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Hydrophilic semconducting micro-chip like Cu doped ZnS thin films grown at room temperature

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ABSTRACT

Copper (Cu) doped ZnS thin films were prepared by means of electrodeposition method on conducting substrate at applied constant deposition potential. The deposition potential of ZnS and Cu doped ZnS thin films were obtained by cyclic voltammetry (CV). The prepared films were characterized by X-ray diffraction (XRD) study, Scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, UV-Vis absorption spectroscopy and contact angle measurements. XRD study reveals that the electrodeposited 3 % of Cu doped ZnS thin films are polycrystalline in nature. The SEM images show micro-chip like microstructure with uniform depsoition of Cu doped ZnS grains. The semiconducting property of Cu doped ZnS thin film was confirmed from the UV-Vis absorption study having band gap energy 4.1 eV. The maximum value of contact angle was found to be 25° for the 3% Cu doped ZnS thin films, which confirms the hydrophilic nature of the Cu doped ZnS.

KEYWORDS

Electrodeposition;
XRD;
Thin film;
Semiconductor;
Microstructure;
ZnS.

INTRODUCTION

ZnS, an important semiconductor compound of the II-VI group, has a wide band gap of 3.7 eV at room temperature and relatively large exciton binding energy (approximately 40 meV)[1]. Now days, much exertion has been devoted to the research of doped metal chalcogenide materials. The chalcogenide exhibits remarkable physical and chemical properties in evaluation with their bulk materials, such as size-dependent variation of the band gap energy. Additionally, impurity ions doped into these nanostructures can influence the electronic structure and transition probabilities. a ZnS is chemically more stable and technologically better than other chalcogenides, so it is considered to be a promising host material[2]. Also manganese (Mn) doped ZnS nanoparticles have been extensively studied for their better emission efficiencies,[3]. Cu doped ZnS nanoparticles with their excellent luminescent properties have attractive applications in LEDs, plasma displays, sensors and lasers[4].

Mostly Cu doped ZnS nanoparticles are studied for the luminescence properties, but luminescence properties are still controversial in the case of nanosized Cu doped ZnS. Lee et al[5] shows that two emission bands (blue and green) were often observed simultaneously in the same sample, such as 420 and 520 nm. There have been many research groups studied Cu doped ZnS nanoparticles through chemical

methods. Geng et al.[6] have explained the synthesis of Cu^{2+} doped ZnS nanorods using a solution phase thermal decomposition molecule precursor route and Cu2+ can able to tune the optical properties by changing Cu doping concentration. Datta et al.[7] has reported the effect of Cu incorporation on the phase transition from wrutzite to Cubic structure prepared by solvothermal process. Peng et al[2] shows the Low temperature syntheses of Cu doped ZnS nanoparticles and its photoluminescence properties. Now recently Yao et al,[8] reported super hydrophobic surface ZnS thin film chemical vapor deposition technique.

In the present investigation Cu doped ZnS thin films were prepared by simple electrodeposition technique at room temperature. The deposited thin films were characterized by using XRD, SEM, Fourier transform Infrared spectroscopy (FTIR), UV-Vis spectroscopy and surface wettability were studied.

EXPERIMENTAL

Synthesis

Cu doped Zinc sulfide thin films are prepared by electrochemical synthesis at room temperature. The electrolytic bath consist of 0.1 M Zinc sulphate ($ZnSO_4$), 0.05 M Sodium thiosulphate ($Na_2S_2O_3$) and 0.01M Copper sulphate ($CuSO_4$). The Cu doping is done by taking the volumetric proportion of precursors (Zn and Cu). Actual electrodeposition set up consists of cylindrical glass beaker and three electrodes such as working, reference and counter electrodes. The stainless steel and tin doped indium oxide (ITO) glass substrates which act as working electrode with respect to saturated calomel electrode (SCE) as reference electrode. The graphite plate is act as counter electrode. All the potentials were measured with respect to SCE. The deposition potential of ZnS and Cu doped ZnS thin films were determined by cyclic voltammetry (CV). The deposition of Cu doped ZnS a thin film was made at -0.85 V vs SCE. The deposited films were further characterized for structural, morphological, optical and surface wettability study. ITO's are used for the SEM and optical study and steel substrate are used for XRD, FT-IR and Wettability test.

