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Preparation and Characterization of Copper Doped $Cd_{0.7}Zn_{0.3}S$ Thin Film and Evaluation of Doping Effect of Copper

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$Cd_{0.7}Zn_{0.3}S$ was doped for different mol % of Cu was prepared by chemically deposited technique. The film has been characterized by X-ray diffraction, scanning electron microscope, energy dispersive spectroscopy and ultra violet spectroscopy. The result of X-ray diffraction showed that the films are polycrystalline in nature with a hexagonal structure. SEM studies revealed the size of the sphere increases initially with the increase in Cu concentration. The presence of elemental constituent has been confirmed by energy dispersive X-ray analysis. Results obtained from optical studies showed that the band gap energy varied from 4.650 to 3.265 eV, which confirmed the decrease of band gap with increase in the concentration of Cu on $Cd_{0.7}Zn_{0.3}S$.

Keywords: Chemical bath deposition, XRD, Thin film, SEM, Copper.

INTRODUCTION

Study of $Cd_{(1-x)}Zn_{(x)}S$ semiconductors received attention of academicians and technologists because of their energy gap can be tuned and the lattice parameters can be varied suitably with the variation of x. This material can be used as a photovoltaic solar cell [1]. CdZnS thin films have been widely used as a wide band gap window material in heterojunction solar cells [2]. Recently there will be a lot of gain in the solar cell and increases in the field on thin film semiconductor [3-5]. $Cd_{(x)}Zn_{(1-x)}S$ nanostructures film made a potential, in various optoelectronic nano devices [6].

The $Cd_{(x)}Zn_{(1-x)}S$ films were used in solar cells [7]. Copper on $Cd_{(x)}Zn_{(1-x)}S$ thin film is being prepared by several techniques like CVD, MOCVD, sputtering, spray pyrolysis, electro deposition, successive ionic layer absorption and reaction (SILAR), chemical bath deposition (CBD) *etc.* [8]. All these techniques are highly sophisticated as well as cost-effective. Therefore, work has been continued to find out ways to prepare films by simple methods so as to reduce the cost of solar cell.

Chemical bath deposition is one of the most convenient, reliable, simplest and less expensive methods used to prepare films at close to room temperature. The technique offers many advantages over the more established vapour phase synthetic routes to prepare semiconductor material. Another advantage of chemical bath deposition method than other methods is that the films can be deposited on different kinds, shapes and sizes of substrates.

EXPERIMENTAL

The doping of copper on $Cd_{0.7}Zn_{0.3}S$ was done by chemically deposited method. The glass slides were cleaned by liquid detergent in an ultrasonic bath and then dipped into a chromic acid bath for 2 h at room temperature, further washed with distilled water and acetone then dried. A Cu: $Cd_{0.7}Zn_{0.3}S$ bath containing 0.1 M of copper nitrate, 0.1 M of cadmium chloride, 0.1 zinc chloride of and 1 M of thoiurea. The pH was adjusted to 10 by adding NH_4OH. The glass substrates were immersed vertically in the reaction vessel and the bath was set to a desired temperature as 80 °C for 120 min and the slides were in the bath for 24 h at room temperature. The deposited films were washed with distilled water then dried in air.

Thickness of the film was measured by interference technique. Structural, optical, morphological and compositional properties of these films have been characterized using XRD technique using a Philips PW1840 instrument with a CuKα target. An UV-visible spectrometer (Jenway 6800) has been utilized to measure the absorbance and transmittance of films in the wavelength (λ). SEM studies revealed the size of the sphere and EDAX confirmed the presence of elemental constituents. The formation of $Cd_{(1-x)}Zn_{(x)}S$ and its reactions are given below:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Cadmium tetra amine $[Cd(NH_3)_4]^{2+}$ and zinc tetra amine $[Zn(NH_3)_4]^{2+}$ was formed by adding the ammonia solution to Cd and Zn as follow:

$$Cd^{2+} + 4NH_3 \rightleftharpoons Cd(NH_3)_4^{2+}$$

$$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$$

Due to the decomposition of thiourea in alkane medium the sulfide ions were released, which is described by the following chemical reactions:

$$SC(NH_2)_2 + 3OH^- \rightleftharpoons Cd(NH_3)_4^{2+}$$

$$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$$

$$HS^- + OH^- \rightleftharpoons S^- + H_2O$$

All the source ions combined in the reaction mixture, which led to the formation of $Cd_{1-x}Zn_xS$.

