Preparation & characterization of CuS thin films via spray pyrolysis technique for photovoltaic applications.

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Abstract. Copper Sulphide (CuS) is a p-type semiconductor material widely used in photovoltaic applications. CuS thin films have been coated on a glass substrate at 300°C by spray pyrolysis technique. Copper Sulphate in different concentrations with constant concentration of Thiourea (without any complexing agent) was used as a precursor to fabricate the films. The different properties of the films were characterized. Their structural properties were done by X-ray diffraction. XRD analysis showed that the films are high crystalline in nature. The morphological properties were done by SEM and EDX. The atomic percentage of CuS particles were recorded by EDX. The optical properties were studied by UV-Spectrometer in visible to infrared region. The band gap value of the film varied from 2.2eV to 2.7 eV with the different concentration of Copper Sulphate.

Keywords. CuS, Spray pyrolysis, XRD, SEM-EDAX, UV-VIS.

1. Introduction

Copper sulphide (CuS) is one of the potentially useful P-type semiconductor material. It has excellent optical, electronic, physical and chemical properties [1,2]. CuS thin films have great scientific attention due to the semi conductive and non-toxic properties. It is used in multiple applications such as solar cells, photo thermal conversion of solar energy, microwave shielding coatings, chemical sensors, cathode material of lithium ion batteries and in hard coatings etc [3, 4]. Copper sulphide thin films could be prepared by variety of deposition techniques like chemical bath deposition(CBD) [5], chemical vapour deposition technique(CVD) [6], sol gel [7], spray pyrolysis [8], sputtering [9], thermal oxidation method [10], vacuum evaporation [11], electro deposition and molecular beam epitaxy etc. Among these methods, spray pyrolysis is a low cost and non-vacuum required technique to synthesize material in the form of thin films. In this method precursor is sprayed onto a heated substrate and provides a high quality and large area deposition.

In the present work, we investigate the deposition of CuS thin films by spray pyrolysis technique. The characterization studies of structural, morphological and optical are carried out. These results together provide the properties of the CuS thin films.

2. Preparation of the film

The non-foggy polished microscopes slides have been used as the substrate for CuS thin films. The thickness of the slides was about 1.3mm and size about 75mm x 25mm respectively. Substrate cleaning is one of the most vital and compelling aspects in the deposition of uniform thin film to attain good stoichiometry. The polished glass slides were first cleaned in ordinary water 2 to 3 times. And
then cleaned with a detergent solution then rinsed with acetone followed by distilled water then drained subsequently.

For the synthesis of CuS thin films Copper Sulphate and Thiourea were utilized as a source of Cu\(^+\) and S\(^-\) respectively [12]. Copper sulphide (CuSO\(_4\).5H\(_2\)O) with different concentrations (0.05M, 0.1M, 0.15M, 0.2M) and thiourea with constant concentration (0.1M) were dissolved in 50ML of distilled water in separate beakers. To form a desired precursor solution Thiourea solution was added gradually to the Copper Sulphate solution under constant stirring. The aqueous solutions of these constituents were sprayed by means of carrier gas. The spray nozzle and the substrate distance were kept at 30cm respectively. The desired precursor was sprayed onto the preheated substrate at 300\(^{\circ}\)c. In order to maintain constant temperature the spraying process was takes place for 5 seconds with 30 seconds of interval. That process was repeated continuously until to form a complete thin film with desired thickness. After deposition the films were washed with distilled water and dried subsequently. This is to be done to remove the weakly bonded atoms on the surface.

X-ray diffractometer was used to analyse the crystalline structure of the thin films. Optical absorption and transmission data were examined with UV–VIS spectrometer in the range of 300nm – 900nm. (SEM) Scanning Electron microscopy and energy dispersive X-ray analysis (EDX) were used to study the surface morphology of CuS thin films.

