Solution processed earth abundant copper iron/manganese tin sulphide thin films for photovoltaic applications

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**SOLUTION PROCESSED EARTH
ABUNDANT COPPER IRON/MANGANESE
TIN SULPHIDE THIN FILMS FOR
PHOTOVOLTAIC APPLICATIONS**

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Abstract

This work focuses on earth abundant $\text{Cu}_2(\text{Fe,Mn})\text{SnS}_4$ (C(F,M)TS) thin films for solar absorber materials. Synthesis of C(F,M)TS by a simple non-toxic spray pyrolysis technique is reported. X-Ray diffraction and Raman spectroscopy confirm the presence of C(F,M)TS in the thin films after sulphurization. CFTS and CMTS exhibited band gaps, carrier density and carrier mobility similar to CIGS and CZTS. CFTS was employed as a counter electrode in dye-sensitized solar cells (DSSCs) and exhibited good conversion efficiencies (8.03%). A photovoltaic device with a structure of Mo/CMTS/CdS/TCO/top electrode was fabricated as a proof-of-concept and yields a preliminary power conversion efficiency of $\sim 0.2\%$. Through analyses of the device characteristics we identify a key problem of very high carrier density in the CMTS absorber that leads to short collection length, low V_{oc} , low quantum efficiency at long wavelength and high shunt conductance that quench the fill factor.

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Chapter 1. Introduction

1.1 Background

Figure 1.1.1 Abundance of elements in the earth's crust .[2]

The energy demands of the world are constantly on the rise and of all the current energy sources, fossil fuels constitute 86% of the current energy supply[3]. The main disadvantages of fossils fuel are that they are a non-renewable source of energy with a significant carbon footprint. The amount of CO₂ released in the earth's atmosphere as a consequence of the burning of fossil fuels is stupendous and contributes significantly to global warming and climate change. This in the future would be disastrous to human population and the survival of the human race. Therefore there is an urgent need to find alternative energy sources that are clean, green and renewable. There are various source of energy such as solar, wind, tidal, geothermal and nuclear. Solar energy is one of the key candidates for

an alternative renewable energy source as the energy from sun is practically unlimited. Harnessing the power of the sun could be a global solution to the energy problems of the human race.

Among the various solar technologies available Silicon solar cells dominate the energy market. Even though Silicon is abundant, it requires high crystallinity and purity to achieve high efficiency solar cells and thus increasing the manufacturing cost. There are other thin film solar cells based on $\text{CuInGa}(\text{S,Se})_2$ (CIGS) and CdTe which provide high efficiency solar cells but materials like In, Ga and Te are expensive and rare. Hence this cannot be used for the development of Terawatt (TW) energy sources to meet the energy demands of the world. There are several emerging technologies like dye-sensitized solar cells (DSSC) and organic photovoltaics (OPVs) but they are still far away from large scale energy generation due to issues with long term stability and energy pay back. Therefore the need of the hour is to develop high efficiency solar cells with earth abundant materials with a low processing cost. There are several candidates for the development of earth abundant photovoltaics such as $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTS), SnS, Cu_2O and FeS_2 . Among these CZTS are very promising as efficiencies exceeding 12% have already been achieved. Therefore materials with analogous structures similar band gaps and absorption coefficients as CZTS such as Cu_2MSnS_4 where (M = Fe, Mn) have attracted a great deal of attention for earth abundant thin film solar cells. Also replacement of Zn with more earth abundant elements like Fe and Mn would provide a significant leap forward for developing photovoltaics which can be used for terawatt electricity generation (**Figure 1.1.1**). There is also another key motivation: in CZTS based solar cells, the Cu-Zn antisite defects such as $[\text{Cu}_{\text{Zn}}^- + \text{Zn}_{\text{Cu}}^+]$ are suspected to be abundant, as they are next to each other in periodic table, which lead to severe potential fluctuations and tail states[4]. A severe tail states in CZTS is one of the dominant factor responsible for low open circuit voltage (V_{oc}), which is the number one problem in the current CZTS technology.