RESULTS AND DISCUSSION

X-ray diffractions: The X-ray diffraction of $Cu:Cd_{0.7}Zn_{0.3}S$ compounds prepared by chemical bath deposition method are shown in Figs. 1 and 2, respectively. Sharp diffraction peaks indicating that they have polycrystalline nature.

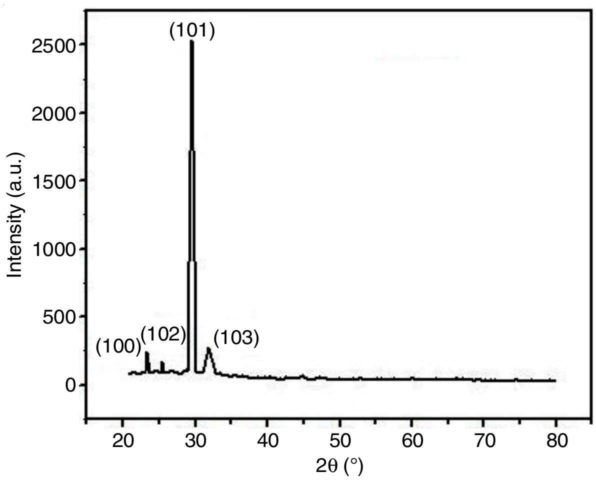

Fig. 1. XRD specttra of $Cd_{0.7}Zn_{0.3}S$

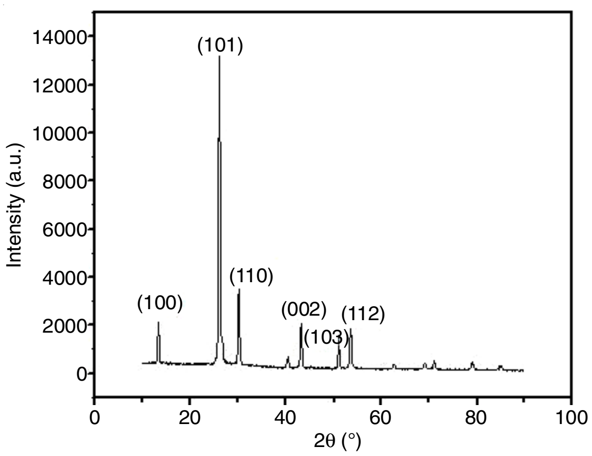

Fig. 2. XRD spectra of $Cd_{0.7}Zn_{0.3}S$:5 % Cu

The peaks were indexed by comparing their positions with the standard ASTM data (JCPDS card 65-5915) of $Cd_{0.7}Zn_{0.3}S$ (Hexagonal) structure. The well defined (002), (100) and (110) peaks were observed in the XRD patterns.

Optical characterizations: The optical absorption coefficient (α) near the absorption edge is evolved from the equation:

$$\alpha(\nu) = 2.303A/d \quad (1)$$

where d is the thickness of each sample and A, the absorption, respectively. The band energy gap are determined from the following equation:

$$h\nu = A\ (h\nu - E_g)^n \quad (2)$$

where A is constant, E_g is the optical band gap of the material and n assumes values of 1/2,2,2/3 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. The absorption curves *versus* hν were plotted are shown in Figs. 3-6.

