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Influence of Copper Concentration on the Structural and Optical Properties of Chemically Deposited $CuSbS_2$ Thin Films

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Abstract: *Thin films of $CuSbS_2$ have been deposited on ultrasonically cleaned glass substrates using a simple chemical bath deposition technique. Prepared films have been characterized using X-ray diffraction, Field Emission Scanning Electron Microscopy and UV-Vis-NIR spectroscopic techniques, respectively. X-ray diffraction analysis revealed that the prepared films possess polycrystalline in nature with orthorhombic $CuSbS_2$ in addition to secondary phase of monoclinic Cu_3SbS_3 and cubic $Cu_{12}Sb_4S_{13}$ for different copper concentrations. Field Emission Scanning Electron Spectroscopic analysis showed that the prepared films possess spherical shaped grains with irregular shaped clusters. Optical absorption analysis showed that the prepared films possess band gap value in the range between 1.7 and 2.4 eV.*

Keywords: $CuSbS_2$; Chemical Bath Deposition; Field Emission Scanning Electron Microscopy

1. INTRODUCTION

In recent years, there is need for semiconductors made from light absorbing materials, which can be used for the fabrication of more efficient devices like light emitting diodes, solar absorber coatings etc [1]. Semiconducting chalcogenide materials which have attracted researchers attention because of their device conversion efficiency upto 20.3% [2]. The toxicity of cadmium along with scarcity of tellurium, indium and gallium are the major problems for the fabrication of devices using these materials. Fabrication of solar cells using CdTe as absorber material reached conversion efficiency up to 17.3% [2]. copper antimony sulphide ($CuSbS_2$) is a relatively new material with narrow band gap value of around 1.5 eV received much attention because of its various applications in solid state devices such as optoelectronic devices and solar cells [3]. Thin films of $CuSbS_2$ are usually crystallized in orthorhombic structure (JCPDS ICDD 2003, File No: 44-1417) with lattice constants (a=14.50Å, b=6.019Å and c=3.796Å). The addition of sulphur (S) with copper (Cu) and antimony (Sb) which make the material in the form of thin film was found to be essential to enhance the photovoltaic properties of the material [4]. Thin films of $CuSbS_2$ have been prepared by a number of techniques such as vacuum evaporation [5], spray pyrolysis [6], thermal diffusion [7] and electrodeposition [8]. When compared to the above mentioned techniques used for the preparation of $CuSbS_2$ thin films, chemical bath deposition is now recognized as a versatile, low cost method to produce thin films for device fabrication. Also, it must be simple, more convenient and easy way of process to reproduce films with device quality [9].

In the present work, thin films of $CuSbS_2$ have been prepared on ultrasonically cleaned glass substrates using a simple chemical bath deposition technique at various copper (Cu) concentrations. Simple chemical reactions are used to analyze growth mechanism

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of the deposited films. The deposited films have been subjected to X-ray diffraction, Field Emission Scanning Electron Microscopy and Optical absorption techniques for the determination of structural, morphological and optical properties of the deposited films. The effect of copper (Cu) concentrations on above mentioned properties of the deposited films is investigated. The experimental observations are discussed in detail.

2. EXPERIMENTAL DETAILS

All the chemicals used in the present work were of Analar Grade (AR) grade reagents. The deposition bath used for the preparation of films containing reaction mixture of copper nitrate pentahydrate ($Cu(NO_3)_2$. $5H_2O$), antimony trichloride ($SbCl_3$) and sodium thiosulfate ($Na_2S_2O_3$). $SbCl_3$ with 1 M concentration was prepared in 5 ml of organic solvent acetone. In addition to that, 1 M $Cu(NO_3)_2$ was dissolved in 15 ml double distilled water and 1 M of $Na_2S_2O_3$ dissolved in 25 ml of double distilled water. Finally we obtained 80 ml of solution by the addition of distilled water. Finally, the solution was stirred continuously with the help of magnetic stirrer cum heater. After 30 minutes of stirring, the colour of the solution becomes brown. Ultrasonically cleaned glass substrates immersed vertically in the deposition bath which is maintained at room temperature for the time duration of 3 hours. After 3 hours of deposition, the substrates were removed from the deposition bath and well cleaned with double distilled water. Further, the deposited films were subjectd to the process of annealing at 250°C in air for 30 minutes. Similar procedure was followed for the preparation of film with different Cu concentrations. X-ray diffraction data of the prepared films was analyzed using an X-ray diffractometer (XPERT PRO PAnalytical, Netherland) with CuK_α (λ = 1.5406 Å) radiation. Surface morphology of the deposited films was analyzed using Field Emission Scanning Electron Microscope (BRUKER- QUANTAXEDS). Optical absorption analysis of the prepared films was analyzed using SPECORD210 PLUS UV-Vis-NIR spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Growth Mechanism

