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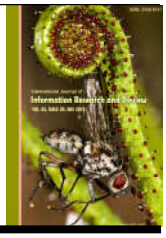

Research Article

TUNING THE STRUCTURAL PROPERTIES AND FLOWER-LIKE MORPHOLOGIES OF CU_2S THIN FILMS THROUGH ZN DOPING

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ABSTRACT

Zinc -doped Cu_2S thin films have been deposited onto a glass substrate using simple and economical chemical bath deposition technique (CBD). The Zn doping concentrations vary from 0 to 6 at. % in the step of 2 at. %. X-ray diffraction (XRD) measurement shows a hexagonal structure with the average crystalline size from 26.91 nm to 14.20 nm. The Fourier transform infrared (FTIR) studies have revealed the confirmation of a functional group of Cu-Zn- S lattice. The photoluminescence (PL) studies showed the occurrence of energy transition from Cu_2S to dopant material of Zn sites. The blue shift observed in the transmittance spectra is due to the interstitial incorporation of Zn in the CuS matrix. The field emission scanning electron microscope (FESEM) images indicate that there is a gradual decrease in the grain size with increase in the Zn doping concentration and the flower-like structure appeared for 6 at. % of Zn. The optical energy band values are varying from 2.6 eV to 3.35 eV.

INTRODUCTION

Metal chalcogenide thin films, like metal sulphide, metal selenides, and metal tellurides, possess useful electrical and optical properties and can be found in many technical applications (Mortazavi-Derazkola *et al.,* 2015; Sahar Zinatloo-Ajabshir *et al.,* 2015; Sobhan Mortazavi-Derazkola *et al.,* 2015). The particle size and shape of the nanomaterials thin films have a great impact on their properties (Sahar Zinatloo-Ajabshir *et al.,* 2015). Copper sulphide is a promising material with wide-range applications for solar selective coatings, solar cells (Mukherjee *et al.,* 2011), flat panel displays (Ali Yildirm, 2012), sensors (Galkidas *et al.,* 2000), photovoltaic devices (Hamid Reza Pouretedal and Mahammad Hossein Keshavarz, 2010), Lithium ion batteries (Chung and Sohn, 2002) and superconductor devices (Ali Yildirim *et al.,* 2009). A copper sulphide (CuxS) thin film is one of the potentially useful metal chalcogenides with signification variation in properties depending on the stoichiometry, $1 \leq x \leq 2$. Copper sulphide forms five stable phases such as Chalcocite, djurleite, digenite, anilite and Covellite. Copper sulphide is a P-type semiconducting material with a band gap of 2.6 eV (Lin Chen *et al.,* 2012) with the hexagonal system (Ramasamy *et al.,* 2012). Doping is one of the most intensively used methods to modify the electrical and Optical properties of semiconducting materials. Copper sulphide is one of the Parent compounds like CuXS (X = Ag, Zn, Mn, Co, Ni, Cd) (Jun Liu *et al.,* 2014). Zinc sulphide is an n-type semiconducting material with an energy band gap of 3.35 eV (Mehdi Adelifarda *et al.,* 2012) and it has a hexagonal structure.

Different concentrations of zinc doped Copper sulphide films were prepared. CuZnS ternary alloy compounds are promising material for optical device applications. Depending upon the applications, thin film preparation technique varies like spray pyrolysis (Yongjuan Lu *et al.,* 2011), chemical bath deposition (CBD) (Bollero *et al.,* 2009), thermal Co-evaporation (Jing Li *et al.,* 2013), electro deposition (Schneider *et al.,* 2007), chemical vapour deposition (Schneider *et al.,* 2007), Successive Ionic Layer Adsorption and Reaction (SILAR) (Fuwei Zhuge *et al.,* 2009). Among these methods the chemical bath deposition technique is very simple, low cost, mild reaction and controllable reaction conditions. In this report, thin films were deposited by CBD technique and investigated for tuning the structural properties and Flower-like morphologies of chemical bath deposited Cu_2S thin films through Zn doping.