3. Results and discussion

3.1. X-Ray Diffraction analysis.

X-ray diffraction was performed for the structural analysis of the CuS thin films. The XRD pattern indicates a strong intensity peaks at \(2\theta = 20.40^{\circ} \& 11.33^{\circ}\). It indicates high crystalline nature of the films. When the size of the particle increased, it shows high intensity peaks with good crystallinity [13]. Broad peaks are observed for low intensity values, and the size of the particle also very low. \(2\theta = 68.58^{\circ}\) has low intensity value with small particle size. Crystalline structure has been depending on the precursor composition and the substrate temperature. The surfactants and complexing agents were added to the solutions to increase the stability of the solutions and the uniformity of the deposited film [14]. But here in the absence of complexing agents and surfactants the precursor solution is stable only a limited period of time after some precipitates are formed. Because of the instability the solutions cannot be used any more for film formation. The various crystalline size CuS was attributed due to the precursor concentration. The crystalline size was calculated by Debye Scherrer’s formula mentioned in equation (1)[15]. The obtained crystalline size was in the range from 1nm – 7nm. The broadening of diffraction peaks (\(\beta\)) influenced by the strain and crystalline size of the film. Strain is attributed due to the imperfection and distortion in the crystal lattice. The greater crystal size has lower dislocation and strain. Strain is calculated by Stokes Wilson equation mentioned in equation (2)[16]. If the value of strain is low then it may be said that the dislocations are the important reason for the broadening of the peaks. Dislocation density calculated by the equation (3).

\[
\text{Crystalline Size} \quad D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)
\]

\[
\text{Strain} \quad \varepsilon = \frac{\beta \cos \theta}{4} \quad (2)
\]

\[
\text{Dislocation density} \quad \delta = \frac{1}{D^2} \quad (3)
\]

The calculations done by the above equations are shown in table (1)
Table 1. Showing 2θ, FWHM, interplanar spacing, dislocation density, strain of CuS thin film

| 2θ°  | FWHM | d-spacing | Grain size D (nm) | Dislocation density δ | Strain ε (x10^-3) |
|------|------|-----------|-------------------|-----------------------|-------------------|
| 11.35| 2.88 | 7.80      | 5.48              | 3.32                  | 6.2               |
| 20.41| 2.3616| 4.35     | 6.76              | 2.1878                | 5.06              |
| 68.58| 1.1808| 1.37     | 1.61              | 3.855                 | 2.1               |

Figure 1. X-Ray Diffraction patterns of CuS

3.2. Scanning Electron Microscopy (SEM).
The surface morphology of the CuS thin films was seen under scanning electron microscopy. It shows that the films are smooth and covered the substrate. It shows particles in different shapes. Elongated, ellipsoidal and spherical shaped particles are noted. And also regular and irregular shape and form of the particles also seen in the SEM image. This is because of the polycrystalline nature of the film. The ratios of copper sulphate and thiourea (0.05M; 0.1M) and (0.15M; 0.1M) shows smooth films without any pores. Some dark spots are also deposited over the film because of the nucleation over growth. EDX confirms that the Cu & S particles present in the CuS films. The reducing reactions not occurred because the deposited films contain only CuS. It gives the strong information about the atomic percentages of the particles which is present in the film. Proper concentration of copper and thiourea is more important to obtaining smooth and continuous films.
Figure 2. SEM images of CuS

Figure 3. EDX results of CuS
3.3. Optical Properties.

UV-spectrometer has been used to carry out the optical study of the CuS thin films. It exhibits strong absorption in the range of 325nm to 625nm. It shows a desirable absorption at visible range. The transmission value increases from 400nm – 700nm wavelength range.

An absorption co-efficient can be calculated from Lambert’s relation $\alpha = 2.303A/t$ [17], where A is the optical absorption and t is the thickness of the film. The band gap value was calculated by Tauc’s relation [18]

![Figure 4. (a) Absorption and (b) Transmission spectrum of CuS thin films.](image)

![Figure 5. Optical band gap of CuS](image)

The optical energy band gap of CuS thin films was calculated by plotting a graph based on $(\alpha h\nu)^2$ vs $(h\nu)$. The band gap of CuS found to be varying from 2.2eV to 2.7eV [19]. The ratio of 0.05: 0.1M has 2.3eV energy, which is good agreement with the band gap of bulk covellite CuS. The wide band gap and high absorption is the most important reason for their application in opto electronics [20].
4. Conclusion

In accordance with our studies, optimal conditions for chemical spray deposition of CuS films, for solar cell applications were established. Solution containing Copper Sulphate, thiourea (TU) was used. The substrate temperature was maintained about 300°C. The film thickness lies between 400-650 nm. The optical band gap of CuS found to be varying from 2.2eV to 2.7eV. CuS thin films produced in this study can be used in heterojunction solar cells due to their better crystalline structure and good energy band gap value. Spray pyrolysis deposition represents a low cost technique, empower the development of large area thin films for solar energy conversion devices.

5. Reference

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