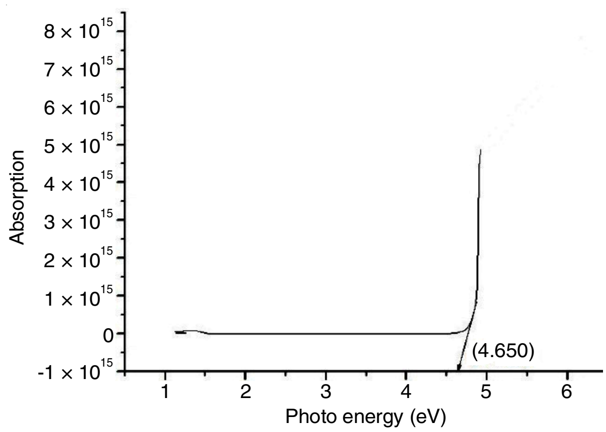

Fig. 3. Optical absorption of CdZnS thin film

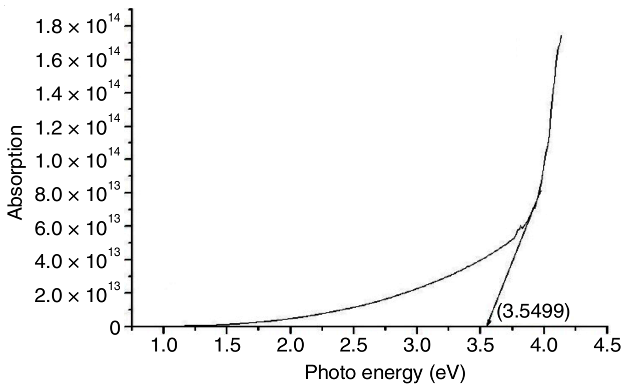

Fig. 4. Optical absorption of 1 % Cu on $Cd_{0.7}Zn_{0.3}S$ thin film

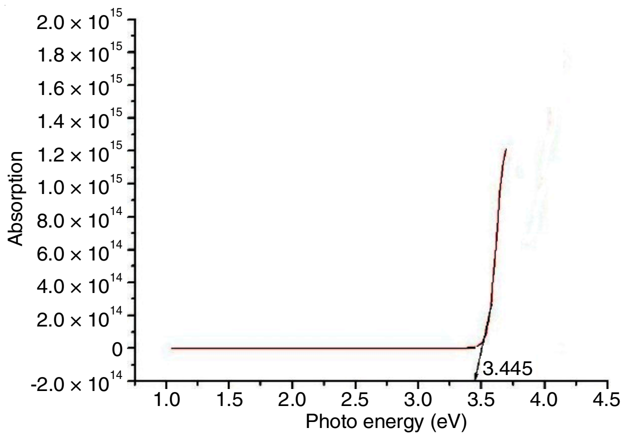

Fig. 5. Optical absorption of 3 % Cu on $Cd_{0.7}Zn_{0.3}S$ thin film

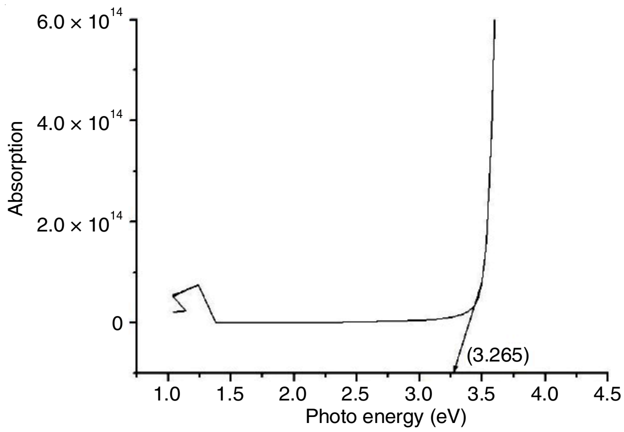

Fig. 6. Optical absorption of 5 % Cu on $Cd_{0.7}Zn_{0.3}S$ thin film

The band gap energy of $Cd_{0.7}Zn_{0.3}S$ is 4.650 eV is continuously decreased to 3.265 eV for $Cd_{0.7}Zn_{0.3}S$:5 % Cu as shown in Table-1.

TABLE-1
OPTICAL BAND GAP OF Cu:$Cd_{0.7}Zn_{0.3}S$

S. No.	Samples	Band energy gap (eV)
1	$Cd_{0.7}Zn_{0.3}S$	4.650
2	$Cd_{0.7}Zn_{0.3}S$:1 % Cu	3.549
3	$Cd_{0.7}Zn_{0.3}S$:3 % Cu	3.445
4	$Cd_{0.7}Zn_{0.3}S$:5 % Cu	3.265

SEM studies: Scanning electron microscope is a convenient method for studying the microstructure of thin films. The microstructure of $Cd_{0.7}Zn_{0.3}S$: 3 % Cu film on glass substrate is shown in Fig. 7. It reveals that the formation of sub-micrometer crystalline more or less uniformly distributed to the surface.

