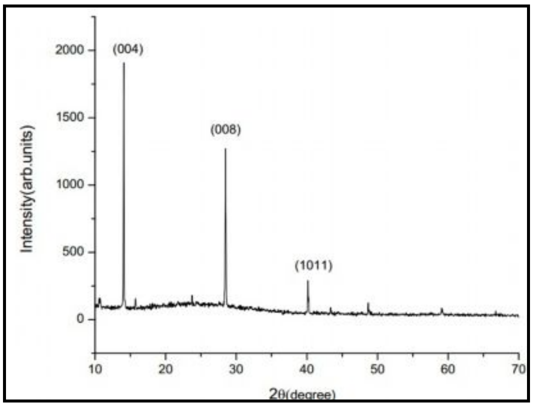

Fig 1. XRD Pattern of as prepared ZnS thin film

SEM Analysis

SEM is a convenient technique to study the microstructure of thin films. Figure 2 shows the surface morphology of ZnS thin films as deposited at room temperature observed by SEM. From the micrographs, it is observed that the as-deposited films are not uniform throughout all the regions but the films are without any void, pinhole or cracks and they cover the substrates well. From the figure, it is clearly observed that the small grains engaged in a fibrous-like structure. The energy dispersive X-ray (EDAX) analysis was used to determine the percentage of zinc and sulfur present in the deposited ZnS film.

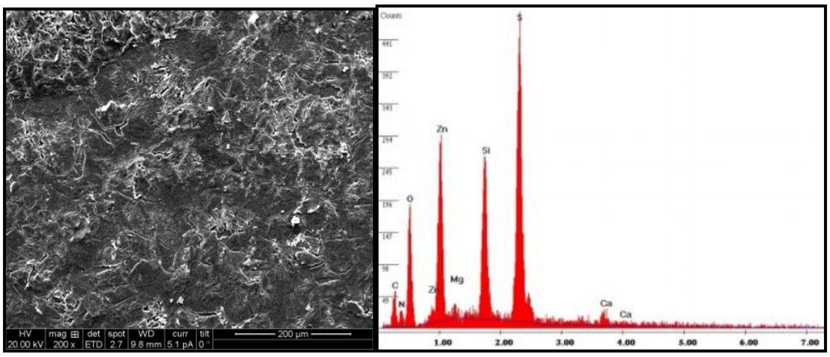

Fig 2 SEM & EDAX of as prepared ZnS thin film

Optical properties

The optical properties were studied by using a UV–Visible Spectrophotometer (JASCO Corp., V – 570). The optical properties of the film deposited on glass substrates were determined from the absorbance measurement in the range of 300–700 nm. Figure. 3 the absorption spectra ZnS thin films. It can be seen that the transmission of the film is greater than ~ 64% for the wavelength values greater than the wavelengths that corresponds to optical band gap [12][13].

Absorbance coefficient α associated the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t) using relation [14] [15]

$\alpha = 2.3026\ A/t$ (2)

The absorption coefficient α was analyzed using the following expression for optical absorption of semiconductors [16]

$(\alpha h\upsilon) = K\ (h\upsilon - E_g)\ n/2$ (3)

Where k is Boltzmann's constant, E_g is separation between valence and conduction bands and n is constant that is equal to 1 for direct band gap semiconductor

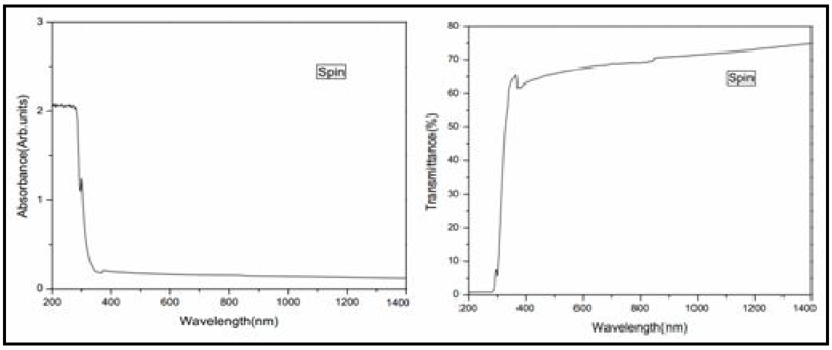

Fig 3 The Absorbance and Transmittance spectra of as deposited ZnS thin film

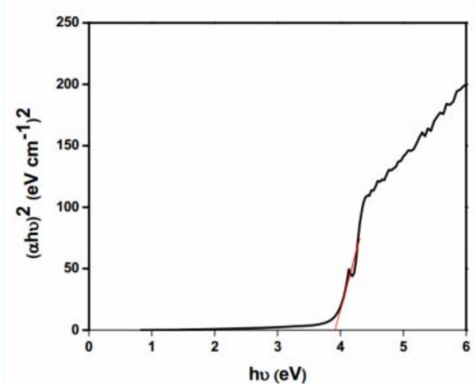

Fig 4 The optical band gap of as deposited ZnS thin film

The optical band gap *Eg* can be estimated from the Tauc plot [17]. Figure 4 shows the optical bandgap of as deposited ZnS thin film. For crystalline semiconductors, n can take values l/2, 3/2, 2 or 3 depending on whether the transitions are direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [18]. The exact values of band gap were determined by extrapolating the straight line portion of the $(\alpha hv)^{1/2}$ versus hv graphs to the hv axis, where *a* is the optical absorption coefficient, hv is the incident photon energy and n depends on the kind of optical transition.

Conclusion

The goal of sol-gel processing is to provide nanoscale control over the structure of a material from the earliest stages of processing. We successfully prepared ZnS thin film through spin coating technique. The films are polycrystalline with hexagonal wurtzite structure. The major peak observed at 14.9^{o} corresponds to (004) crystallographic plane. The bandgap energy value of 3.90 eV was on higher side compared to bulk value indicating quantum confinement.

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