$CuSbS_2$ thin films have been prepared using chemical bath deposition technique. Antimony trichloride ($SbCl_3$) was mixed with sodium thiosulphate ($Na_2S_2O_3$) leading to form antimony thiosulphate which is explained by eq.(1) [9]. The dissociation of Sb^{3+} ions takes place from antimony thiosulphate $Sb_2(S_2O_3)$ according to eq.(2). The production of S^{2-} from $S_2O_3^{2-}$ ion takes place according to eq.(3). $Cu(NO_3)_2$ dissolved in water maintained at 300°K, decomposition of $Cu(NO_3)_2$ takes place leading to generate Cu^+ ions according to eq.(4). The released ions such as Cu^+, Sb^{3+} and S^2 from their corresponding solutions finally combined with each other leads to condense on the surface of the substrate producing $CuSbS_2$ film on the substrate.

$$2SbCl_3 + 3Na_2S_2O_3 \rightarrow Sb_2(S_2O_3)_3 + 6NaCl \quad (1)$$

$$Sb_2(S_2O_3) \rightarrow Sb^{3+} + 3S_2O_3^{2-} \quad (2)$$

$$S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2S^{2-} + 2H^- \quad (3)$$

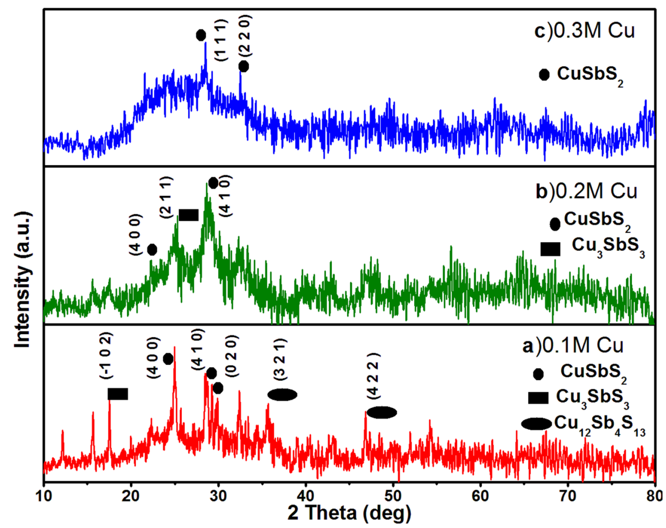

Figure 1. X-ray diffraction pattern of $CuSbS_2$ thin films annealed at 250°C prepared at various Cu concentrations: (a) 0.1 (b) 0.2 (c) 0.3 M.

$$Cu(NO_3)_2 + H_2O \xrightarrow{300K} Cu^+ + 2NO_2 + 4OH^{2-} \quad (4)$$

$$Sb^{3+} + 2S^{2-} + Cu^+ \rightarrow CuSbS_2 \downarrow \quad (5)$$

3.2. X-ray Diffraction

X-ray diffraction analysis has been carried out to determine crystalline nature and phases of the deposited film. Figure 1 shows X-ray diffraction (XRD) pattern of $CuSbS_2$ thin films deposited on glass substrates at various Cu concentrations. The different peaks in the diffractogram are indexed and the corresponding values of the inter planar spacing "d" is calculated and compared with standard JCPDS ICDD file for orthorhombic $CuSbS_2$, cubic $Cu_3SbS_3$and monoclinic $Cu_{12}Sb_4S_{13}$ [10 - 12]. The observed diffraction peaks of orthorhombic $CuSbS_2$ are found at 2θ values of 24.98º, 28.71º, 29.23º corresponding to the lattice planes (400), (410) and (020) respectively, which is shown in Figure 1a. It is also observed that the crystallites are preferentially oriented along (400) plane [10]. There is an additional appearance of diffraction peaks at 2θ values 32.38° and 42.94° corresponding to the lattice planes (3 2 1) and (4 2 2) of cubic $Cu_{12}Sb_4S_{13}$ which is denoted in Figure 1[11]. The diffraction peak appeared at 2θ value around 17.54 corresponds to the monoclinic phase of Cu_3SbS_3 [12]. All the identified peaks are in close agreement with corresponding phases of JCPDS ICDD 2003 file for $CuSbS_2$, $Cu_{12}Sb_4S_{13}$and Cu_3SbS_3. XRD pattern recorded for $CuSbS_2$ thin film obtained at 0.2 M and 0.3 M Cu concentrations are shown in Figures 1b, 1c. It is observed that the crystallites are preferentially oriented along (410) plane. It is also observed that the intensity of cubic $Cu_3SbS_3$and monoclinic $Cu_{12}Sb_4S_{13}$planes are found to decrease while increasing the concentration of Cu from 0.2 to 0.3M, and finally planes of cubic $Cu_3SbS_3$and monoclinic $Cu_{12}Sb_4S_{13}$ are disappeared which is denoted in Figure 1c.

