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# Electrical transport in layer-by-layer solution deposited $Cu_2SnS_3$ films: Effect of thickness and annealing temperature

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ABSTRACT

Thermoelectric and photothermoelectric analysis have been employed to determine the carrier transport in solution deposited $Cu_2SnS_3$ films in temperature range 120–273 K. The effect of varying thickness and annealing temperatures on the electrical conduction are studied. The variation in conductivity is found to be thermally activated. The change in conductivity with thickness and annealing temperature is resolved into individual contributions of carrier concentration and mobility. Both carrier concentration and mobility change have been found to affect the conductivity under different variations. The changes observed have been qualitatively correlated with incorporation of defects during layer by layer deposition of films. The change in concentration and distribution of these defects are suggested to alter observed electrical transport of $Cu_2SnS_3$ films of different thickness and after annealing at different temperatures.


## 1. Introduction

For development of low-cost solar cells, newer absorber materials capable of replacing conventional thin film solar cell (TFSC) materials CIGS and CdTe are being intensely investigated [1–3]. These new absorber materials are expected to lower the cost in two ways: (i) by using earth-abundant and low-cost elements and (ii) by means of non-vacuum systems based on direct liquid coating (DLC) methods, thus offering advantages of low input capital, high throughput and material utilization, ease of large area roll to roll deposition [4]. In this direction, high efficiency TFSC utilizing copper zinc tin sulphide and its selenium derivatives (CZTS) beyond 11% is reported. It must be emphasized that this and other high efficiency TFSC based on CZTS are fabricated using direct liquid processing methods such as spin coating, doctor blading etc. [4–6]

In last report, we had proposed an even simpler alternative, copper tin sulphide, $Cu_2SnS_3$ (CTS) for low cost TFSC [7]. CTS has been reported to have a direct energy band gap of 1.1 eV and a high absorption coefficient of $>10^5\ cm^{-1}$ (for wavelength <1400 nm), properties enabling CTS for maximal utilization of terrestrial solar radiation with minimal thickness of absorber. A proof-of-concept solar cell with photo-conversion efficiency above 2% and high open circuit voltage of 816 mV was demonstrated based on solution deposition from single metal-organic solution [7].

Unlike controlled environments of vacuum deposition systems, solution processing may yield films with unpredictable carrier transport due to inherent proclivity of gettering defects during processing. Thus understanding the nature of carrier transport in these films becomes crucial from basic and application perspective. This will suggest the scope of improvement for fabricating better thin film solar cells. Thermoelectric and photothermoelectric power analysis have been employed reliably for seeking insight into carrier transport in semiconducting thin films [8,9]. In this report, an in-depth analysis of temperature dependence of basic semiconducting thin film parameters such as carrier concentration and mobility, derived from conductivity and thermoelectric power measurements, is presented. The experiments have been performed for layer by layer solution processed CTS films of different thickness and after annealing, under dark and illumination to provide information relevant to solar cells. At the end, a qualitative physical model for understanding the influence of deposition and post-deposition work-up parameters on carrier migration in these films is proposed.

## 2. Experimental

The synthesis of the films has been reported earlier, utilized layer by layer deposition of precursor films drawn from single metal-organic complex precursor solution [7]. As studied with

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the help of Thermogravimetric analysis/Diffrential Calorimetry (TGA/DSC) in the earlier report, the conversion of the precursor to $Cu_2SnS_3$ takes place at around 473 K. Thus for the synthesis of $Cu_2SnS_3$ films, precleaned glass substrates are first dip-coated with precursor solution and then heated at 473 K in air for 10 min. To increase the thickness of the film, the above cycle is repeated and at each step an increment of ~75 nm in the thickness is achieved.

For the purpose of the present study two different kinds of thin films of $Cu_2SnS_3$ are considered:

1. Films of $Cu_2SnS_3$ of varying thickness in the range of 75–500 nm. These films are prepared by the above described procedure layer-by-layer.
2. Films of $Cu_2SnS_3$ of thickness ~500 nm (prepared by above described procedure) annealed at three different temperatures: 523 K, 623 K and 673 K. As studied by TGA/DSC (in the earlier report), heating the precursor at temperatures above 523 K in air will cause the oxidation of sulphide. Thus annealing of films at temperatures of 523 K, 623 K and 673 K was carried out under inert atmosphere of nitrogen gas. For annealing the films, the samples are kept in a controlled quartz tubular furnace (MTI: OTF-1200X) and heated upto the target temperature (523 K, 623 K and 673 K) at 5 K/min. The films are annealed at the dwelling temperature (523 K, 623 K and 673 K) for 2 h. The samples are then allowed to cool naturally (~20 K/min.) up to 373 K and then taken out of the furnace. Throughout the annealing procedure the nitrogen gas is purged through the furnace at a flowing rate of 150 ml/min.

