Optimization of low cost, non toxic, earth abundant p-type Cu$_2$SnS$_3$ thin film for Photovoltaic application

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 Abstract. Cu$_2$SnS$_3$ (CTS) is one of promising candidate as an absorber material for thin film solar cell. Because of relatively higher prize of Indium and hazardous environmental impact of processing of Gallium, CTS is suitable alternative candidate to CuInGaS2 (CIGS) based solar cell as its constituent elements such as copper, tin and sulphur are abundantly available in earth's crust. CTS is ternary semiconductor and its energy band gap is 1.5eV, which is perfectly matched with solar energy spectrum for maximum transfer of solar energy into electrical energy through photovoltaic action. The primary methods for the synthesis of CTS are Thermal evaporation, electrochemical, sputtering and wet chemical methods. Here in this paper we have optimized a low cost non-vacuum solution process method for the synthesis of CTS without any external sulfurization. The X-ray diffraction studies showed the formation of phase with the peaks corresponding to (112), (220) and (312) planes. Chemical Solution Deposition (CSD) for the synthesis of CTS is suitable for large area deposition and it includes several routes like solvothermal methods, direct liquid coating and nano ink based technique. The metal Chloride salts and thiourea is used as a source of sulphur to synthesize CTS solution and homogeneous thin films of CTS deposited on glass substrate using spin coating method. Use of abrasive solvent like hydrazine and hydrogen sulphide gas which are used to synthesize CTS thin film have detrimental effect on environment, we report eco friendly solvent based approach to synthesize CTS at low temperature 200 ˚C.

Keywords: Cu$_2$SnS$_3$ thin films; Spin coating; Optical properties; Photovoltaic.

1.   Introduction

Nowadays, the use of chalcopyrite materials has been considered for many years as a promising alternative to silicon for the production of solar cells at a lower cost. Ternary chalcopyrite thin film

made by Cu_2SnS_3 (CTS) is used as absorber layer of tin film solar cell. The optical energy band gap of CTS thin film is between 0.5 to 1.5eV [1], which is perfectly matched with solar energy spectrum for maximum transfer of solar energy into electrical energy. The industrial development of large scale CTS-based thin film photovoltaic has already started with pilot plants being run and mass production feasible in the near future. Nevertheless, to become cost competitive with other energy sources and achieve grid parity, the production costs of CTS-based thin film solar cells must be lowered even more. For this, both wet deposition techniques such as electrodeposition and short processing times are being optimized to achieve higher photovoltaic conversion efficiencies. The Thin film of CTS can be synthesized by various technique like successive ion layer adsorption and reaction (SILAR) [2], sputtering [3], solvothermal synthesis [4]. In the present study, we have optimized low cost, solution process technique for the synthesis of stoichiometic CTS followed by heat treatment up to 400 ℃ in argon atmosphere.

2.   Experimental Details

The precursor solution was prepared by dissolving Copper (II) chloride $CuCl_2.2H_2O$ (0.01 mol L^{-1}), Tin (II) chloride $SnCl_2.2H_2O$ (0.005 mol L^{-1}) and thiourea NH_2CSNH_2 (0.05 mol L^{-1}) in 20 ml 2-methoxyethanol. Molar ratio of precursors Cu/Sn/S of 2:1:5 was used. Excess amount of thiourea was required to avoid secondary phases and precipitation of metal sulfides and hydroxides since thiourea makes complexes with metal hydroxide and sulfide [5].

Glass substrates (2.5 X 2.5 cm^2) were cleaned with detergent and distilled water then they were sonicated in the mixture of Isopropylalcohol and acetone (1:1) for 10 min. After that RCA cleaning of glass substrate ware done in the mixture of (NH_4OH + H_2O_2 + Distilled water) (1:1:5) at 80 ℃ for 10 min. To prepare thin films of CTS, precursor solution was spin coated on cleaned glass substrate at 2,500 rpm for 30 sec. (Apex Instruments, model SCU 2005). The precursor layer was then dried in air at 200 ℃ for 10 min. to remove any residue of organic solvent. The process of coating to drying of thin films was repeated nine times until desired thickness (approximately 900 nm) was obtained. The as-grown films were then annealed in an Argon atmosphere at 400℃ for 1 h.

The structural properties of CTS films were analyzed using X-ray diffraction (XRD) (BRUKER D2 PHASER) using CuKα radiation (λ = 1.5418 Å). Surface morphology was studied by atomic force microscopy (AFM) (Easyscan 2, Nanosurf). Charge carrier concentration was estimated by Hall effect measurements (HSM-3000, ECOPIC Corp.). Also optical properties of CTS films were studied by UV-Visible infrared spectrophotometer (Shimadzu UV 2600).