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Experimental Procedure

Substrate cleaning

The Substrate cleaning process is one of the important roles in the deposition of thin films. The contaminated substrate surface provides nucleation sites facilitating the growth which results in the non-uniform film growth. Glass slides of dimensions 26 x 76 x 2 mm were used as substrates. These substrates were boiled (80 ˚C) in concentrated Chromic acid for one hour and rinsed in acetone. Finally, the substrates were cleaned with double distilled water before the deposition of the films.

Sample preparation

$Cu_{2-x}Zn_xS$ thin films were deposited using CBD at elevated temperatures. All the chemicals were purchased from Merck Company. The analytical grade chemical reagents were used without further purification. For the preparation of undoped Cu_2S thin films, 0.1 M of Copper sulphate pentahydrate ($CuSO_4$. $5H_2O$) were dissolved in 50 ml of double distilled water and it was stirred well. Now a few drops of Triethanolamine (TEA) were added to the above solution until the pH of the bath were found to be 10. The well-cleaned glass substrates were immersed vertically into the beaker using a slide holder. Then 1.0 M of thiourea ($(CS(NH_2)_2)$) was slowly added to the solution. The temperature was slowly increased to 90 C and this temperature was maintained throughout the experiment. During the whole reaction process, the reactants were vigorously stirred under air atmosphere. The chemical reaction was started at the mixture of solutions. The films deposited on glass substrates have been taken out after 2 h when it became brown in colour. The same procedure was carried out for the Zn-doped Cu_2S films with 2, 4 and 6 at %. The elevated temperature is used for two fold purposes, to improve the deposition of copper and to ensure synthesis for the duration of two hours.

Characterization techniques

The crystal structure of all the samples of Cu_2S and $Cu_{2-x}Zn_xS(0 \leq x \leq 0.6)$ thin films has been determined by powder XRD. The XRD patterns were recorded (Make: RigaKu, Model: C/max-2500) using CuKα radiation (k = 1.54056 A) operated at 40 kV and 30 mA in the wide angle region from 10 to 70 . Surface morphology was studied using a Hitachi S-4160 Field emission scanning electron microscope (FESEM). The UV–visible optical absorption and transmittance spectra of Cu_2S thin films have been carried out to explore their optical properties. The spectral absorption was determined by using UV-visible spectrometer (Make: Perkin Elmer, Model: Lambda 35) in the wavelength ranging from 200 to 1200 nm using cm^{-1} quartz cuvettes at room temperature. Halogen and deuterium lamps were used as sources of visible and UV radiations, respectively at room temperature. The presence of chemical bonding in Cu_2S thin films was studied by FTIR spectrometer (Make: Perkin Elmer, Model: Spectrum RX I) in the range of 400–4000 cm^{-1}.

Structural Analysis

Fig. 1 shows XRD patterns of undoped and Zn-doped copper sulphide thin films with concentrations of zinc varies from 0 to 6 at. % in the step of 2 at. %.. From the XRD pattern, for all the films (110) plane is the preferential orientation because it has the lowest surface energy. For the undoped film, all the diffraction peaks were exhibited with the hexagonal phase and it matches well with the JCPDS card number for Cu_2S (JCPDS Card No: 84-0209). For the Zn- doped pattern, secondary phases are introduced (102) plane for the corresponding 2θ values of 28˚. The change in peak intensity may be attributed to the crystallinity of the films. The crystallinity of the films is improved with an increase in the Zn concentration. After doping, the peaks slightly shifted towards the lower angles of 2θ position and this is due to the quantum confinement effect. The shift of the peak implies the systematic incorporation of the Zn^{2+}(74 pm) ions for the Cu^{2+}(73 pm) ions in the lattice parameter. Because Zn^{2+} and Cu^{2+} are having similar ionic radii. From the above result, it was observed that when 6 at .% of Zn was doped, the lattice well matched and exhibited between ZnS and CuS. The full-width half- maximum (FWHM) value of the diffraction peaks of Cu_2S films is broader than the doped films. The average Crystallite size (D) were calculated using the Debye- Scherrer's formula (Sahar Zinatloo Ajabshir and Masoud Salavati Niasari, 2014)

