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Preparation and Characterization of Zinc Sulfide thin film deposited by Dip Coating Method

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Abstract

Dip coating method was utilized to fabricate Nanocrystalline Zinc Sulfide(Zns) thin films from a sol – gel method. The sol – gel comprised of Zinc Nitrate, Thiourea and Isoproponal. Samples were prepared on glass substrates by multiple dips on optimization. The as-deposited films were highly adherent and homogeneous. All the films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV – visible spectroscopy. Compositional studies were carried out by EDAX. 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, Dip coating method, structual and optical properties

1. Introduction

Nanomaterials are widely seen as having huge potential to bring advantages to many areas of research and applications. Research work has focused on nanosize devices because of their unique and novel properties and their potential application in various fields of science and technology. Semiconductor nanocrystals, especially II–VI semiconductors, have attracted great deal of attention in the past few decades due to their unique properties and potential applications[1]. ZnS is a direct-transition semiconductor with the widest energy band gap among the groups II–VI compound semiconductor materials, and it is an important material with an extensive range of applications including light-emitting diodes, flat panel displays, infrared windows, optical sensors, optical coating etc.[2]

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 [3], evaporation [4], chemical bath deposition (CBD) [5], SILAR [6], 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 [7–9] 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[10]. 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 bandgap 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 Dip coating techniques. The coated film was characterized to examine their physical properties.

2. 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. Dip 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 This solution was stirred continuously for 2 hours at room temperature for obtaining clear homogenous solution. The stirred solution was taken in a beaker and the well cleaned glass substrates were dipped in the solution for five times at regular intervals at room temperature using automatic dip coating system (Holmarc - HO-TH-02).

3. Result & Discussion

3.1 **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 [11]. The phase purity and crystal structure of these samples were analyzed by using CuKα radiations source in the range of 20^0 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 $\alpha = 3.820$ A˚.[12]

From the X-ray diffraction peaks in Figure1 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.

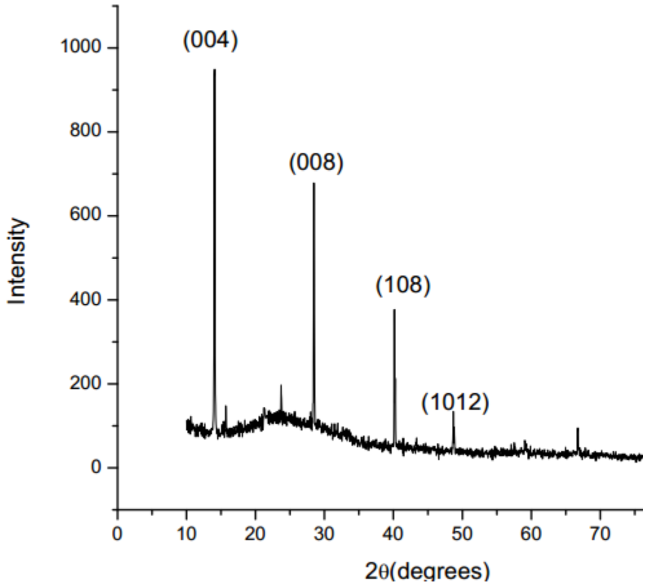

Fig 1. XRD Pattern of as prepared ZnS thin film

3.2 **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 petals-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.

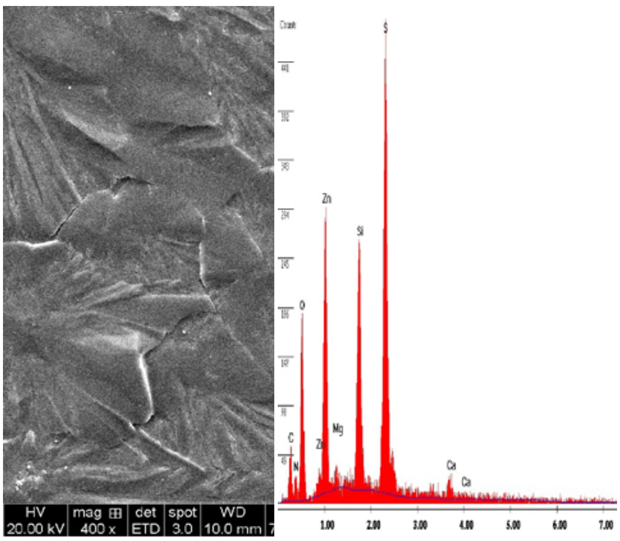

Fig 2 SEM Micrograph & EDAX of as prepared ZnS thin film

3.3 **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 200–1000 nm. Figure. 3 the absorption spectra ZnS thin films. It can be seen that the transmission of the film is greater than 60% for the wavelength values greater than the wavelengths that corresponds to optical band gap [13][14].