3.   Result and discussion
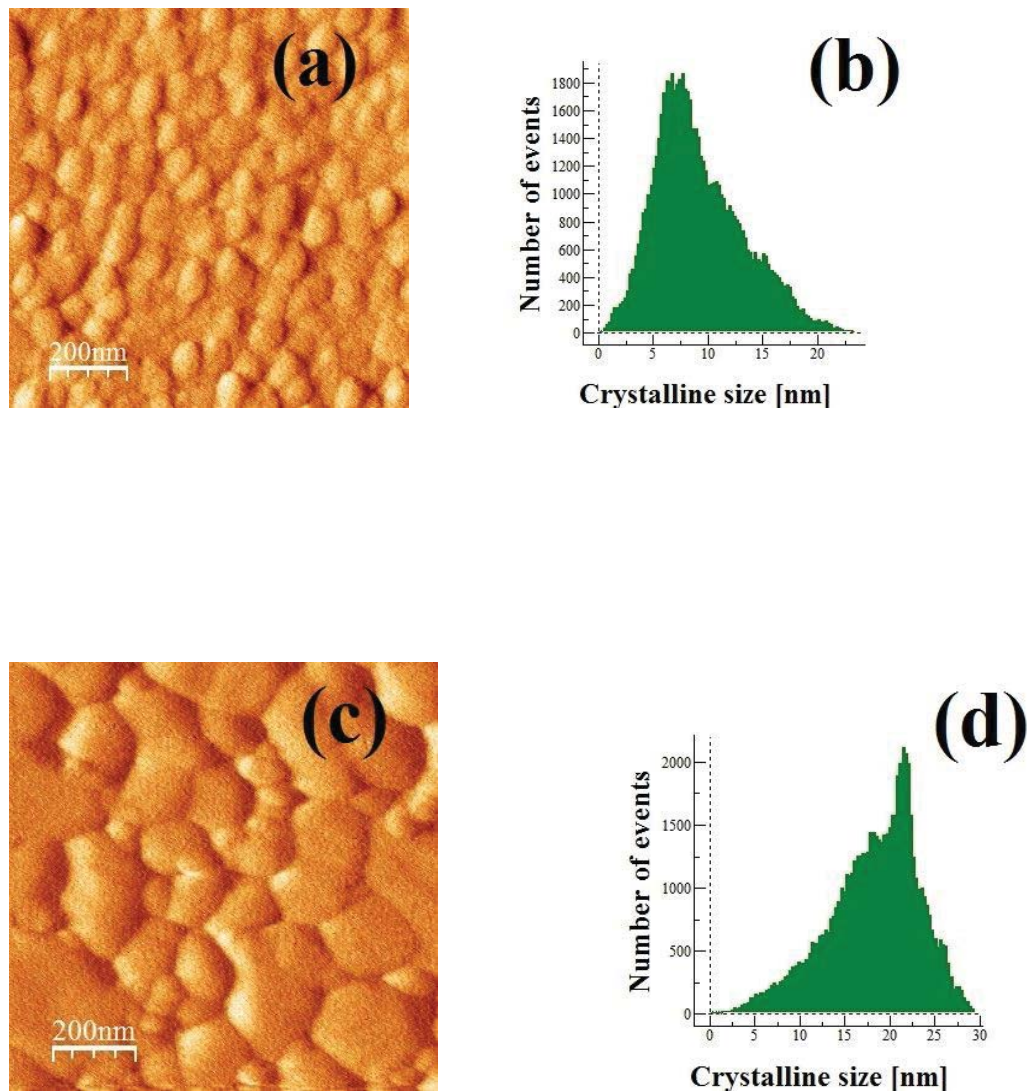### 3.1 Atomic Force Microscopy (AFM)

Figure 1 (a) and (c) are two dimensional AFM image of Cu_2SnS_3 thin film and (b) and (d) are Line profile of AFM image.

Surface morphology of the thermally treated CTS thin film was studied by atomic force microscopy (AFM). Fig. 1(a) displays the two dimensional AFM image of CTS film grown on glass substrate and dried in air at 200ºC [6]. It can be observed that the CTS grains are densely packed and they are in definite spherical shape. Average grain size of CTS thin film estimated from the AFM image fig 1(a) is of the order of 8 nm with smooth surface morphology. Whereas AFM image of fig 1(c) reveals that CTS film annealed at 400 ºC in argon has average grain size is of the order of 23 nm. An analysis of AFM data conform that size of the grain in CTS film increases as it is annealed in argon atmosphere at 400 ºC. Smooth surface of CTS is beneficial to decrease the dark current in photovoltaic device also decreases number of interface states between absorber layer and window layer [7].