The composition of films is analyzed by X-ray diffraction (D2 Phaser, Bruker). The morphology and thickness of films are determined using scanning electron microscopy (Leo 440*i*). For electrical measurements graphite is used as Ohmic contact. The electrical measurements i.e. conductivity and thermoelectric power, of the films are carried using a cryostat fitted with a quartz window. All the measurements are done in the temperature range of 120–273 K. The measurements are repeated for dark and under illumination of white light from halogen lamp (Phillips 50 W, 12 V) with intensity at sample surface of 30 mW/cm$^2$ (measured with pyranometer, National Instruments). For thermoelectric power a temperature gradient of $3 \pm 0.1$ K is maintained between the two ends of films by a resistance heater regulated by PID controller (Selec 500).

The X-ray diffractogram (XRD) of $Cu_2SnS_3$ films on glass substrate with different thickness and after annealing at different temperature is shown in Fig. 1. The diffractograms show broad peaks at 2$\theta$ values of 28.6, 33.1, 47.6 and 56.3° which match with standard for tetragonal $Cu_2SnS_3$ (JCPDS file: 089–4714) and are found to be reflections from (1 1 2), (2 0 0), (2 0 4) and (3 1 2) planes. The XRD patterns show no change in shape of peaks with varying thickness, although the intensity of peaks increases. The average crystallite size, calculated using Scherrer relation from the broadening of (1 1 2) peak is ~7 nm, which remains same for all the samples of different thickness. This suggests that each layer grow independently of previous. Upon annealing, the peaks becomes slightly sharper and the average crystallite size calculated using Scherrer relation from the broadening of (1 1 2) peak, after annealing at 523 K, 623 K and 673 K, are 9, 12, 14, 16 nm, respectively.

Figs. 2 and 3a,c,e show the surface topology CTS films of different thickness and after annealing at different temperatures, as revealed by scanning electron microscopy. The films are in general homogenous, compact and smooth for all samples. Annealing of the films results in slight ripening of grains and increase in average grain size of size in the films. Fig. 2b,d,f shows the cross sectional SEM views suggesting the thickness of the films after two intervals of depositions. Fig. 3b,d,f shows the cross section view of the samples annealed at different temperature and show increased grain sizes with increasing annealing temperature. Fig. 3 (a,b); (b,d); (e,f) shows films annealed at 673 K, 623 K and 523 K, respectively.

## 3. Results

### 3.1. Variation of conductivity with temperature

In the previous study, the temperature variation of CTS films was studied in the temperature range of 5–290 K. Analysis of the data suggested presence of three different transport mechanisms: (i) from 5 to 50 K: variable range hopping, between 150 and 290 K: thermoionic emission over grain boundaries and the intermediate range (50–150 K) shows a transition between the two behaviors, and expected to follow nearest neighbour hopping type conduction.

In the present study, the temperature range considered for elucidation of carrier transport is 120–273 K. General behavior of variation in conductivity with temperature shows existence of two different slopes at extremes of the temperature range considered. As in the previous study [7], in the present case too; observed data for variation of conductivity with temperature can be explained by amalgamation of two different conduction mechanisms i.e.: in temperature range of 120–160 K carrier conduction is due to nearest neighbour hopping whereas between 160 and 273 K conductivity is governed by thermoionic emission over grain boundaries. The

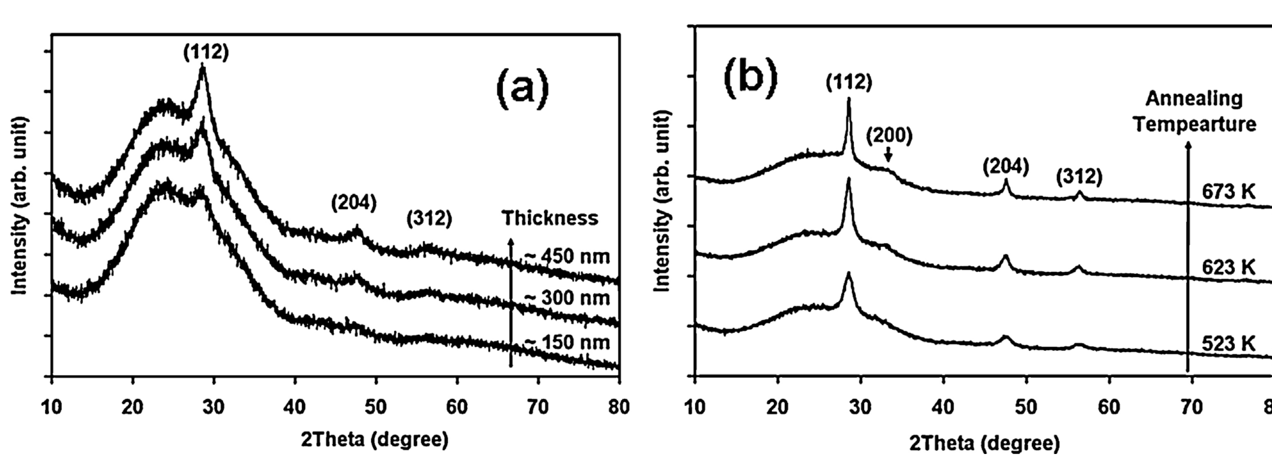


**Fig. 1.** X-ray diffractograms of $Cu_2SnS_3$ films: (a) different thickness and (b) after annealing at different temperatures.