Hence, replacement of Zn with other metals could provide a route to alter the defects and tail states in the absorber and to eventually improve the V_{oc} . [1]

1.2 Objectives

The objective of this work is to synthesize $Cu_2(Fe,Mn)SnS_4$ (C(F,M)TS) thin films and investigate its electrical and optical properties and utilize it in photovoltaic devices. The first step towards achieving these goals is to synthesize $Cu_2(Fe,Mn)SnS_4$ thin films using a simple, facile and solution processed technique like spray pyrolysis. This will be followed by sulphurization to investigate its effect on the phase purity, electrical and optical properties. The research novelties would be the synthesis of crystalline C(F,M)TS thin films by a solution processed technique and understanding the electrical transport and photocarrier generation in these thin films. The sub-objectives of this work are as follows.

I. Synthesis of C(F,M)TS thin films

- A. Synthesis of C(F,M)TS thin films by a simple solution processed technique like spray pyrolysis followed by sulphurization.
- B. Morphological characterization by SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy) to study the grain size of the thin films.
- C. Structural characterization by X-Ray Diffraction (XRD) and Raman spectroscopy to understand the phase purity of the thin films.

II. Electrical Transport and Optical characterization

- A. Electrical transport properties of thin films by Hall measurements such as carrier density and carrier mobility to find whether the properties are suitable for solar cell application.

- B. Photoconductivity of thin films by using 2- probe current – voltage characteristics to know the potential of CFTS and CMTS as an absorber in solar cells.
- C. Study photoconductivity decay by transient photocurrent measurements to investigate its optoelectronic properties.
- D. Estimate the Optical band gaps from UV-Vis absorption spectroscopy, a key property for solar cell application.

III. Applications in Photovoltaics of C(F,M)TS

- A. Employ CFTS as a counter electrode in Dye-sensitized solar cells for Pt replacement.
- B. Utilize CMTS as an absorber layer in Thin film solar cells.

1.3 Thesis Organization

In this report, the synthesis and application of CFTS and CMTS thin films in photovoltaics are discussed. Chapter 1 provides a brief introduction of photovoltaic technology and the need to develop solar cells using non-toxic and earth abundant materials to realize the goal of terawatt electricity production. Chapter 2 provides a literature review on the current earth abundant thin film solar cells based on Cu_2O , SnS , FeS_2 and CZTS and then introduces works related to CFTS and CMTS. Chapter 3 explains the various experimental techniques and characterization techniques utilized to achieve our goals. The detailed physical, electrical and optical characterization techniques used to study the thin films and the solar cell fabricated are described. Detailed discussion on the results obtained is provided in chapter 4. The crystal structure, electrical and optical properties of CFTS thin films with varying sulphurization conditions is discussed. CFTS thin films as a counter electrode in DSSCs is demonstrated and its electrochemical properties are discussed. Then the optical and electrical properties of CMTS thin films is analysed to investigate its feasibility for employing CMTS as an absorber in

solar cells. Thin films solar cells were fabricated with CMTS and hence showing the potential of CMTS as a potential new solar absorber. Chapter 5 concludes the thesis by pointing out the salient features of this work. Chapter 6 summarizes future work that could be accomplished to further the fundamental understanding of these thin films and improve the power conversion efficiencies of these solar cells.

1.4 Novelty and Scientific contribution

Original contributions achieved by this Master thesis include

- i. Successful synthesis of CFTS and CMTS thin films via a water based non-toxic solution processed spray pyrolysis technique.
- ii. First report on the electrical properties (carrier mobility, type of carriers and carrier density) of CFTS and CMTS thin films in literature.
- iii. High efficiency dye sensitized solar cells (DSSCs) demonstrated with CFTS as a counter electrode rivalling power conversion efficiencies obtained with Pt as a counter electrode and hence providing a low cost earth abundant replacement for Pt in DSSCs.
- iv. Photovoltaic effect observed for the first time in CMTS thin films and achieved a proof of concept efficiency of 0.2 %.
- v. Identified the key problem with the CMTS thin films (High charge carrier density) that limit the current photovoltaic device and thus paving way for the development of high efficiency earth abundant solar cells by addressing this problem.

Chapter 2. Literature Review

2.1 Earth Abundant Materials for Photovoltaics

There are several materials that have been investigated for earth abundant photovoltaics like Cu_2O , SnS , CZTS and FeS_2 .