3.2 X-ray Diffraction (XRD)

Crystallographic structures of the CTS films were analyzed by X-ray diffraction (XRD) in powder mode. Fig. 3 shows typical XRD pattern of the CIS film. Sharp peaks are located at $2\Theta = 28.8°$, $33.4°$, $47.6°$, $56.5°$ are corresponding to the single tetragonal planes, viz., (112), (200), (204) and (116) respectively. We notice that these diffraction peaks are in agreement with PCPDF file no 89-2877. XRD data reveals that as deposited film at 200 ℃ in air has less intense peaks and there are many secondary phases. Whereas CTS film thermally treated at 400 ℃ in argon atmosphere are more intense and number of secondary phases are reduced.
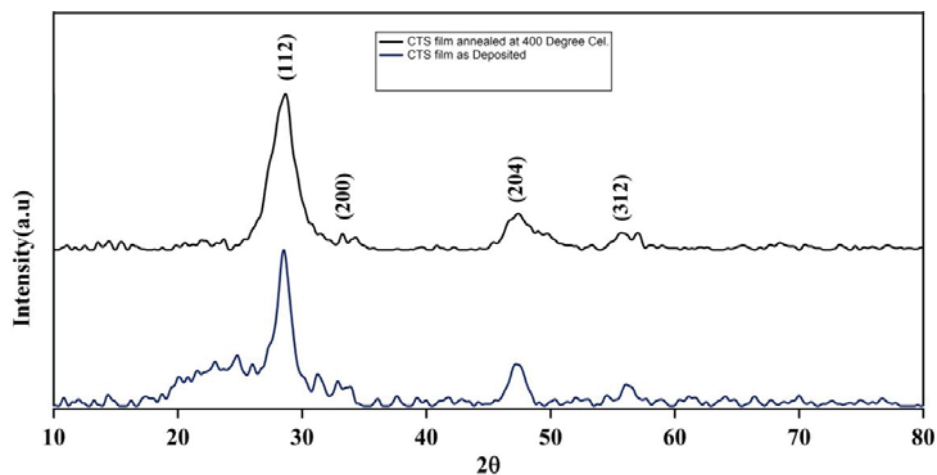

Figure 2 X-ray diffractogram of Cu_2SnS_3 thin film grown on glass.

3.3 *Optical properties*

Optical properties of CTS thin films were measured by UV-visible spectrophotometer. Optical energy band gap of CTS thin film can be calculated by Tauc relation [8, 9] for direct energy bad gap semiconductor.

$$\alpha h\upsilon = B (h\upsilon - E_g)^{1/2}$$

Where,
α is absorption coefficient in (cm^{-1}),
h is plank constant in (Js),
υ is the frequency of radiation (Hz),
B is proportionality factor called Tauc parameter,

E_g is the optical energy band gap (eV),

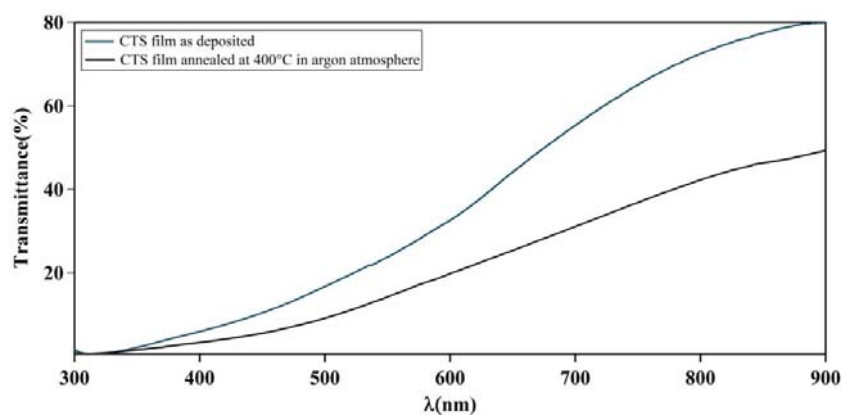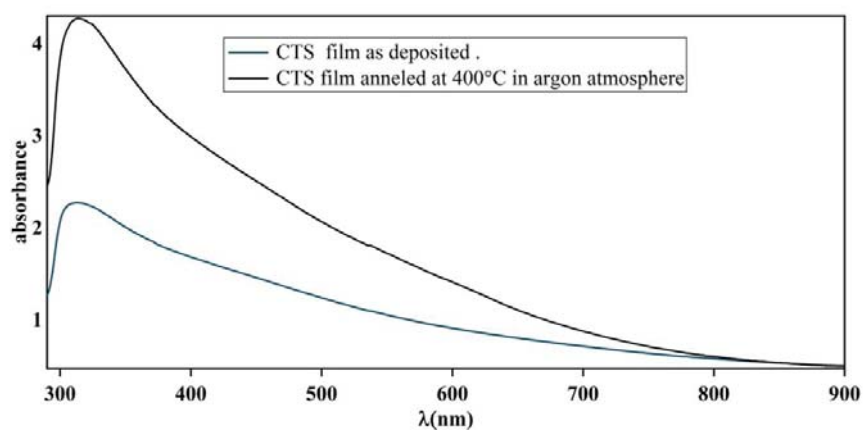**Figure 3** Transmittance spectra of Cu_2SnS_3 thin film grown on glass.