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where 'λ' is the wavelength of X-ray used (1.54056 Å), 'β' is the angular peak width at half maximum in radians, and 'θ' is the Bragg's diffraction angle. The microstrain (ε) can be calculated using the formula (Callister, 1997)

$$\varepsilon = \frac{\beta \cos\theta}{4}$$

Additionally, the dislocation density (δ), defined as the length of dislocation lines per unit volume has been estimated by the equation (Ravichandran and Thirumurugan, 2014)

$$\delta = \frac{1}{D^2}$$

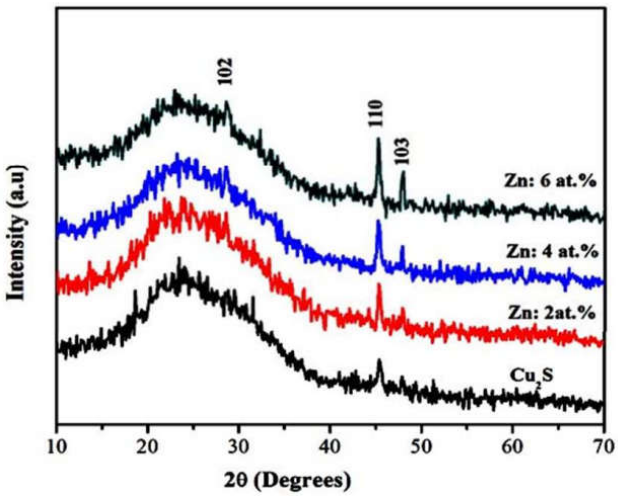

Fig. 1. XRD patterns of undoped and Zn-doped Cu_2S thin film

Where D is the crystallite size. The microstrain gets increased, whereas the average crystallite size decreased from 26.91 to

14.20 nm. The dislocation density has a low value (13.8 X 10^{14} lines/m^2) for undoped Cu_2S thin films, but for the Zn-doped film, the dislocation density gradually increased from 13.8 to 49.55 lines/m^2 as the doping level increases.

Fourier transform of infrared studies (FTIR)

Fourier transform of infrared spectra for Cu_2S thin films and Zn-doped films with concentrations from 0 to 6 at. % in step of 2 at. %. were recorded at room temperature in the wavelength range of 400 - 4000 cm^{-1} are shown in the Fig. 2. This measurement is used to identify the functional groups of the deposited films. The broad absorption peaks attributed nearly from 2799- 3400 cm^{-1} are due to O-H stretching vibrations of Cu-S lattice parameters (Vasuhi *et al.,* 2014). From the spectrum, it is observed that only minimum absorption peaks are present undoped and 2 at.%) and it reveals the poor crystalline quality of the films. The peaks at 3410-3465 cm^{-1} reveal the high binding energy of the – OH group in the ZnS matrix. By increasing the Zn doping, the absorption peaks obtained are more and they correspond to the Zn-doped Cu_2S (Murugadoss, 2013). The frequencies in the range of 1666 - 1677 cm^{-1} are assigned to H-OH bending vibration of water in Cu-Zn-S lattice (Muthukumaran and Ashokkumar, 2013). For the doping of 6 at.%, more absorption peaks are present which reveals the good crystalline quality of the film. All the FTIR spectra show close similarities which indicate that Zn has entered the CuS lattice substitutionally. These results are in good agreement with the XRD pattern.

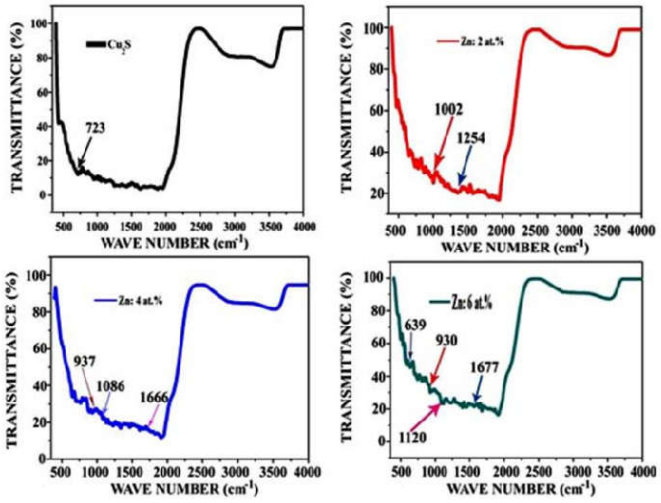

Fig. 2. FTIR spectra of undoped and Zn-doped Cu_2S thin films for different Zn concentrations