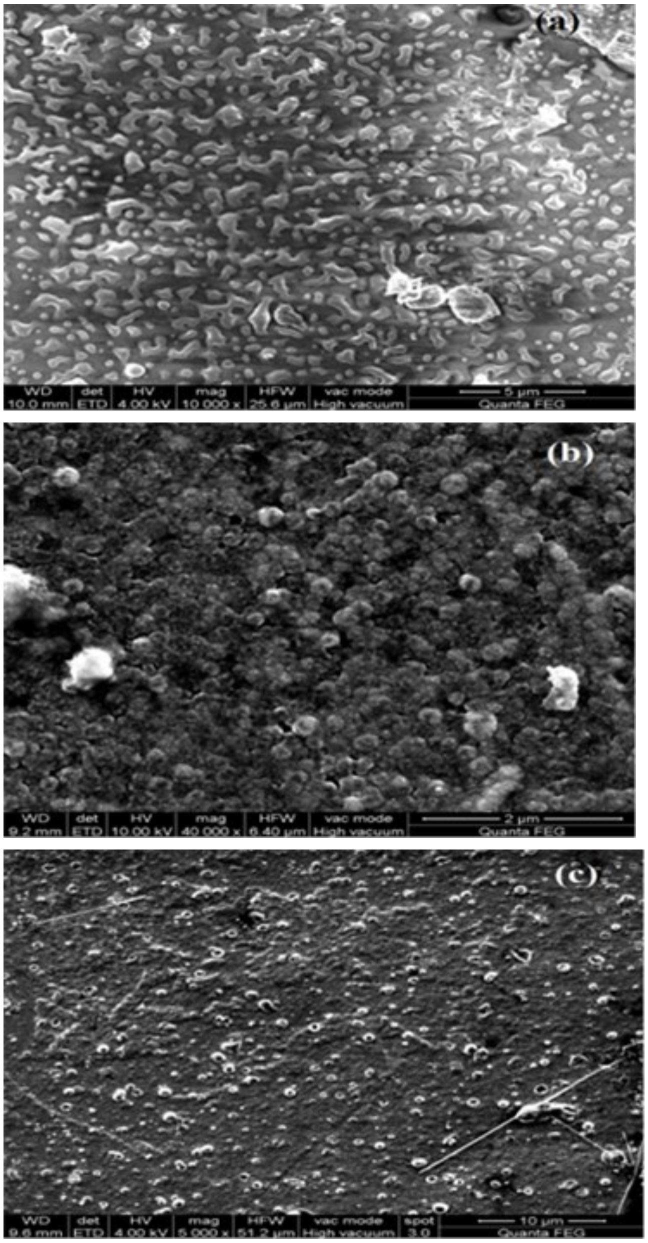

Figure 2. a. FESEM image of $CuSbS_2$ film obtained at 0.1 M Cu concentration and annealed at 250°C, b. FESEM image of $CuSbS_2$ film obtained at 0.2 M Cu concentration and annealed at 250°C, c. FESEM image of $CuSbS_2$ film obtained at 0.3 M Cu concentration and annealed at 250°C.