2.1.1 Cu_2O

Cuprous oxide (Cu_2O) was considered as a promising candidate for thin film solar cells due to its abundance, p-type conductivity and relatively high absorption coefficients[5]. Cu_2O exhibits band gaps ~ 2.0 eV. Ideally efficiencies close to 20 % theoretically can be achieved for a single junction but Cu_2O based solar cells have been limited due to interfacial recombination originating from non-ideal band alignment with the n-type buffer layer and high trap density near the heterojunction interface[6]. Recent developments on engineering the interface at the surface of the Cu_2O by using atomic layer deposition have resulted in record efficiencies of 2.85 % (**Figure 2.1.1.1**) [7].

Figure 2.1.1.1 (A) Cross section SEM image of Cu_2O thin film solar cell **(B)** NREL certified efficiency of Cu_2O solar cell[7]

2.1.2 SnS

Tin Sulphide (SnS) is a chalcogenide semiconductor with a band gap of 1.1 eV (close to that of silicon) and high absorption coefficient ($>10^5 \text{ cm}^{-1}$) and hence a promising material for photovoltaic applications [8, 9]. The elements tin and sulphur are abundant and hence making it an ideal candidate for earth abundant photovoltaics. Also SnS stability in oxygen and water makes it attractive in comparison to perovskite solar cells that are not stable in oxygen and air[9]. SnS based solar cells have been fabricated with Zn (O, S) as a buffer layer and efficiencies of 2 % was achieved[10]. By doping N in the Zn (O,S) buffer layer and depositing a thin layer of SnO_2 on the absorber layer to reduce recombination, NREL certified efficiencies of 4.36 % have been achieved in SnS solar cells (**Figure 2.1.2.1**).

Figure 2.1.2.1 (A) Device architecture of SnS solar cell **(B)** NREL certified efficiencies of SnS solar cells.[9]

2.1.3 FeS₂

FeS_2 was considered as a promising material for photovoltaics due to its low cost and natural abundance and high absorption coefficient [11]. Although conversion efficiencies of 3 % have been obtained from pyrite solar cells the open circuit

voltage obtained from them were very low ~ 200 mV[12]. FeS₂ nanocrystals were used as an absorber with different device configurations as a solar cell and all these devices exhibited 0% efficiency (**Figure 2.1.3.1**)[13]. Although FeS₂ is very promising due to its low cost and earth abundance, there are certain serious issues which need to be overcome before it can be viable photovoltaics. Issues related to non-radiative recombination, Fermi level pinning and presence of lower band gap impurity such as marcasite have to be addressed before considering development of FeS₂ based thin film solar cells[14].

Figure 2.1.3.1 I-V curves of different device configurations of solar cells fabricated with FeS₂ nanocrystal based solar cells[13].

2.1.4 CZTS

Among all the earth abundant photovoltaic absorbers, CZTS shows that the thin films based of CZTS usually exhibit kesterite structure or stannite structure. **Figure 2.1.4.1 (a)** illustrates the kesterite crystal structure of CZTS. The electrical and optical properties of a material are the key factors that decide its performance in a solar cell. Selenium free CZTS has an optical band gap of 1.5 eV and sulphur free CZTS has a band gap of 0.8 eV [15]. The band gap can be tuned by varying the sulphur to selenium ratio. The ideal band gap required for high efficiency photovoltaics is 1.2-1.4 eV and CZTS fulfils that requirement. Another important optical property is the optical absorption coefficient which determines how much light can be absorbed by a material. The absorption coefficient of CZTS is of the order of 10^4 cm^{-1} which suggests that the absorption of CZTS is high. The absorption spectrum is shown in **Figure 2.1.4.1(b)**. The electrical resistivity of CZTS was found to be around 10^{-3} to $10^{-1} \Omega\text{cm}$. The hole concentration in CZTS was found to vary from 10^{16} to 10^{18} cm^{-3} . This hole concentration can also be changed by controlling the ratio of the Cu, Zn and Sn in CZTS [16]. The hole carrier mobility was also found to vary between 0.1 and $30 \text{ cm}^2/\text{Vs}$. Due to all these desirable electrical and optical properties (Good absorption coefficient, ideal band gap and fast carrier mobility), CZTS can be used as an absorber in thin film solar cells. Another important aspect of CZTS is that it does not contain any rare metals. All the metals in CZTS are earth abundant unlike CIGS based solar cells which contain indium and gallium which are relatively rare metals. This is a very important concern when dealing with large scale and mass production of solar cells to meet the energy demands of the world.