Characterizations

X-ray powder diffraction patterns of the potentiostatically deposited samples were obtained on diffractometer D8 ADVANCE (Bruker) using filtrated Cu-Kα irradiation in the range of 2θ=20-70° with 0.05° increment and signal acquisition interval of 50 s. The surface morphology of ZnS and Cu: ZnS thin films were made by scanning electron microscopy (Model: JEOL 6360). FTIR spectra of ZnS and Cu: ZnS samples in KBr tablets were recorded by SPECTRUM ONE (PerkinElmer) with an accuracy of 2 cm^{-1}. For contact angle measurement, a water droplet of about 50μL was placed on the surface of ZnS and Cu: ZnS thin films using micro syringe. Static contact angles (θ) of ZnS and Cu: ZnS thin films were measured from a water drop placed on the sample surface using Rame–Hart contact angle meter, USA. The absorption spectra measurements were performed with a Shimadzu UV-3600 UV-vis spectrophotometer in the wavelength range 300–900 nm.

RESULTS AND DISCUSSIONS

X-ray diffraction (XRD) study

Figure 1 shows the XRD patterns of electrodeposited ZnS and Cu doped ZnS thin films. It shows the ZnS and 3 % Cu doped ZnS thin films are cubic zinc blende in nature (JCPDS No. 05-0566). We also find out the crystallite size (D) using Scherer formula from eq 1,

$$D = \frac{0.9\lambda}{\beta \mathrm{Cos}\theta} \quad (1)$$

The crystallite size found to be 20 nm and 18 nm for ZnS and 3% Cu^{2+} doped ZnS respectively. very small change is observed in the crystallite size because ionic radius of Zinc is 0.74 A° and ionic radius of copper is 0.73 A° both are nearly same but ionic radius of copper little more smaller than the zinc, so when cooper replaced by zinc atom small change is observed in the crystallite size. The strain ε values are evaluated by the following relation eq. 2,

$$\varepsilon = \frac{\beta \mathrm{Cos}\theta}{4} \quad (2)$$

Strain is found to be 0.262×10^{-3} ($lin^{-2}m^{-4}$) and

0.273×10^{-3} ($lin^{-2}m^{-4}$) for ZnS and Cu doped ZnS respectively.

The number of crystallites per unit area (N) of the films was determined with the using formula eq. 3,[9,10]

$$N = \frac{t}{D^3} \quad (3)$$

Where, "t" is the thickness of the ZnS and Cu doped ZnS thin film. The number of crystal per unit area for ZnS was found to be $25X10^{15}$ m^{-2} and for Cu doped ZnS was $34X10^{15}$ m^{-2}.

Surface morphological study (SEM)

The surface morphological study of ZnS and 3 % of Cu doped ZnS thin films were carried out by SEM images. Figure 2 shows the formation of micro-chip like structure of ZnS thin films. The size of the micro-chip was found to be 2.5 μm in length while the thickness of the micro-chip was found to be very small as compared to length. Upon Cu doping, the shape of the ZnS grains not changes but there is change in length also change in the width of the micro-chips. The sharp wedge shaped micro-chips of Cu:ZnS shows random distribution upon the substrate surface. This doping dependent morphology evolution of the ZnS micro-chip indicates that there exist an initial nucleation and fast axial growth process followed by formation of long and thin micro-chip gradually grow shorter and wider. In addition we obtain thinner micro-chips by 3 % of Cu doping and keeping other reaction parameters constant, which indicates that the presence of Cu^{2+} dopants could also alter the growth kinetic of the micro-chip. Similar study has been reported upon Mn^{2+} doping in the ZnS quantum rods[11].

Fourier transforms infra-red (FTIR) microscopy

To study the interaction between ZnS and Cu doped ZnS, FTIR spectra were measured. The FTIR spectra of the as synthesized ZnS thin film, shown in Figure 3. The band at 3586 cm^{-1} due to the stretching of O-H & H-O-H bond in the water in the crystal structure. The band at 1389 cm^{-1} originates from = $ZnOHCO_2$. The band at 2086 cm^{-1} is a band associated with bending mode of water[12,13]. The band at 1380 cm^{-1} indicates CH_3 bending vibration. The spectra for ZnS exhibit one peak at 3250 cm^{-1} which corresponds to the O-H stretching mode of water indicating the presence of moisture in the sample. The peak at 660 cm^{-1} is assigned to Zn-S bond and 1146 cm^{-1}, assigned to the rocking mode of NH_2, the C=C stretching bonds, and the CH_2 twist band[14].

