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Effect of complexing agent: Comparative study of copper based ternary thin films by chemical bath deposition technique

E. Anuja[a]*, R. Thiruneelakandan[a] and K. Manikandan[b]

[a]Department of Chemistry, University College of Engineering, Anna University, BIT Campus, Tiruchirappalli-620 024, Tamilnadu, India

E-mail: anuja.tau@gmail.com

[b]Department of Physics, Bharathidasan University Constituent Model Arts and Science College for Women, Veppur-621 717, Tamilnadu, India

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Thin films of $FeCuS_2$ and $ZnCuS_2$ at varying complexing agents were deposited by chemical bath deposition method. Ultrathin ternary films were grown on glass plate and the structural, morphological and optical characteristics were analyzed using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-Visible spectroscopy techniques. X-Ray diffraction (XRD) pattern of $FeCuS_2$ and $ZnCuS_2$ thin film explains the polycrystalline nature, and also it showed the deposition of cubic phases at room temperature. The SEM images show that the prepared films show clear morphology influenced by the complexing agent Leishman stain. The effect of complexing agents on the material absorbance and band gap energy of the deposited thin films were analysed using UV-Vis spectrometry. From these results, it is indicated that the prepared films are suitable candidate for solar cell applications.

Keywords: EDTA, copper iron sulphide, copper zinc sulphide, chemical bath deposition, absorbance, band gap.

Introduction

In the present scenario, solar energy can be effectively converted as thermal energy as solar heat or electric current termed as solar photovoltaic[1]. Thin films are highly popular as transducers for harnessing the solar energy[2]. In general, total energy acquired by these transducers are linearly proportional to the surface area. Hence, solar energy devices might have large surface area in order to acquire large amount of energy[3]. The researchers today focus their research mainly on thin film materials that have versatile applications in photovoltaic, solar cell, photo-catalysis and superconducting materials having exponential growth[4]. The substrate and reagent materials are extensively used for making thin films are abundant and cheap without toxic nature with wide applications.

The thin film making technique should be done inquisitively in order to achieve an ultrathin and uniform film coating. The intrinsic interest on making and research on ternary chalcogenide materials are growing exponentially[5]. There are huge depositions techniques available such as chemical bath deposition[6], spray pyrolysis[7], metal organic chemical vapour deposition[8], sputtering[9], electrodeposition[10], sol-gel[11], Successive Ionic Layer and Reaction (SILAR)[12], etc. are in usage for the deposition of thin films. Ternary thin films have been deposited and characterized by various researchers possess specific applications includes $CuSbS_2$[13], CuNiS[14], Cu_2SnS_3[15], etc.

In the present research work, $FeCuS_2$, $ZnCuS_2$ thin films were deposited using chemical bath deposition method with the influence of complexing agents EDTA and Leishman's stain. Structural, surface morphology and optical investigations of the prepared thin films were carried out. With these investigations the prepared thin films are considered as a suitable material for solar cell applications.

Experimental

Preparation of thin films:

All the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionized water (Alpha-Q Millipore). The $FeCuS_2$ and $ZnCuS_2$ thin film was

prepared from bath using aqueous solution of ferrous sulphate, copper sulphate, zinc sulphate and sodium sulphide. The microscopic glass was used as the substrate for the chemical bath deposition of the thin film. Before chemical bath deposition, the glass was degreased with acetone for 10 min and the ultrasonically cleaned with distilled water for 10 min and dried in desiccator.

The $FeCuS_2$ thin film deposit were carried out room temperature by using following procedure 20 ml $FeSO_4$ (0.05 *M*) was taken in 100 ml beaker and 20 ml $CuSO_4$ (0.05 *M*) was mixed in it with constant stirring and also 10 ml of (0.1 *M*) Na_2S was also added along with constant stirring with using magnetic stirrer. The $CuZnS_2$ thin film deposition was done at room temperature by the procedure of 20 ml $ZnSO_4$ (0.05 *M*) was taken in 100 ml beaker and 20 ml $CuSO_4$ (0.05 *M*) was thoroughly mixed with constant stirring and also 10 ml of (0.1 *M*) Na_2S was also added and magnetic stirring was performed. The clean glass substrate was immersed vertically in to the beaker for 120 (min) without disturbing. The deposition was carried out using various complex agent 5 drops EDTA and 5 drops Leishman's stain in a separate 100 ml beaker. After completion of films deposition, the deposited films were washed distilled water and dried in air for further characterization.

