JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Structural and Morphological Properties of CuS Thin Films Prepared By Spray Pyrolysis Technique

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Abstract: Copper Sulphide thin films were prepared at 300^0C temperature by using the thio urea and copper (II) chloride aqueous solutions .The structural, surface morphological and EDS properties of the as deposited thin films were investigated via X-ray diffraction, Scanning electron microscopy, and EDS. Thickness of the thin films determined by using gravimetric weight difference method. Thickness of the as deposited thin films were found t=0.5384 µm, 0.5174 µm and 0.4482µm. X-ray diffraction pattern reveals that all the prepared thin films are polycrystalline in nature and crystallized in hexagonal structure with atomic planes preferential orientation along (102), (103) (112)and (110) direction . The crystalline size increases from 35 nm to 57 nm. Uniform deposition having nanocrystalline granular morphology distributed over the entire glass substrate was observed through FESEM studies. EDS spectra showed the chemical purify of the films. X-ray diffraction (XRD) patterns show that crystallinities of the films are dependent on the copper concentration in the solutions.

***Index Terms* – CuS Thin film, Spray pyrolysis, Structural, Morphological, EDS Properties.**

I. INTRODUCTION

Copper sulphide is an important material from the point of basic research, because it is known to exist in several crystallographic and stoichiometric forms. They are chalcocite (Cu_2S, orthorhombic), djurlite ($Cu_{1.96}S$, orthorhombic), digenite ($Cu_{1.8}S$ .orthorhombic), anilite ($Cu_{1.75}$ S, orthorhombic) and co-vellite (CuS-Hexagonal) [1-3]. Different techniques have been used for the CuS thin films deposition, such as chemical bath deposition [4], photochemical deposition [5], metal organic chemical vapour deposition [6] and spray pyrolysis deposition [7] .Spray pyrolysis is a simple and low – cost technique used to deposit thin films at nano scale or micro scale [8]. Among all mentioned previous techniques, spray pyrolysis deposition is the promising one, for its simplicity, the ability to cover effective large area and low cost deposition, so no need of any advanced instrumentation in this technique. By changing some deposition parameters such as composition of precursors solution (Cu: S) molar ratio or the substrate temperature; the composition, morphology and structural properties of CuS thin films were be designed and changed [9-10]. The as deposited films were characterized for their structural, surface morphological and compositional properties [11]. CuS has been used in photovoltaic conversion [12], catalysis [13-14], electrode [15], hydrogen and ammonia gas sensor [16-17], cathode material in lithium rechargeable batteries [18] and conductive coating [19-20].

II. SYNTHESIS METHOD

Spray pyrolysis technique gives very good adhesion for CuS thin films that deposited on glass substrate unlike most of other techniques [10]. Copper trichloride $CuCl_3$ and thio urea were used to prepare the solution for depositing CuS thin films by spray pyrolysis deposition. The solution was sprayed on glass substrate at 300^0C temperature which is suitable for deposition CuS thin films .The distance between the nozzle and the substrates was 30 cm ,which is the best spray distance because more than this will cause spray flight out the substrate [21]. The as deposited films are characterized for their structural, surface morphological and compositional properties using X - ray diffraction (XRD), Scanning electron microscope (SEM) and EDS. X-ray diffractions (XRD) are recorded with a Philips X' pert X-ray diffractometer using CuKα monochromatic radiations [11].

III. RESULTS AND DISCUSSION

Fig.(1) shows the XRD pattern of CuS thin film deposited onto glass substrate .XRD pattern revealed that the CuS thin film was polycrystalline in nature with orthorhombic (Covellite) crystal structure . XRD pattern of the CuS thin films showed sharp peaks (102) along with other minor peaks corresponding to (103), (110) and (112) planes. Moreover the presence of number of peaks corresponding to CuS indicates that the film is polycrystalline with preferred orientation along (102) plane [22]. Crystalline grain sizes (D) of the film was determined from the full -width at half maximum height (β) of the predominant peak at $2\theta=29.19^0$ corresponding (102) orientation. This was done using the Debye –Scherrer formula [23-24].