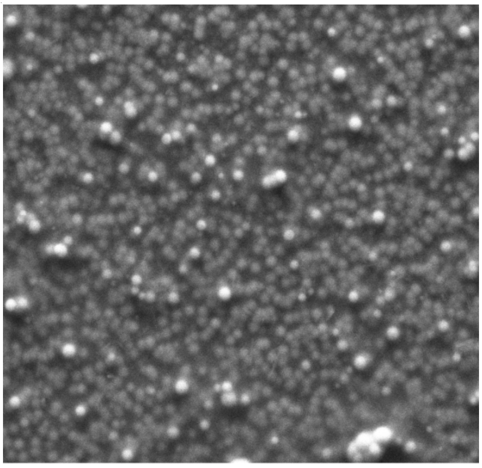

Fig. 7. Scanning electron microscope of $Cd_{0.7}Zn_{0.3}S$: 3 % Cu thin film

For $Cd_{0.7}Zn_{0.3}S$: 5 % Cu we obtained the polycrystalline and porous nature with agglomeration of small crystalline also seems to be present in certain regions on the film surface. The sizes of the sphere were significantly increased due to increasing the percentage of copper was shown in Fig. 8.

Composition analysis: Fig. 9 shows the EDAX of deposited $Cd_{0.7}Zn_{0.3}S$: 5 % Cu thin films. The EDAX peaks confirmed the presence of Cu, Cd, Zn and S.

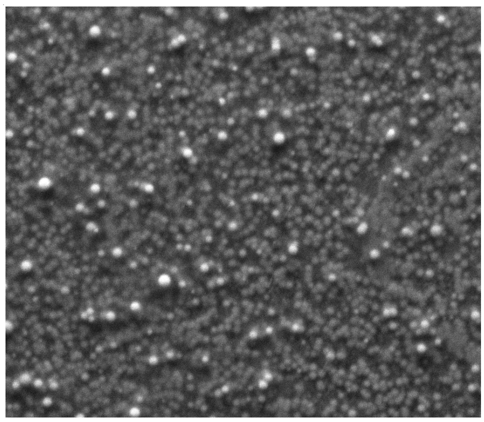

Fig. 8. Scanning electron microscope of $Cd_{0.7}Zn_{0.3}S$: 5 % Cu thin film

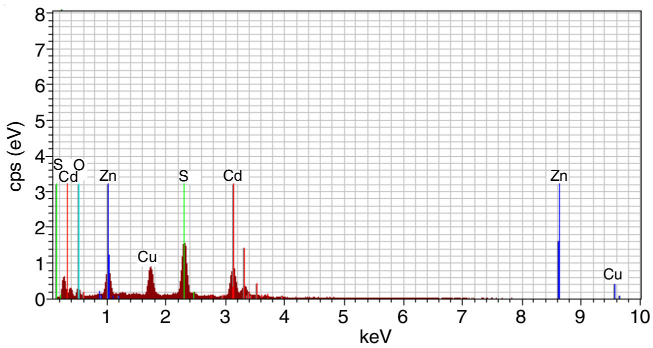

Fig. 9. EDAX spectra of $Cd_{0.7}Zn_{0.3}S$: 5 % Cu thin film

Conclusion

Cu:$Cd_{0.7}Zn_{0.3}S$ thin films were formed on glass substrate by chemical bath deposition technique. XRD results indicated that $Cd_{0.7}Zn_{0.3}S$:Cu thin films are in the polycrystalline form with a hexagonal structure. The energy band gap of the Cu:$Cd_{0.7}Zn_{0.3}S$ samples obtained using optical absorption spectra varied from 4.650 to 3.265 eV. SEM studies revealed that the film was a fine sphere cluster of grain. The presence of elemental constituents has been confirmed by EDAX.

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