Materials characterisation:

The structural characterization of $FeCuS_2$ thin films deposited on glass substrates was carried out by analysing the XRD patterns which were obtained using Ultima3 theta-theta gonio X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å) with a scan rate of 4° min^{-1} from 2θ ~20° to 60°. For surface morphology studies of the film deposited on glass substrate, scanning electron microscopy technique was used. The films were loaded in the sample holder of VEGA3 TESCAN unit for SEM analysis. Optical absorption studies were carried out using a UV-VIS-NIR spectrophotometer (Agilent Ultraviolet Spectrum) in the wavelength range of 300–900 nm.

Results and discussion

XRD analysis:

The deposited films were analysed for X-ray diffraction studies using Cu-Kα radiation (λ = 0.15406 nm) to understand the crystalline nature of the films.

Fig. 1 shows the X-ray diffraction patterns of the as grown

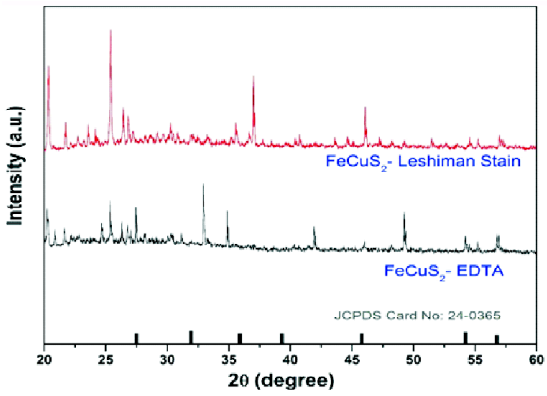

Fig. 1.

film $FeCuS_2$ with EDTA added and $FeCuS_2$ added with Leshiman stain. The XRD patterns are having characteristic peaks at 2θ = 25.36°, 32.93°, 37.08°, 41.95°, 46.13°, 49.36°. No added impurities were found[16]. All the diffraction peaks are well agreement with the JCPDS standard file number: 24-0365 having cubic structure. The lattice constants for $FeCuS_2$ with EDTA added and $FeCuS_2$ added with Leshiman stain are 5.606 Å and 5.608 Å respectively.

Fig. 2 shows the X-ray diffraction patterns of the as deposited thin films $CuZnS_2$, $CuZnS_2$ with EDTA added and $CuZnS_2$ added with Leishman stain. The XRD patterns are having peaks at 2θ = 22.05°, 23.50°, 29.06°, 30.99°, 31.88°, 52.01°. No impurities were observed[13]. All the diffraction peaks are well agreement with the JCPDS standard file number: 65-7736 for CuS and 65-5476 for ZnS with cubic structure.

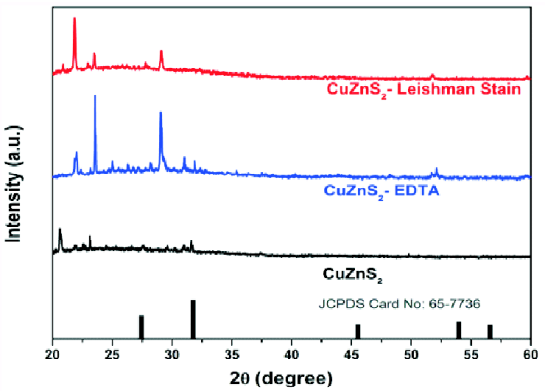

Fig. 2.

The crystallite size (*D*) of the $FeCuS_2$ that were formed in the film during deposition are calculated from the diffrac-

tion peaks. Average crystallite size (*D*) has been estimated by using Scherrer formula[12,17],

$$D = \left(\frac{0.9 \times \lambda}{\beta \cos \theta} \right) \quad (1)$$

where λ is the wave length of X-rays (0.1541 nm), β is FWHM (full width at half maximum), 'θ' is the diffraction angle and '*D*' is crystallite size.

