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Solution processed Cu$_2$SnS$_3$ thin films for visible and infrared photodetector applications

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The Cu$_2$SnS$_3$ thin films were deposited using an economic, solution processible, spin coating technique. The films were found to possess a tetragonal crystal structure using X-ray diffraction. The film morphology and the particle size were determined using scanning electron microscopy. The various planes in the crystal were observed using transmission electron microscopy. The optimum band gap of 1.23 eV and a high absorption coefficient of $10^4$ cm$^{-1}$ corroborate its application as a photoactive material. The visible and infrared (IR) photo response was studied for various illumination intensities. The current increased by one order from a dark current of 0.31 $\mu$A to a current of 1.78 $\mu$A at 1.05 suns and 8.7 $\mu$A under 477.7 mW/cm$^2$ IR illumination intensity, at 3 V applied bias. The responsivity, sensitivity, external quantum efficiency and specific detectivity were found to be 10.93 mA/W, 5.74, 2.47% and $10^4$ × $10^{10}$ Jones respectively at 1.05 suns and 16.32 mA/W, 27.16, 2.53% and $5.10 \times 10^{10}$ Jones respectively at 477.7 mW/cm$^2$ IR illumination. The transient photoresponse was measured both for visible and IR illuminations.

INTRODUCTION

Image sensors used worldwide rely on visible wavelength photodetectors. Infrared (IR) photodetection finds varied use in medical diagnostics, optical fibre communication, night time surveillance, environmental monitoring and remote sensing. PbS and CdTe have been used in visible wavelength photodetection. Hg$_{1-x}$Cd$_x$Te and CuIn$_{1-x}$Al$_x$Se$_2$ have been used as IR photo detectors and in photovoltaic applications. However the high cost and rarity of indium and tellurium as well as the toxicity of cadmium and lead are issues of concern fuelling the need for the lookout for alternative materials. Cu$_2$SnS$_3$ consists of earth abundant and non-toxic elements. It has a band gap in the near IR range from 0.93 to 1.51 eV and a high absorption coefficient of $10^4$ cm$^{-1}$ to $10^5$ cm$^{-1}$ which yields its use in both IR detection and photovoltaic applications. It has a hole concentration of $10^{18}$ cm$^{-3}$, electrical conductivity of 0.5 - 10 S/cm and a hole mobility of 1 - 80 cm$^2$/V/s. It can be grown by simple and low cost techniques like spin coating, dip coating, spray coating and screen printing which can be used for large area coatings thus overcoming the cost and formation of secondary phases associated with vacuum based techniques.

Until now the visible and infrared photodetection properties of Cu$_2$SnS$_3$ thin films has not been studied. So in this paper we have studied the photo response of solution processed Cu$_2$SnS$_3$ thin films under different sun illuminations. Also the IR photo response for different intensities has been studied hence proving that Cu$_2$SnS$_3$ can be used as both a visible and IR wavelength photodetector.

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EXPERIMENTAL

The Cu$_2$SnS$_3$ (CTS) film was deposited onto soda lime glass (SLG) substrates by spin coating a CTS precursor solution. The SLG substrates were pre-cleaned with soap solution followed by boiling in acetone, isopropyl alcohol and deionized water for 15 min each and then flush dried with nitrogen gas. The CTS precursor solution was prepared by the dissolution of 1M CuCl$_2$, 0.5M SnCl$_2$ and 3M thiourea into anhydrous 2-methoxyethanol followed by stirring for one hour. The solution was dropped onto SLG substrates and spin coated at 2500 rpm for 30 sec and dried at 50°C for 5 min and subsequently the second coating was made. Finally the film was dried at 135°C for 10 min and then annealed in a tube furnace at 250°C for one hour.

The phase formation of the CTS films was confirmed using X-ray diffraction (XRD) (PANalytical X’Pert PRO Diffractometer). The morphology of the films was examined using field emission scanning electron microscopy (FESEM) (ULTRA 55, FESEM (Carl Zeiss)). The morphology and crystal structure of the CTS nanoparticles obtained by sonication the film was studied using transmission electron microscopy (TEM) (Jeol JEM-2100F). The optical studies of the film were done using UV-Vis-NIR spectrophotometer (Perkin Elmer-Lambda 750). Photoluminescence was measured using Edinburgh Instruments Fluorescence Spectrometer under a laser excitation of 1.84 eV. Raman spectroscopy was analysed using Raman spectrometer (LabRAM HR) with 514 nm line of Ar$^+$ laser. The X-ray photoelectron spectroscopy was done using AXIS Ultra DLD X-ray photoelectron spectrometer with Al K$_\alpha$ X-ray source. The device was fabricated by depositing an interdigitated circuit pattern on to the film by thermal evaporation of silver. The photo response of the film was measured under different sun illuminations using an Oriel Sol-3A solar simulator under AM 1.5 G conditions with a KG5 filtered lamp source which was calibrated using an NREL calibrated reference Si visible cell (Oriel P/N-91150 V) to 100 mW/cm$^2$. The IR photodetection was carried out using an IR lamp of 150 W and 750 nm – 1150 nm wavelength. The voltage was sourced using a Keithley source meter (SMU-2400). External quantum efficiency was measured using Oriel Newport quantum efficiency system.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern (XRD) of the CTS thin film. The reflections were indexed to the JCPDS 01-089-4714 and the crystal structure was found to be tetragonal with lattice