Absorbance coefficient α associated the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t) using relation [15] [16]

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

The absorption coefficient α was analyzed using the following expression for optical absorption of semiconductors [17]

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

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. The optical band gap *Eg* can be estimated from the Tauc plot [18]

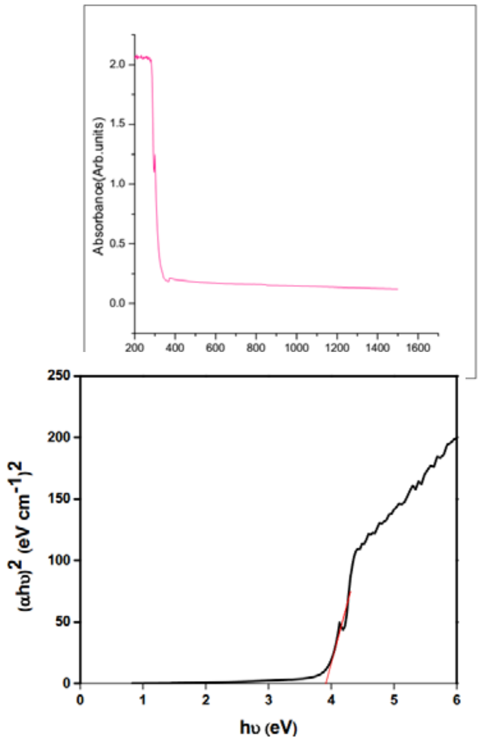

Fig 3 The Absorbance spectra & Band gap of as deposited ZnS thin film

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 [19]. The exact values of band gap were determined by extrapolating the straight line portion of the $(\alpha h v)^{1/2}$ 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.

4. 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 Dip coating technique. EDAX analysis confirms the presence of Zinc and Sulphur. 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 3.70 eV was on higher side compared to bulk value indicating quantum confinement.

Reference

[1] C.S. Pathak, M.K. Mandal, Chalcogenide Lett. 8 (2011) 147.
[2] Xiaosheng Fang, Tianyou Zhai, Ujjal K. Gautam, Liang Li, Limin Wu, Yoshio Bando, Dmitri Golberg, Prog. Mater. Sci. 56 (2011) 175

[3] PORADA Z., OSIOWSKA E.S.: ‘Surface electrical conductivity in ZnS (Cu, C1, Mn) thin films’, Thin Solid Films, 1986, 145, pp. 75–79

[4] ELIDRISSI B., ADDOUA M., REGRAGUI M., BOUGRINE A., KACHOUANE A., BERNE` DE J.C.: ‘Structure, composition and optical properties of ZnS thin films prepared by spray pyrolysis’, Math. Chem. Phys., 2001, 68, pp. 175–179
[5] RABAH M., ABBAR B., AL-DOURI Y., BOUHAFS B., SAHRAOUI B.: ‘Calculation of structural, optical and electronic properties of ZnS, ZnSe, MgS, MgSe and their quaternary alloy Mg1_xZnxSySe1_y’,Mat. Sci. Eng., 2003, B100, pp. 163–171

[6] MONROY E., OMNES F., CALLE F.: ‘Wide-bandgap semiconductor ultraviolet photodetectors’, Semicond. Sci.Technol., 2003, 18, pp. 33–51

[7] A. Goudarzi, G.M. Aval, R. Sahraei, H. Ahmadpoor, Thin Solid Films 516 (2008) 4953.

[8] Y. Fu, N.A. Allsop, S.E. Gledhill, T. K¨ ohler, M. Kr¨ uger, R. Sa´ez-Araoz, U. Block, M.C. LuxSteiner, C.H. Fischer, Adv. Energy Mater. (2011).

[9] K. Catchpole, S. Pillai, J. Lumin. 121 (2006) 315.

[10] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, R. Noufi, Prog. Photovolt. Res. Appl. 16 (2008) 235.

[11] J.A. Ruffiner, M.D. Hilmel, V. Mizrahi, G.I. Stegeman, V. Gibson, Appl. Opt. 28 (1989) 5209.

[12] U. GANGOPADHYA., K. KIM., S. K. DHUNGEL., H. SAHA., J. Yi.: ‘Application of CBD-Zinc Sulfide Film as an Antireflection Coating on Very Large Area Multicrystalline Silicon Solar Cell’, Advances in OptoElectronics Volume 2007, Article ID 18619,5pages

[13] BUSARIN NOIKAEW., PANITA CHINVETKITVANICH., INTIRA SRIPICHAI., CHANWIT CHITYUTTAKAN., ‘The Influence of Growth Conditions on the Chemical Bath Deposited ZnS Thin Films’ Journal of Metals, Materials and Minerals, Vol.18 No.2 pp.49-52, 2008

[14] P. VINOTHA BOORANA LAKSHMI., K. SAKTHI RAJ., K. RAMACHANDRAN.: ‘Synthesis and characterization of nano ZnS doped with Mn ‘ Cryst. Res. Technol. 44, No. 2, 2009, pp 153 – 158.

[15] A.COTTRELL, Intorduction to Mettallurgy ,Arnold, Londan, 1975,P.173

[16] R.S.LONGHURST, Geometrical & physical optics ,Longmans green,Londan 1957.

[17] VIPIN KUMAR , K.L.A. Khan ,G. Singh and T.P. Sharma , Appl .Surf. Sci., 2007, 7, 253

[18] J. Tauc, Amorphous and Liquid Semiconductors, Plenum Press, London and New York (1974), p. 159.

[19] J.R. Rani, V.P. Mahadevan Pillai, R.S. Ajimsha, M.K. Jayaraj and R.S.Jayasree, "Effect of substrate roughness on photoluminescence spectra of silicon nanocrystals grown by off axis pulsed laser deposition," J. Appl. Phys, vol. 100, pp. 014302- 1-014302-6, July 2006.