Surface wettability study

Surface wettability of ZnS thin film was studied by contact angle measurement (CA). When double distilled water droplets about 5 μL are dropped on

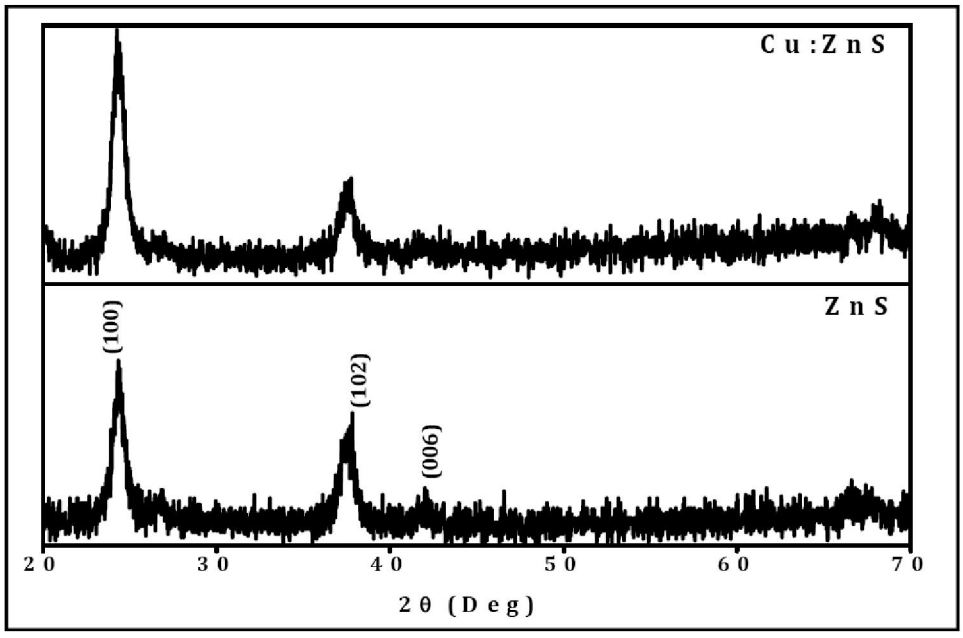

Figure 1 : XRD patterns of (a) ZnS and (b) 3 % Cu doped ZnS thin film

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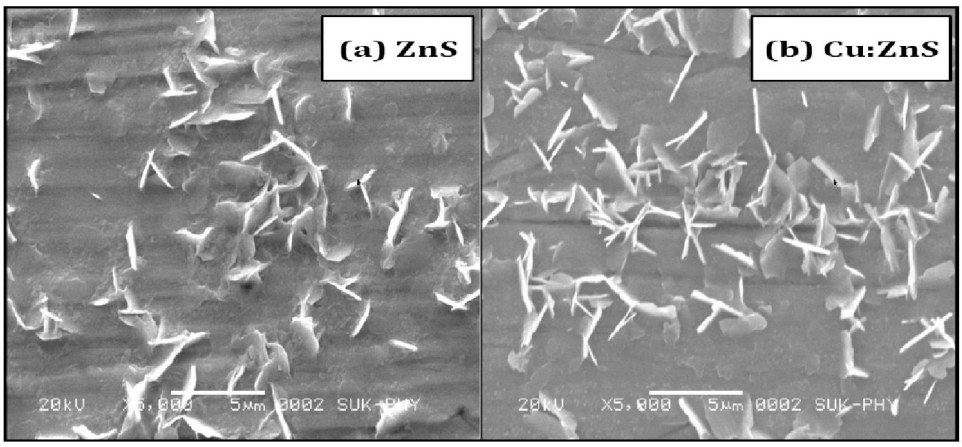