Photoluminescence

The photoluminescence (PL) spectra of undoped and Zn-doped Cu_2S films with Zinc concentration of 0 to 6 at.% are shown in the fig. 3 and are investigated at room temperature. The operation of PL spectrum is formed as a result of the combination of electron-hole separation and recombination from the electron-phonon scattering process. It can be attributed to the variation of the optical band gap of the material. The near band emission of the undoped films appears at 392nm (Mehdi Adelifard *et al.,* 2012). With the increase in doping concentration of Zn, the peaks shift towards the higher wavelength (red shift) region. The intensity of the peak increases with increase in Zn doping concentration, which may be attributed to the improvement of the crystalline quality of the film. This result correlates with the XRD and FTIR spectrum.

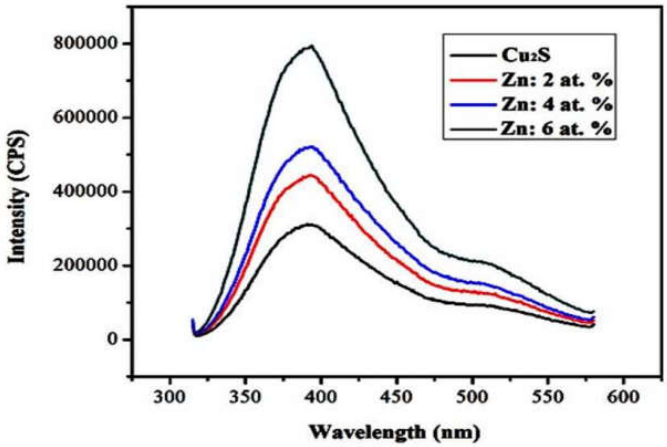

Fig. 3. Photoluminescence spectra of undoped and Zn-doped Cu_2S thin films for different concentration at room temperature

Optical Studies

Fig. 4 shows the transmission spectra of undoped and zinc doped copper sulphide thin films The Zn doping concentrations varies from 0 to 6 at. % in steps of 2 at. %. For the undoped films, the transmittance is very low. When the dopant was added to the Cu_2S films, the percentage of transmittance increases with increase in Zinc concentration. It reaches a maximum value of nearly 55% in the visible region which may be due to the sulphur deficiency, the surface roughness of the film and impurity centres. Here the sharpness of the absorption edge is high for the Zinc with (at. 6%) indicating the better crystalline quality of the films when compared with the other films. Fig. 5 shows the optical band gap (Eg) values calculated using Tauc's plot relation (Farshad Beshkar *et al.,*) ofa bsorption coefficient (α) *Vs* and the photon energy (hν) as

$$Ahv = A(hv \quad Eg)^{\upsilon}$$

Here h*v* is the photon energy and *A* is constant. The Energy gap is found to be 2.6 eV (Abdel Rafea *et al.,* 2012) for undoped films and its value increases with doping, which was tabulated in the table(1). Fig. 6 shows the absorption spectra of undoped and Zn-doped Cu_2S thin films at room temperature from the range of 300-1100 nm. The broad absorption peak is in the visible region and hence it is used for the windows layer in the solar cells.

Surface Morphological Studies

Field emission scanning electron microscope is one of the promising techniques to investigate the surface morphology, shape and size of the particles in the films. Here the formation of morphologies is interesting to notice the great difference between the morphologies. Fig. 7 shows the surface morphology of undoped and Zn-doped Cu_2S films which vary from (0 to 6 at.% of Zn). Fig. 7(a) shows the undoped film of Cu_2S and it revealed the uniform distribution of particles with the size nearly about 40 nm. Fig. (b) shows some well agglomerated spherical grains uniformly distributed over the surface.