Crystallite size is defined as the number of crystallites formed along the surface of the substrate and it has been calculated using FWHM data with Debye Scherrer's formula [13-15].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{6}$$

where λ is wavelength of CuK_α radiation (λ =1.54060 Å), β is

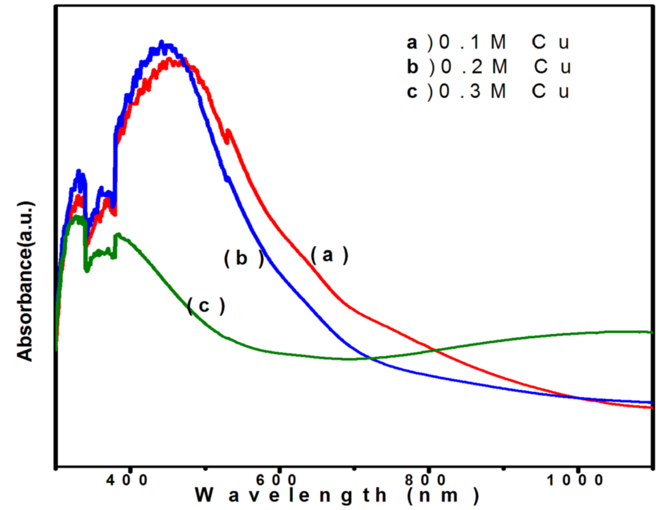

Figure 3. Optical absorption spectra of $CuSbS_2$ films annealed at 250°C for various Cu concentrations: (a) 0.1 (b) 0.2 (c) 0.3M.

Full Width at Half Maximum (FWHM) of the peak position in radian and θ is Bragg's diffraction angle at peak position in degree. The sizes of the crystallites obtained in the present work are found to be in the range between 27 and 45 nm.

3.3. Morphological Analysis

Surface morphology of the deposited films has been analyzed using Field Emission Scanning Electron Microscopy (FESEM). FESEM image of $CuSbS_2$ thin film prepared at 0.1 M Cu concentration and annealed at 250ºC is shown in Figure 2a. It is observed that the surface is covered with small spherical shaped grains and presence of voids at few places of the films. If the concentration of Cu is increased to 0.2M, there is change in surface morphology observed which is indicated in Figure 2b. This may be due to the fact that smaller grains are grouped together to form larger grains. The sizes of the grains are found to be in the range between 75 and 100 nm. Further increasing Cu concentration above 0.2 M, the film is covered with uniform spherical shaped nanopores implemented the uniform growth of film on the surface of the substrate which is denoted in Figure 2c. This may be due to the diffusion of Cu ions taking place at higher concentration and the surface is found to be uniform with well-defined surface morphology [7].

3.4. Optical Absorption Analysis

Optical absorption analysis of the prepared films has been carried out using an UV-Vis-NIR spectrophotometer in the wavelength range between 300 and 1200 nm. Figure 3 shows the optical absorption spectra of $CuSbS_2$ thin films obtained at various Cu concentrations. All the prepared films are found to exhibit maximum absorption in the wavelength range between 300 and 500 nm which must be useful for photovoltaic applications. It is clearly noticed that absorption edge of the films shift towards shorter wavelength while increasing the concentration of Cu from 0.1 to 0.3 M. Since the diameter of the crystallites is found to be less than 30 nm, the absorption depends upon only the oscillation of the dipoles. It is observed that diameter of crystallites decreases, the absorption

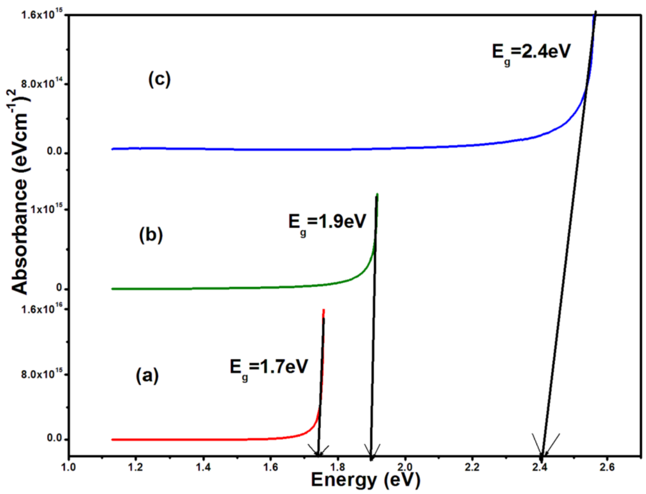

Figure 4. Plot of (hυ) versus $(\alpha h\upsilon)^2$ for $CuSbS_2$ thin films annealed at 250 °C for various Cu concentrations: (a) 0.1 (b) 0.2 (c) 0.3M.