Figure 2 : SEM images of (a) ZnS and (b) Cu doped ZnS thin film

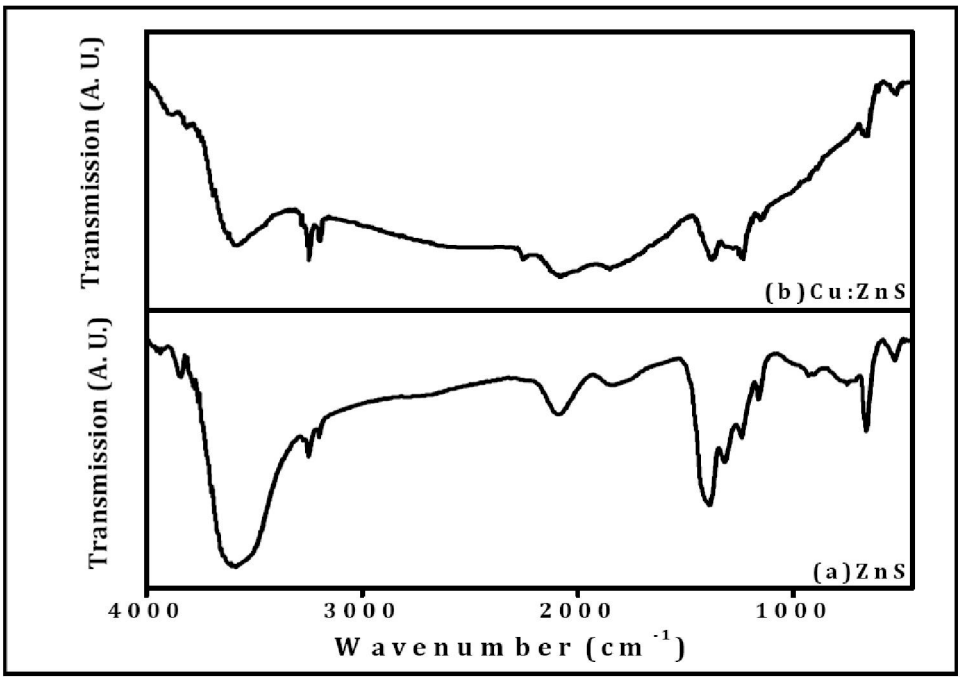

Figure 3 : (a) FTIR spectrum of ZnS and (b) 3 % Cu doped ZnS thin films

the surface, it yielded almost spherical shape at the microscopic level (shown in Figure4 (a, b)). The ZnS and Cu doped ZnS thin films shows the CA 19° and 25° which reviles that the ZnS and Cu doped ZnS thin films are hydrophilic in nature. The contact angle was increased after addition of copper content in ZnS, because of decrease in the crystallite size. The calculated Surface energy using Newman's method[15] was 70 mJ/cm^2 and 70.5 mJ/cm^2 for ZnS and Cu doped ZnS respectively.

UV-Vis absorption spectroscopy

Figure 5 exhibits the UV–visible absorption spectra of the ZnS and Cu doped ZnS thin film over spectral range 350–850 nm for the films deposited as it is electrodeposited ZnS and 3% Cu doped ZnS. The absorbance peak at 290 nm and 308 nm for ZnS and Cu doped ZnS respectively. After Cu content doped in the ZnS absorbance peak is clearly blue shifted because quantum size effect. The optical band gap energy of ZnS and Cu doped ZnS thin films are determined by using the equation,

$$\alpha = \frac{\alpha_o (h\nu - E_g)^{1/2}}{h\nu} \quad (4)$$

Where, hν is the photon energy and E_g is the optical band gap. The plot of $(\alpha h\nu)^2$ vs. hν shown in inset of Figure 5. The band gap energy is found to