The broad nature of the diffraction peaks at 2θ = 25.36 clearly indicates that the crystallite size of the samples is the order of 5.56 nm and 6.21 nm for $FeCuS_2$ with EDTA added and $FeCuS_2$ added with Leshiman stain respectively. From the XRD patterns, it is clearly suggested that the reflection peaks are in phases of nature, thus the film deposited is in polycrystalline nature.

The broad nature of the obtained diffraction peaks suggest the crystallite size of the samples is of the order of 5.55 nm, 5.86 nm and 6.21 nm for for $CuZnS_2$, $CuZnS_2$ with EDTA added and $CuZnS_2$ with Leishman stain respectively. From the XRD patterns, it is clearly indicates that the diffraction peaks are in phases of nature.

SEM analysis:

Scanning electron microscopy is a good method for studying microstructure of thin films. The microstructure of $FeCuS_2$ films without complexing agent, with EDTA added and with Leishman stain added is shown in Fig. 3(a), 3(b) and 3(c) respectively. The thin film deposition process on a glass substrate relies mainly on the formation of nucleation sites and subsequent growth of thin films. It is observed from SEM micrograph studies that the as-deposited $FeCuS_2$ films are homogeneous, without pinholes, without cracks, and are well covered uniform coating to the substrates[18]. From Fig. 3(a-c) SEM micrographs, it is seen clearly that the iron copper sulfide deposits for all the complexing agent. Each unit has a non-porous structure. The increased grains are formed in the surface morphology with the varying complexing agents[19]. However, the pinholes of the thin film are reduced on surface; this may be due to the influence of EDTA.

The microstructure of $CuZnS_2$ films without complexing agent, with EDTA added and with Leishman stain is depicted in Fig. 4(a), 4(b) and 4(c) respectively. It is understood from SEM studies that the as-deposited $CuZnS_2$ films are highly

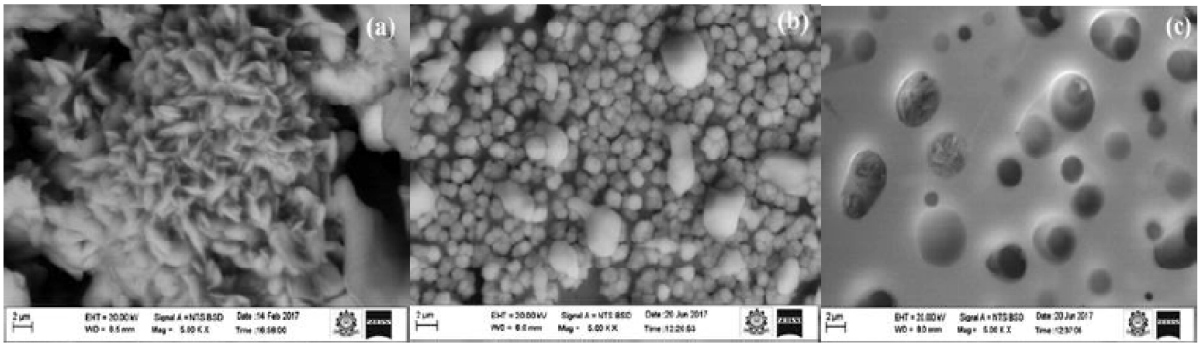

Fig. 3.

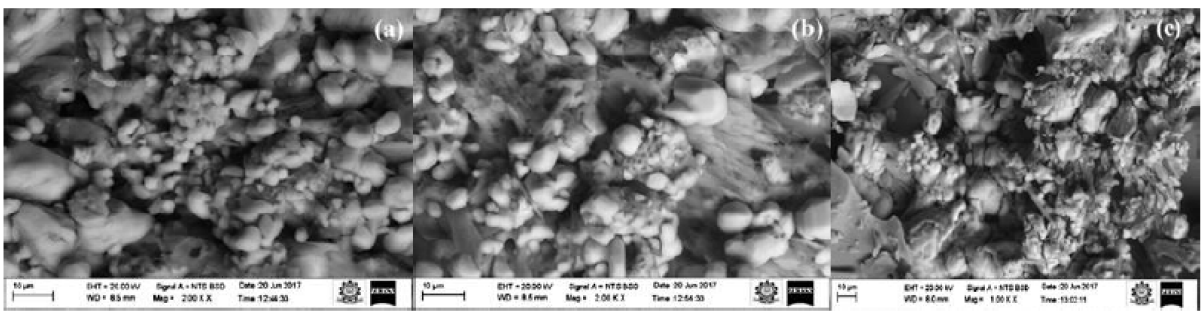

Fig. 4.

uniform, without pinholes and cracks, and are having uniform coating to the substrates[16].