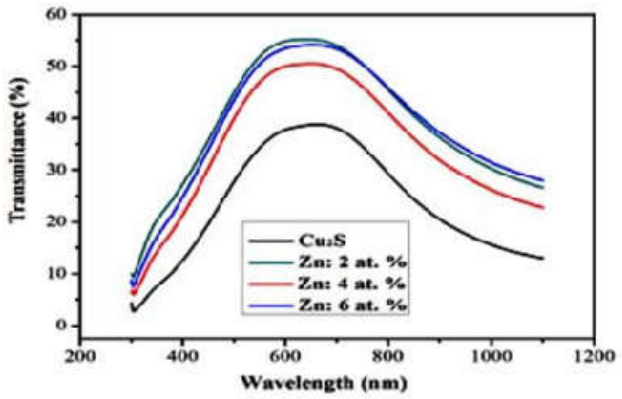

Fig. 4. Transmittance spectra of undoped and Zn-doped Cu_2S thin films

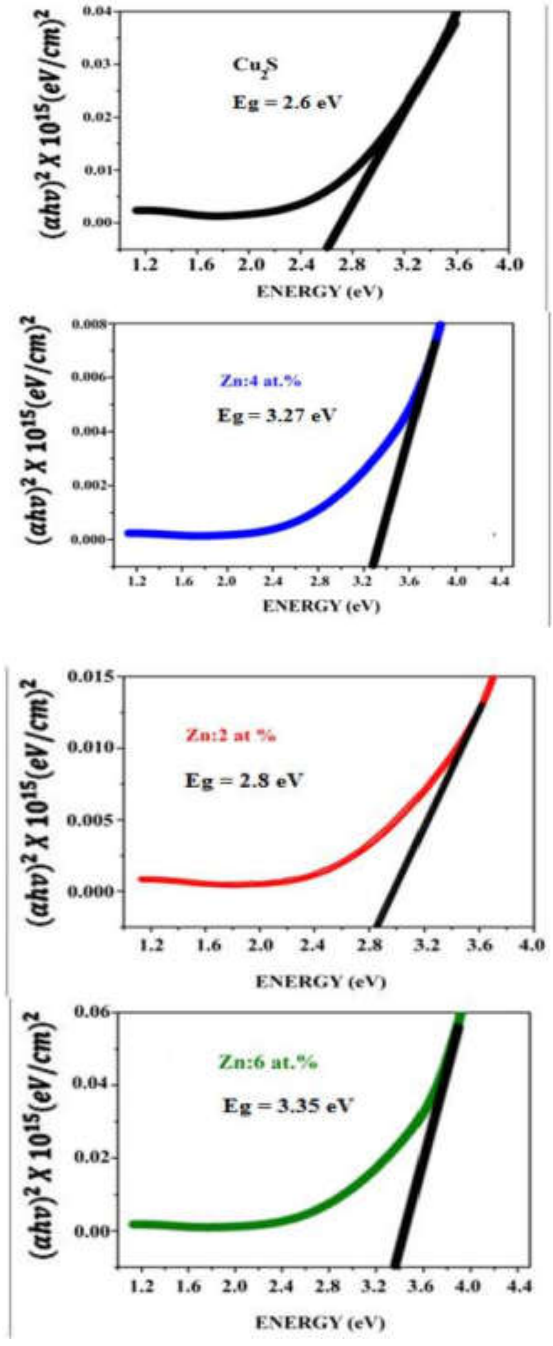

Fig. 5. (αhν)2 versus hν plots of undoped and Zn-doped Cu_2S thin films

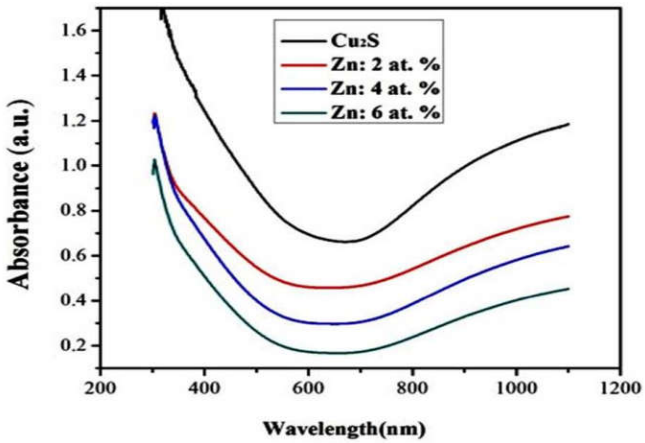

Fig. 6. Absorbance spectra of undoped and Zndoped Cu_2S thin films

Table 1. Structural and optical parameters of undoped and Zn-doped Cu_2S thin films

S.No	Samples	D (nm)	ϵ X 10^{-2} (Lines^{-2}m^{-4})	δ X 10^{14}lines/m^2	Eg (eV)
1.	Undoped-Cu_2S	26.91	0.08	13.8	2.60
2.	Zn: 2 at. %	21.48	0.10	21.66	2.85
3.	Zn: 4 at. %	16.46	0.13	36.87	3.27
4.	Zn: 6 at. %	14.20	0.15	49.55	3.35

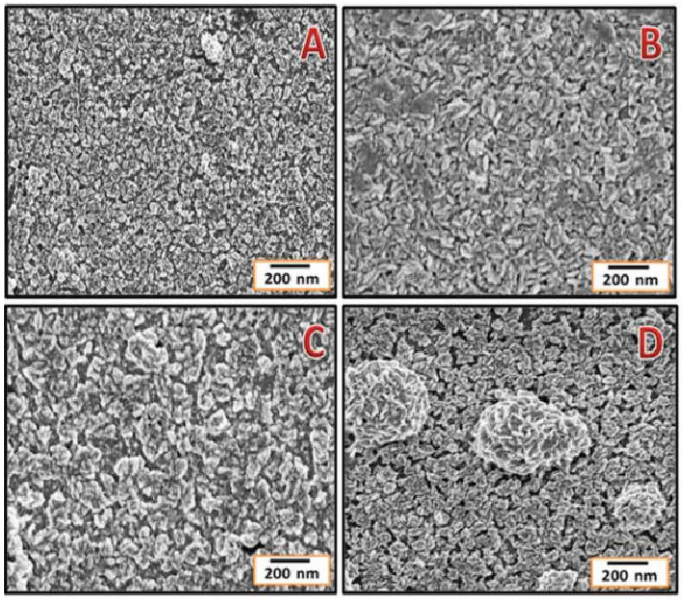

Fig. 7. FESEM images of undoped and Zn-doped Cu_2S thin films

When the dopant was added with 2 at. % of zinc, the particle size changes due to the chemical reaction. The particle size varies from 40 nm to 78 nm. Fig. 7(c) shows the Zn dopant with 4 at.%. From the morphology, it was observed that these grains are loosely bounded and the large grains (~72 nm-125 nm) are exhibited. The particles become larger than the critical size for nucleation and further nucleation occurs on it (29). Fig. 7(d) shows 6 at % of Zn with the well-defined very small uniform distribution of particles. From Figure. 7 (b) & 7(c), it revealed that the agglomerated particles are combined to form a well-defined flower–like structure, which corresponds to the 6 at.% of Zn.

Conclusion

Nanocrystalline CuZnS thin films were deposited onto glass substrates by CBD method. The structural analyses of prepared films suggest that the Zn successfully occupied the Cu sites and did not change the hexagonal structure of Cu_2S. The dopant concentration of Zn with 6 at. % film was found to be the best crystalline quality with improvement in the surface morphology as monitored using FESEM. These films exhibited high absorbance in the visible region. The band gap of the films showed a blue shift with increasing Zn concentration (2.6 eV to 3.35 eV). As a result, it can be argued that the structural and optical properties of the Cu_2S films can be improved by Zn doping. From the properties of doping Zn on Cu_2S the films confirm that these films can be used for eye glasses coating, solar thermal conversion, anti-reflection coating and solar cell fabrications.

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