$$D=K.\lambda/\beta.Cos\theta$$

Where k is a constant (0.94), λ is wavelength of X-ray, β is broadening of diffraction line measured at full width at half of the peak maxima in radians and θ is Bragg's angle .We found that the crystalline size ranges between 35-57 nm for thin film [22].
Scanning electron microscope (SEM) is one of the promising techniques for the topography study of the samples and it gives important information regarding the surface morphology, shape and size of the particles in the film [25]. The FESEM picture of the CuS film. Fig. (2) Shows that the film was relatively uniform, homogeneous with the average grain size (d) was 100 nm [8].and having dense microstructures. The film surface looks smooth and uniform. It is well clear from the micrographs that the particles are spherical and adherent. It is seen that these spherical grains are uniformly distributed to cover the surface of the substrate completely [26]. The presence of nominal compounds and chemical purity of the CuS thin film is confirmed by EDS .The typical EDS of as deposited CuS thin film shown in the Fig.(3) [25]. The elemental composition of the as –deposited CuS thin film was investigated using EDS and the pattern is shown in Fig (3). Peaks of Cu and S exhibit the presence of these elements in the as-deposited film. The average atomic percentage of Cu: S in the as deposited film was calculated as 63; 37[24].

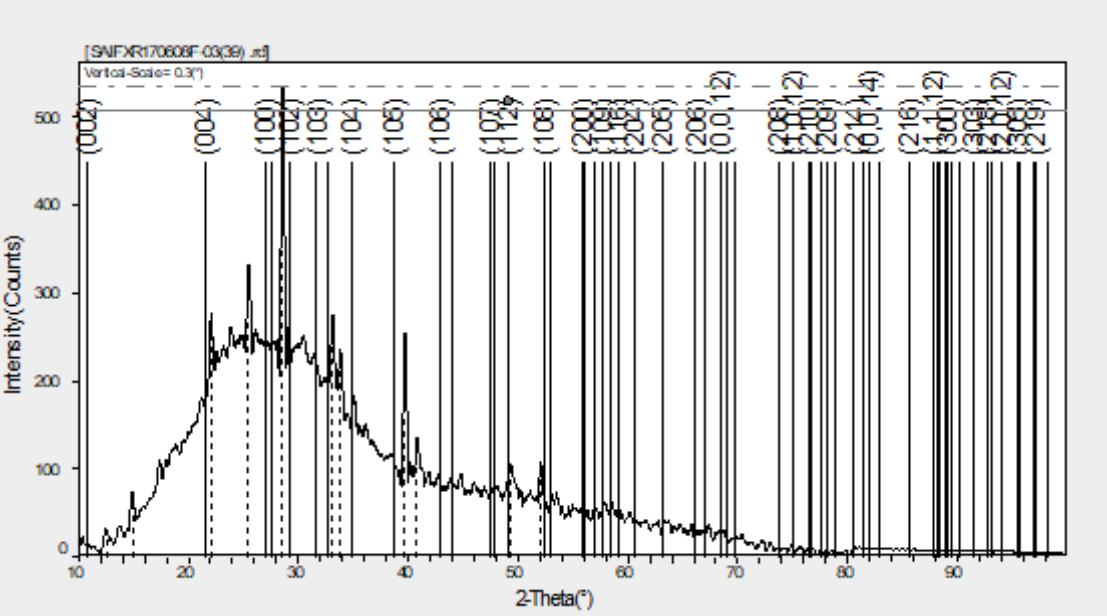

Figure 1. XRD Pattern of CuS Thin Film

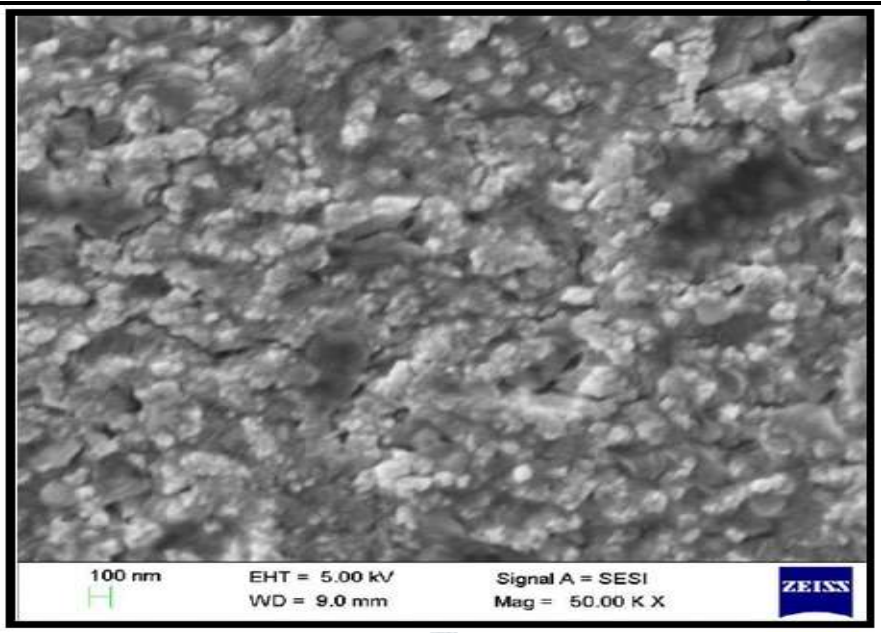

Figure 2. FESEM Image of CuS Thin Film

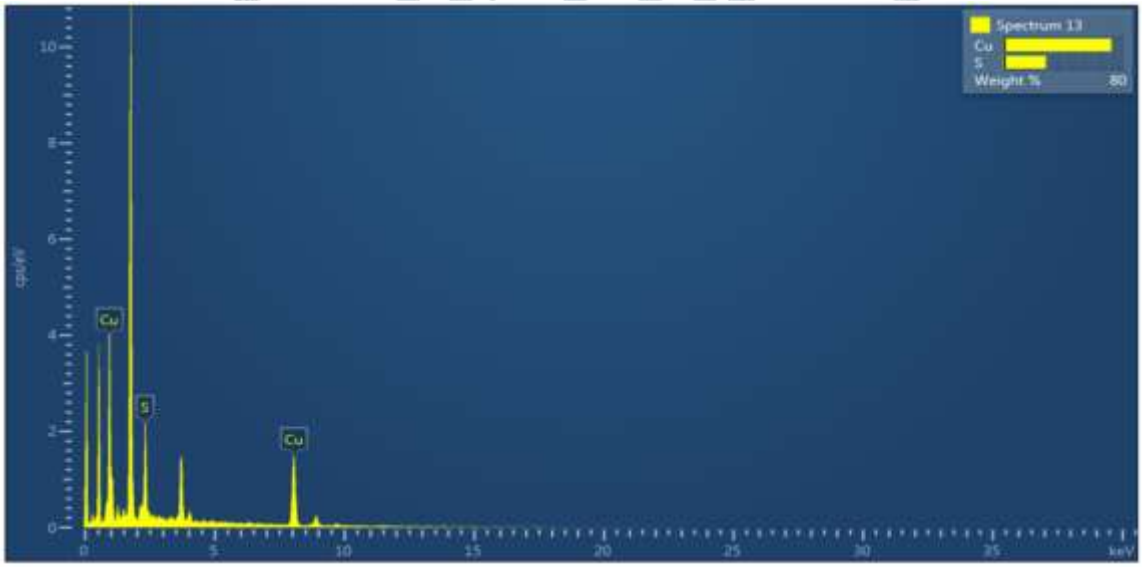

Figure 3. EDS Spectra Of CuS Thin Film.

Conclusions

Homogeneous and relatively uniform thin film of covellite (CuS) with hexagonal crystalline structure is deposited at 300^0C temperature by chemically spray pyrolysis from aqueous solutions containing CuCl2 and thio urea as precursors. XRD measurement shows that the prepared film is polycrystalline hexagonal in nature. A morphological study shows that the film is smooth, dense and homogeneous without any pinholes and cracks. The quantitative elemental analysis of the CuS thin film was carried out using EDS and the result revealed that the atomic percentage ratio of Cu: S in the as deposited film was about 63:37.

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