Optical analysis:

The optical properties of the $FeCuS_2$ thin films are obtained from Fig. 5 for $FeCuS_2$ films without complexing agent, with EDTA added and with Lesihman stain added respectively. Absorbance spectral measurements are in the range of 300 to 800 nm as obtained from the UV-Vis spectrophotometer. As the wavelength increases, the absorbance possess a maximum at 305 nm for $FeCuS_2$ films without complexing agent, 296 nm for $FeCuS_2$ with EDTA added and 288 nm for $FeCuS_2$ films with Lesihman stain added. Absorption edge shifted towards lower wavelength side with varying complexing agents[20].

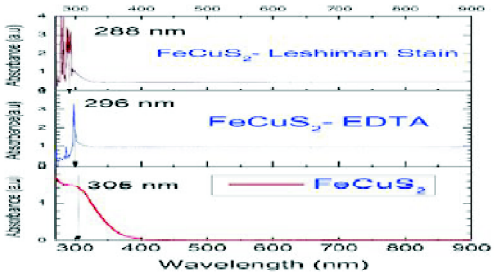

Fig. 5.

From Fig. 6 for $CuZnS_2$ films without complexing agent, with EDTA added and with the addition of Leishman stain respectively. The absorbance spectral measurements are given in the range of 250 to 900 nm as available from the UV-Vis spectrophotometer. As the wavelength increases, the absorbance shows a maximum at 298 nm for $CuZnS_2$ films without complexing agent, 295 nm for $CuZnS_2$ with the addition of EDTA and 293 nm for $CuZnS_2$ films with Lesihman stain. Absorption edge is getting shifted towards lower wavelength with the different complexing agents[17]. The UV region is possesses high absorbance properties which shows that the present material could be used as a window for photovoltaic cells.

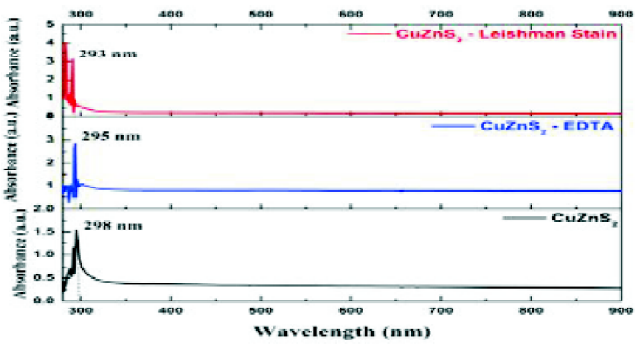

Fig. 6.

Conclusion

Thin films of copper iron sulfide ($FeCuS_2$) were prepared using without complexing agents and with EDTA and Leishman stain as complexing agents by chemical bath deposition method. XRD analysis suggests crystalline nature of the films without any impurities. Also, the XRD pattern suggests that the crystalline nature is primitive cubic phases. The SEM image shows the uniform coating without pin holes and larger particle structure of the thin films which reveals that the surface morphology of the films is highly influenced by the complexing agent. From the AFM results, it was understood that the average grain size and roughness values were observed clearly in the dimensions of nanometres. The UV-Vis spectral studies enumerated the influence of complexing agent on the absorbance. The material can be used as direct semiconductor and the values of band gap energy are in the range of 3.57 – 3.85 eV applications.

Thin films of copper zinc sulfide ($CuZnS_2$) were deposited without complexing agents and with EDTA and Leishman stain by chemical bath deposition method. XRD patterns suggest crystalline nature of the films with cubic phases and with no impurities. SEM image depicts the highly uniform coating and higher particle structure of the thin films. Also, the surface morphology of the films is greatly dominated by the complexing agent. From the topographical studies, it is known that the average grain size and roughness values were clearly observed. The UV-Vis studies illustrate the effect of complexing agents on the optical absorbance. The present material could be used as direct semiconductor and the values of band gap are in the range of 3.92 – 4.21 eV.

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