![X-ray diffraction pattern of the CTS thin film.](image-url)
TABLE I. Texture coefficient and crystallite size for different planes.

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>(hkl)</th>
<th>d (Å)</th>
<th>I/Io</th>
<th>TC (%)</th>
<th>L (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.53</td>
<td>(112)</td>
<td>3.13</td>
<td>0.31</td>
<td>1.67</td>
<td>2.12</td>
</tr>
<tr>
<td>47.46</td>
<td>(220)</td>
<td>1.91</td>
<td>0.13</td>
<td>0.69</td>
<td>2.59</td>
</tr>
<tr>
<td>56.31</td>
<td>(312)</td>
<td>1.63</td>
<td>0.12</td>
<td>0.65</td>
<td>2.59</td>
</tr>
</tbody>
</table>

parameters a = 5.41 Å and c = 10.83 Å. The broad XRD peaks denote the nanocrystalline nature of the films. The crystallite size L was calculated using the Scherrer formula (eq. (1))

\[ L = \frac{0.9 \lambda}{\beta \cos \theta} \]  

where \( \lambda \) is the X-Ray wavelength, \( \beta \) is the full width at half maximum and \( \theta \) is the angle of diffraction. The average crystallite size was found to be 2.4 nm. The preferential orientation of the film was determined from texture coefficient TC (hkl) calculations (eq. (2)).

\[ TC(hkl) = \frac{I(hkl)}{I_0(hkl)} \frac{1}{N \sum I(hkl)} \]  

where, \( I(hkl) \) is the experimentally measured intensity and \( I_0(hkl) \) is the value of intensity obtained from the JCPDS for a given (hkl) plane. N is the number of reflections. For randomly oriented crystallites \( TC(hkl) = 1 \) and for crystallites preferentially oriented along a (hkl) plane \( TC(hkl) > 1 \).

From Table I, the \( TC(112) > 1 \) indicating the preferential orientation of the crystallites along the (112) plane. The calculated values of the interplanar spacings d for different 2θ angles and the crystallite sizes are also shown in the table.

**CU₂SnS₃ PRECURSOR REACTION MECHANISM**

The formation of the Cu₂SnS₃ thin film occurs via the thermolysis of the metal thiourea complex formed by the reaction of the precursor compounds. The metal salts and thiourea undergo hydrolysis in the presence of the solvent anhydrous 2-methoxyethanol as follows.

\[ \text{CuCl}_2 \rightarrow \text{Cu}^{2+} + 2\text{Cl}^- \]  
\[ \text{SnCl}_2 \rightarrow \text{Sn}^{2+} + 2\text{Cl}^- \]  
\[ \text{NH}_2 - C - \text{NH}_2 \rightarrow \text{NH}_2 - C^+ = \text{NH} + \text{H}^+ + \text{S}^{2-} \]

The metal ions attach to thiourea via the sulphur atom to form a metal thiourea complex \([\text{CuSn(CS(NH}_2)_n])^{m+}\) which upon heat treatment undergoes thermolysis to give Cu₂SnS₃.

\[ [\text{CuSn(CS(NH}_2)_n])^{m+} \xrightarrow{\text{Heat treatment}} \text{Cu}_2\text{SnS}_3 + \text{gaseous products} \]

The morphology of the films observed using SEM is shown in Fig. 2. The films are composed of closely packed spherical grains of around 20 nm. These grains could be further composed of crystallites of around 2 nm as obtained from XRD.

The TEM studies were done for the CTS nanoparticles obtained from the film by ultrasonication. The films exhibited polycrystalline nature. The high resolution transmission electron micrograph (HRTEM) of the CTS nanoparticles is shown in Fig. 3(a) with the interplanar spacings d of 3.70 Å and 2.31 Å corresponding to the (112) and (211) planes of CTS. The selected area electron diffraction pattern (SAED) with the various planes indexed is shown in Fig. 3(b).