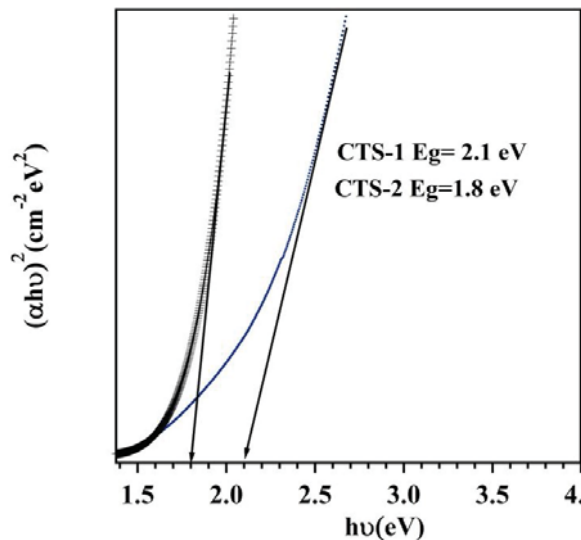**Figure 4** Absorbance spectra of Cu_2SnS_3 thin film grown on glass.

Figure 5 $(\alpha h\upsilon)^2$ vs. $h\upsilon$ plot of Cu_2SnS_3 thin film grown on glass.

As shown in Fig. 3 transmittance of CTS film decreases when CTS film is annealed at 400 ℃ in argon atmosphere and fig (4) demonstrate that absorbance of CTS film increases as CTs film annealed at 400 ℃ in argon atmosphere. This confirms that CTS films are appropriate candidate for absorber layer of thin film solar cell. As shown in Fig. 5 in by extrapolating along the linear portion of the $(\alpha h\upsilon)^2$ versus $h\upsilon$ the direct bandgap of CTS film can be determined by intercept at $h\upsilon$ axis.

3.4 *Electrical properties*

Hall effect measurements were performed to find the electrical properties of CTS thin films and carrier concentration of CTS thin films. CTS-1 demonstrates as deposited CTS film at 200 ℃ while CTS-2 demonstrates CTS film annealed at 400 ℃ in argon atmosphere. Hall measurements demonstrates that, Hall coefficient of all CTS thin films are positive, suggesting the hall induced transport in CTS films and p-type conductivity in CTS films. Table-1 demonstrates that resistivity of CTS film decreased when CTS film annealed 400 ℃ in argon atmosphere. While carrier concentration, conductivity and mobility increased under thermal treatment of CTS film.

Table-1 Electrical properties of Cu2SnS3 thin film grown on glass.

Sample name	Hall coefficient cm^3/C	Resistivity ohm.cm	Carrier Concentration cm^{-3}	conductivity 1/(ohm.cm)	Mobility cm^2/Vs
CTS-1	1.712 X 10^3	1.27X10^5	1.36X10^{15}	7.86X10^{-6}	1.35X10^{-2}
CTS-2	5.97 X 10^2	2.42X10^3	1.04X10^{16}	4.127X10^{-4}	2.46X10^{-1}

4. Conclusion

CTS films have been successively synthesized by spin coating method on glass substrate. An analysis of AFM imaged reveals that CTS thin films have uniform grains distribution and grain size increases with thermal treatment of CTS films at 400 ºC in argon atmosphere. Also, optical energy band gap of as deposited CTS film is about 2.1eV whereas thermally treated CTS film has 1.8eV. An analysis of XRD data reveal singe tetragonal phase of CTS films. An analysis of Hall effect measurements reveals that, electrical resistivity is decreases and charge carrier concentration, mobility and conductivity of CTS thin film increases under thermal treatment at 400 ºC in argon atmosphere .

5. References

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