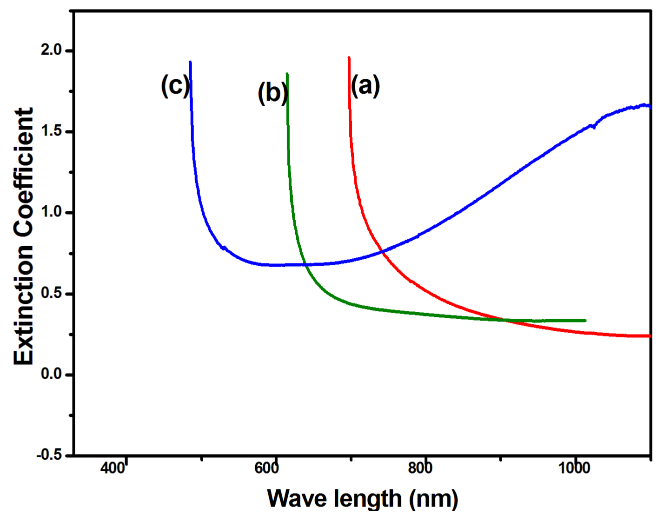

Figure 5. Plot of extinction coefficient (k) with wavelength (λ) for $CuSbS_2$ films annealed at 250°C for various Cu concentrations: (a) 0.1 (b) 0.2 (c) 0.3 M.

peaks on shorter wavelength side shift towards the blue region of the spectrum [17]. Thickness of the prepared films are found to be 176, 181 and 194 nm for films obtained at 0.1, 0.2 and 0.3M Cu concentrations, respectively. The absorption coefficient of $CuSbS_2$ films prepared on glass substrates is calculated using the following eq.(7) [13,15].

$$\alpha = \frac{1}{t}\ln\left(\frac{A}{T}\right) \quad (7)$$

where α is the absorption coefficient in cm^{-1}, t is thickness value of the deposited film in nm, A is absorbance and T is transmittance in terms of percentage. The band gap (E_g) and refractive index (n) value of the deposited films are calculated using the following eqs. [13-15].

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \quad (8)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (9)$$

where $h\nu$ is photon energy in eV, E_g is energy gap in eV, A is energy dependent constant and n is an integer. Optical absorption and transmittance measurements were carried out to determine optical properties of the deposited films. A plot of (hυ) versus $(\alpha h\upsilon)^2$ for $CuSbS_2$ films prepared on glass substrates at various Cu concentration is shown in Figure 4. The plot is linear indicating the presence of direct transition present in the deposited films. Extrapolation of the plot to X-axis (Energy axis) gives band gap value of the deposited films. The band gap value of the deposited films is found to be in the range between 1.7 and 2.4 eV. The increase in value of film thickness thus leads to decrease in band edge sharpness, which result increase in the energy gap value of the deposited films. This is in close agreement with the value reported earlier [1, 17]. Optical constant such as extinction coefficient (k) is calculated using eq.(9). Variation of extinction coefficient (k) with wavelength (λ) for $CuSbS_2$ thin films deposited at various Cu concentrations is shown in Figure 5. It is observed that the value of "k" is found to decrease while increasing the wavelength "λ" and reaching its minimum value in the wavelength region between 480 and 720 nm.

4. CONCLUSIONS

Thin films of $CuSbS_2$ were prepared on glass substrates at various Cu concentrations using chemical bath deposition technique. X-ray diffraction results revealed that the prepared films possess polycrystalline nature with the mixture of cubic, monoclinic and orthorhombic phases. It is also observed that the intensity of orthorhombic phase ($CuSbS_2$) increased and the intensity of cubic and monoclinic phases (Cu_3SbS_3 and $Cu_{12}Sb_4S_{13}$) decreased if the concentration of Cu was increased in the deposition bath. FESEM analysis showed that there is change in surface morphology with irregularly shaped grains due to uniform cluster of Cu-rich particles. Optical absorption analysis revealed that the deposited films were found to exhibit band gap value in the range between 1.7 and 2.4 eV for films obtained at various Cu concentrations. The band gap value observed in the present work was quite closer to the value reported earlier. Further detailed investigation on film composition, Raman spectroscopic analyses are in under process.

5. ACKNOWLEDGEMENTS

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