The CTS film was found to have a high absorption coefficient of 10⁴ cm⁻¹ as shown in Fig. 4(a) and the band gap \( E_g \) was calculated to be 1.23 eV from the Tauc plot in Fig. 4(b) using the relation (eq. (7))

\[ \alpha (\lambda) = A(\hbar \nu - E_g)^n / \hbar \nu \]
where, $\alpha$ is the absorption coefficient, $A$ is a constant and $n = \frac{1}{2}$ for direct band gap. The high absorption coefficient and the optimum band gap of 1.23 eV make CTS a suitable absorber layer for visible applications.

Fig. 5 shows the photoluminescence spectra of the CTS thin film. Luminescence was observed at 1.23 eV under excitation with 1.84 eV laser. This corresponds to the band to band transition in CTS as also determined from the absorbance spectrum in Fig. 4.

Fig. 6 shows the Raman spectrum of the CTS thin film. The Raman peaks at 297 cm$^{-1}$, 336 cm$^{-1}$ and 351 cm$^{-1}$ correspond to the tetragonal phase of CTS. Absence of extra peaks confirms the absence of secondary phases like Cu$_{2-x}$S (475 cm$^{-1}$). In our present case CTS is having tetragonal crystal structure with space group I-42m (No. 121), point group D$_{2d}$ (42m) and contains one formula group per unit cell. The above Raman peaks can be attributed to various phonon modes occurring in the material. There are a total of 36 vibrational modes which can be represented as $M = 2A_1 + A_2 + 3B_1 + 7B_2 + 10E$. Out of these there are 30 optical modes, 3 acoustic modes, 24 infra-red active modes, 29 Raman active modes and 30 hyper Raman active modes. The acoustic and optic modes are given as $\Gamma_{\text{acoustic}} = B_2 + E$, $\Gamma_{\text{optic}} = 2A_1 + A_2 + 3B_1 + 6B_2 + 9E$ respectively. The infra-red (IR) and Raman active and hyper Raman (HR) active modes excluding the acoustic modes are given by $\Gamma_{\text{IR}} = 6B_2 + 9E$, $\Gamma_{\text{Raman}} = 2A_1 + 3B_1 + 6B_2 + 9E$, $\Gamma_{\text{HR}} = 2A_1 + A_2 + 3B_1 + 6B_2 + 9E$ respectively. The $A_2$ mode is hyper-Raman active whereas it is both Raman and IR inactive. The assignment of the various modes were done using Bilbao crystallographic server.

The purity and composition of the samples were found using X-ray photoelectron spectroscopy. Fig. 7(a) shows the survey spectrum and there were no impurities detected from the spectrum.
Fig. 7(b)-7(d) shows the core level spectra for Cu 2p, Sn 3d and S 2p. From the core level spectra the binding energies for Cu 2p3/2 and Cu 2p1/2 were found to be 933 eV and 953 eV respectively which corresponds to the +1 oxidation state of Cu. There is an absence of the satellite peak at 942 eV corresponding to Cu2+ ion. The binding energies for Sn 3d5/2 and Sn 3d3/2 were found to be 487 eV and 495.5 eV respectively which corresponds to the +4 oxidation state of Sn. The binding energies for S 2p3/2 and S 2p1/2 were found to be 162 eV and 163.1 eV respectively which corresponds to the -2 oxidation state of S.

PHOTODETECTION

Fig. 8 shows the device structure of the CTS film with the inter-digitated silver electrodes, used for the photo response measurements. Figs. 9(a) and 9(b) show the current voltage curves obtained for dark and different sun illuminations from 0.88 suns to 1.05 suns and IR lamp illumination intensities from 286.6 mW/cm² to 477.7 mW/cm². There was an increase in the photocurrent by one order from a dark current of 0.3 µA. There was found to be a clear increase in current for higher illuminations in both the cases. The photocurrent increased from 1.34 µA at 0.88 suns to
FIG. 6. Raman spectrum of the CTS thin film.

1.78 μA at 1.05 suns under visible illumination and from 1.83 μA at 286.6 mW/cm² to 8.65 μA at 477.7 mW/cm² under IR illumination, at 3 V applied bias.