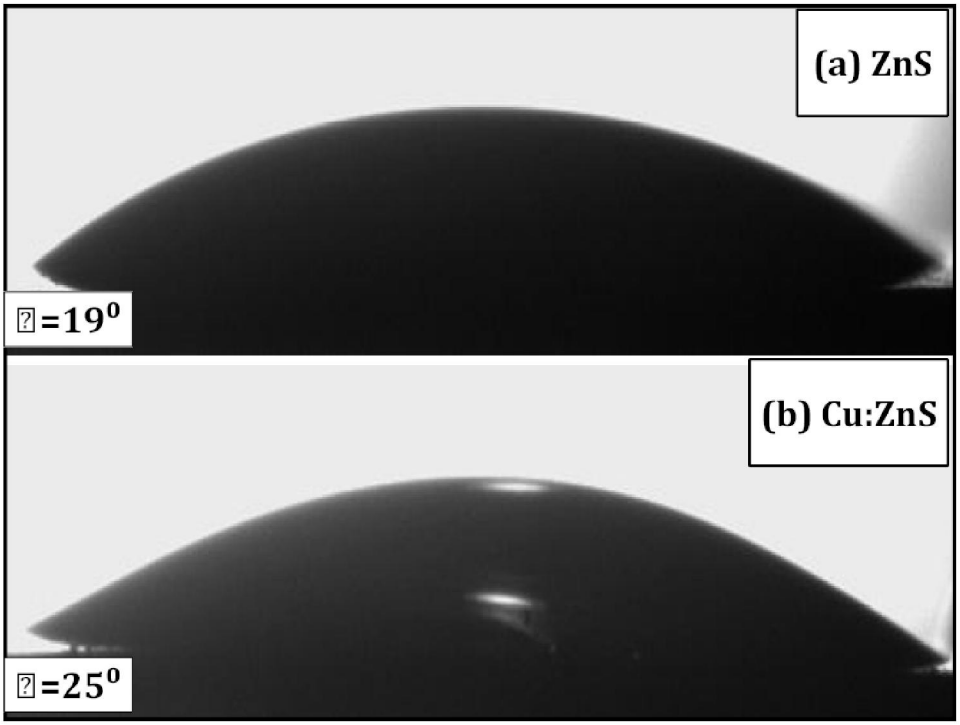

Figure 4 : (a) Contact angle of ZnS and (b) 3 % Cu doped ZnS thin films

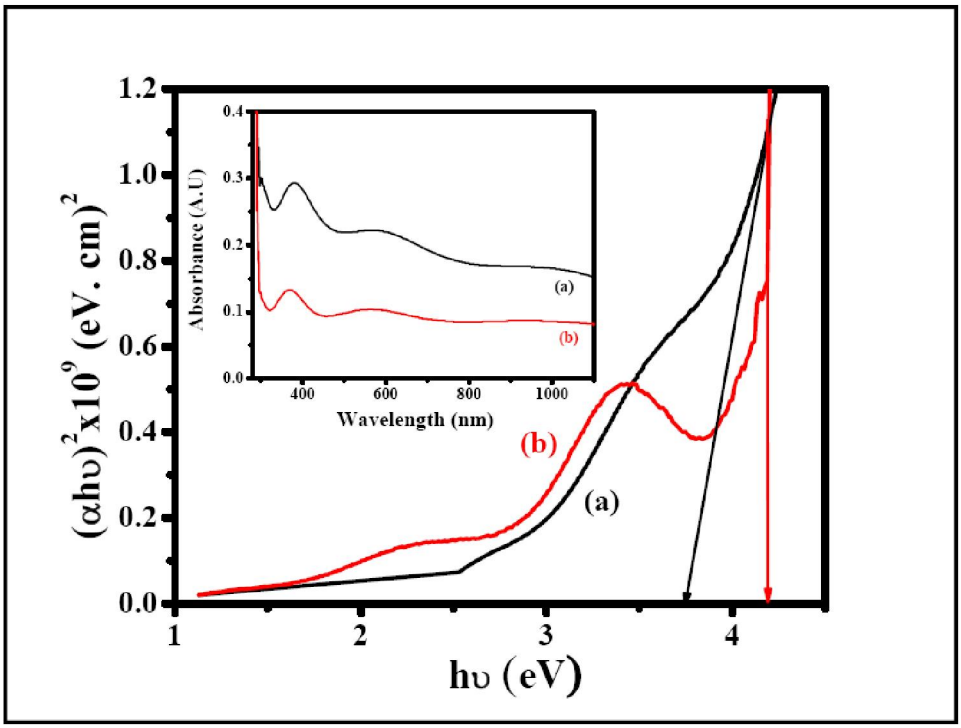

Figure 5 : (a) Optical band energy plot (a) ZnS and (b) 3 % Cu doped ZnS thin films. Inset optical absorption spectra of (a) ZnS and (b) 3 % Cu doped ZnS thin films

be 3.7 eV and 4.1 eV for ZnS and Cu doped ZnS respectively. The band gap energy increased after addition of Fe content in the ZnS due to the quantum size effect.

CONCLUSIONS

We have successfully deposited Cu doped ZnS

thin film by electrodeposition technique. The Cu doped ZnS thin films show the Cubic zinc blende structure. The Cu doped ZnS shows micro-chip like morphology. The FTIR peak at 660 cm^{-1} is confirm that a Zn-S bond. The undoped and Cu doped ZnS thin films are hydrophilic in nature. The optical band gap energy was observed to be increases after addition of Cu content in the ZnS because quantum size effect.

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