Fig. 10(a) and 10(b) show the band diagrams for the CTS/Ag semiconductor-metal junction at equilibrium in dark and under illumination respectively. CTS being a p type semiconductor with

FIG. 7. X-Ray photoelectron spectra of the CTS thin film (a) survey spectrum (b) Cu2p (c) Sn3d (d) S2p core level spectra.
FIG. 8. Schematic of the CTS/Ag device structure used for the photo response measurements.

work function $\phi_p = 5.62$ eV$^{11}$ greater than the work function of Ag, $\phi_m = 4.25$ eV$^{25}$ the semiconductor bands will bend downward in order to align the Fermi level as shown in Fig. 9(a). Since CTS has majority of holes, the holes go from CTS to Ag and electrons from Ag to CTS leading to formation of negative charge on CTS and positive charge on Ag. Upon illumination, electron-hole pairs are generated in the depletion region at the semiconductor-metal interface. The holes get attracted to the negative charge on CTS and go towards CTS and the electrons get attracted to the positive charge on Ag. Thus the CTS gets positively biased with respect to Ag. Since electrons are going to Ag, the Fermi level of Ag rises and since the electrons are removed from CTS, its Fermi level lowers. This separation of the Fermi levels leads to development of photovoltage V as shown in Fig. 9(b).

The sensitivity $S'$ of the device is the ratio of the generated photocurrent to the dark current, given by (eq. (8))$^{26}$

$$S' = \frac{I_\lambda}{I_{dark}}$$  \hspace{1cm} (8)

where $I_\lambda$ is the photocurrent given by $I_\lambda = I_{light} - I_{dark}$. The sensitivity was found to increase from 4.32 at 0.88 suns to 5.74 at 1.05 suns visible illumination and from 5.72 at 286.6 mW/cm$^2$ to 27.16 at 477.7 mW/cm$^2$ IR illuminations.

The photoresponse parameters i.e., responsivity, external quantum efficiency and specific detectivity were calculated for various suns and IR illumination intensities. The responsivity $R_\lambda$ of a photodetector is a measure of the amount of photocurrent generated per unit area per unit illumination intensity$^5$

$$R_\lambda = \frac{I_\lambda}{P_\lambda S}$$  \hspace{1cm} (9)

where, $P_\lambda$ is the incident illumination intensity and $S$ is the effective illumination area.

FIG. 9. Current voltage plots for dark and (a) different suns and (b) different intensities of the IR lamp.
FIG. 10. Band diagrams for the CTS/Ag semiconductor-metal junction (a) at equilibrium in dark (b) under illumination.

The external quantum efficiency EQE is the number of electrons generated per incident photon. \(^{27}\)

\[
EQE = \frac{hcR_4}{q\lambda} \tag{10}
\]

where \(h\) is the Planck’s constant, \(c\) is the velocity of light, \(q\) is the electronic charge and \(\lambda\) is the wavelength of the illuminating source.

The specific detectivity \(D^*\) is the ability of the photodetector to detect the weakest light signal. \(^{28}\)

\[
D^* = \frac{R_4}{(2qI_0)^{1/2}} \tag{11}
\]

where \(I_0\) is the dark current.

The calculated visible and IR photoresponse parameters have been tabulated in Tables II and III respectively. For visible illumination, the responsivity, EQE and specific detectivity values increase and then again decrease at a higher sun value of 1.05 suns. This decrease could be due to the activation of traps at higher light intensities leading to the trapping of charge carriers. \(^{29}\) In the case of IR illumination, all the parameters are found to increase with increase in illumination intensity.

To study the stability and reversibility of the device, the variation of the photocurrent with time was measured for three cycles at different suns and at 286.6 mW/cm\(^2\) IR illumination at an applied bias of 3V as shown in Figs. 11(a) and 11(b). Fig. 11(a) shows an increase in the photocurrent with increase in the sun illumination. The photocurrent showed stability over time in both the cases.

Figs. 11(c) and 11(d) show the rise and decay curves taken for one cycle at 0.92 suns and 286.6 mW/cm\(^2\) IR illumination respectively. The rise and decay curves were fitted to the second order exponential rise and decay equations (eq. (12)) and (eq. (13))

\[
I(t)_{\text{rise}} = I_{\text{dark}} + A \exp\left[\frac{t}{\tau_1}\right] + B \exp\left[\frac{t}{\tau_2}\right] \tag{12}
\]

\[
I(t)_{\text{decay}} = I_{\text{dark}} + A \exp\left[-\frac{t}{\tau_1}\right] + B \exp\left[-\frac{t}{\tau_2}\right] \tag{13}
\]

respectively where \(I_{\text{dark}}\) is the dark current, \(A\) and \(B\) are scaling constants, \(\tau_1\) and \(\tau_2\) are the first and second order time constants and \(t\) is the time of switching on and switching off the light. From the fitting of the curves the rise and decay constants were found. In Fig. 10(c) during rise the current increased rapidly initially in 0.92 s followed by a slower component of 5.99 s during saturation. When the light was switched off, the current decreased quickly initially in 1.46 s followed by a slower decrease of 13.58 s. The slower decay time could be due to the trapping of charge carriers.

<table>
<thead>
<tr>
<th>Suns</th>
<th>Responsivity (mA/W)</th>
<th>Sensitivity</th>
<th>EQE %</th>
<th>Specific Detectivity (Jones)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.88</td>
<td>10.17</td>
<td>4.32</td>
<td>2.29</td>
<td>(3.23 \times 10^{10})</td>
</tr>
<tr>
<td>0.92</td>
<td>13.25</td>
<td>5.47</td>
<td>2.99</td>
<td>(4.21 \times 10^{10})</td>
</tr>
<tr>
<td>1.05</td>
<td>10.93</td>
<td>5.74</td>
<td>2.47</td>
<td>(3.47 \times 10^{10})</td>
</tr>
</tbody>
</table>
by trap states. From Fig. 11(d) initially when the IR lamp was switched on, the rise in the curve was fast with a time constant of 0.59 s and later there was a slower rise leading to saturation with a time constant of 22.74 s. When the lamp was switched off, the current decreased rapidly with a time constant of 0.7 s.

The spectral response of the CTS thin film was measured as shown in Fig. 12. CTS shows good quantum efficiency in the wavelength region of interest i.e. vis-near IR which is required for photodetection.

Fig. 13 shows the plot of log I versus $V^{1/2}$ for the dark current. The plot exhibits two regions of different slopes. The region of the plot below 0.5 V has been fitted to the Schottky emission equation (eq. (14)) and the region above 0.5 V has been fitted to the Poole-Frenkel emission equation (eq. (15)).

$$I \propto \exp \left( \frac{q\beta_S V^{1/2}}{kT d^{1/2}} \right)$$  \hspace{1cm} (14)

$$I \propto \exp \left( \frac{q\beta_{PF} V^{1/2}}{kT d^{1/2}} \right)$$  \hspace{1cm} (15)

### TABLE III. The calculated values of responsivity, sensitivity, EQE and specific detectivity under different IR illumination intensities.

<table>
<thead>
<tr>
<th>Illumination intensity (mW/cm²)</th>
<th>Responsivity (mA/W)</th>
<th>Sensitivity</th>
<th>EQE %</th>
<th>Specific Detectivity (Jones)</th>
</tr>
</thead>
<tbody>
<tr>
<td>286.6</td>
<td>4.91</td>
<td>5.72</td>
<td>0.76</td>
<td>$1.53 \times 10^{10}$</td>
</tr>
<tr>
<td>382.2</td>
<td>14.46</td>
<td>19.53</td>
<td>2.25</td>
<td>$4.52 \times 10^{10}$</td>
</tr>
<tr>
<td>477.7</td>
<td>16.32</td>
<td>27.16</td>
<td>2.53</td>
<td>$5.10 \times 10^{10}$</td>
</tr>
</tbody>
</table>

FIG. 11. Variation of photocurrent with time for (a) 0.92 suns and 1.05 suns (b) 287 mW/cm² IR illumination; Rise and Decay curves for (c) 0.92 suns (d) 287 mW/cm² IR illumination.
where

$$\beta_S = \left[ \frac{q}{4\pi k T} \right]^{1/2}$$

$$\beta_{PF} = 2\beta_S$$

where I is the current, T is the temperature, V is the applied bias, q is the electronic charge, d is the thickness of the film, k is the Boltzmann constant and $\beta_S$ and $\beta_{PF}$ are constants related to the Schottky and Poole-Frenkel effect respectively.

At lower voltages, electrode limited Schottky emission occurs since the electrons have to overcome the contact resistance. However the contact resistance is overcome by the higher electric field at higher voltages and bulk limited Poole-Frenkel emission dominates the transport process.\textsuperscript{31,32}

![Figure 12](image1.png)

**FIG. 12.** Spectral response of the CTS thin film.

![Figure 13](image2.png)

**FIG. 13.** Plot of Log I versus $V^{1/2}$. 
CONCLUSIONS

The Cu$_2$SnS$_3$ thin films were synthesized and its structural, morphological and optical properties were studied. The photocurrent of the films was studied under different sun illuminations. The sensitivity of the device varied from 4.32 to 5.74. It was shown that CTS thin films could be used for IR photo detection applications apart from being a good solar absorber material. The device exhibited a high sensitivity of 5.72 at 286.6 mW/cm$^2$ and 27.16 at 477.7 mW/cm$^2$. The time dependent photo response exhibited stability over different ON/OFF cycles. The rise and decay curves were fitted to second order exponential rise and decay equations respectively and the corresponding time constants were obtained.