$\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTS) based thin film solar cells is a key player in the search for earth abundant photovoltaics.. Solar cells with CZTS as an absorber have already hit an efficiency of 12.1 % (**Figure 2.1.4.2**) [17]. CZTS absorber layers can be prepared by wide variety techniques such as evaporation, sputtering, electrodeposition, nanoparticle based thin film deposition and spray pyrolysis[16,

18-21]. However the best efficiencies have been reported with a hydrazine based solution approach[17].

Figure 2.1.4.1 (a) Kesterite Crystal structure of CZTS[1] (b) Absorption spectrum of CZTS[22]

One of the main limiting factors of the efficiency of CZTS is the large significant V_{oc} deficit. The highest lab scale efficiency CZTS solar cell exhibits a V_{oc} of 513.3 mV which corresponds to a V_{oc} nearly 0.6 V. This is mainly due to severe tail states due to electrostatic potential fluctuations caused by defects in the semiconductor. One of the key defects responsible for limiting the V_{oc} is the Cu-Zn anti site defect in CZTS (**Figure 2.1.4.3**). The Cu-Zn antisite has a low formation energy and also due to the close proximity of Cu and Zn in the periodic table. Therefore the replacement of Zn with other metals like Fe, Mn could help to reduce these defects and hence address the V_{oc} deficit problem to achieve high efficiency solar cells. Therefore there is a need to investigate alternate semiconductors like $\text{Cu}_2\text{FeSnS}_4$ and $\text{Cu}_2\text{MnSnS}_4$ which has similar crystal structure with CZTS for photovoltaic applications.

Figure 2.1.4.2 (a) Top view, (b) cross section and (C) J-V curve of record CZTS device[17]

Figure 2.1.4.3 Illustrates the band tail recombination that is caused due to potential fluctuations.[23]

2.2 $\text{Cu}_2\text{FeSnS}_4$ (CFTS)

2.2.1 Crystal structure of CFTS

Figure 2.2.1.1 Crystal structure of $\text{Cu}_2\text{FeSnS}_4$ stannite[24]

Figure 2.2.1.1 shows the stannite crystal structure of CFTS. This structure is similar to chalcopyrite and sphalerite structure. This was assigned to the space group $I4_2m$. Mossbauer spectroscopy and magnetic susceptibility studies reveal that the oxidation states of Cu, Fe, Sn and S in CFTS were +1, +2, +4 and -2 respectively[25]. CFTS is a tetrahedrally coordinated semiconductor where the sulphur anions are bonded with 4 metal cations (2 copper, 1 iron and 1 tin located at the edges of a tetrahedron) and each cation is bonded with 4 sulphur anions [26].

2.2.2 Nanocrystals (NCs) and Nanoparticles (NPs) of CFTS

Figure 2.2.2.1 (a) low resolution TEM image of CFTS NCs (b) high resolution TEM image of CFTS NCs (c) SAED pattern of CFTS NCs [26]

Figure 2.2.2.1 shows the TEM images of CFTS NCs prepared by hot injection method. In this method a solution of elemental sulphur is inserted into a mixture of Copper acetyl acetonate, iron acetyl acetonate and tin chloride at 280 °C. The SAED pattern from TEM, identifies the tetragonal structure of CFTS and the average diameter was estimated to be around 13 nm. The band gap of such crystals was found to around 1.3 eV which is ideal for solar cells. CFTS NCs were also prepared by hot injection method with different precursors which yielded band gaps of around 1.5 eV[27]. In this method Copper acetyl acetonate, iron acetyl acetonate were mixed with 10 mL oleylamine (OLA). The solution was subsequently heated up to 150 °C and a mixture of 1-dodecanethiol (1-DDT) and tert-dodecanethiol (t-DDT) was injected into the solution and heated up to 210 °C. Using another similar hot injection method CFTS NCs were prepared with a band gap of 1.33 eV (**Figure 2.2.2.2**) [28]. The synthesis involved the copper acetate,

iron chloride, tin chloride and elemental sulphur. The particle sizes were in the range of 15-25 nm. In order to improve their electrical conductivity the long chain organic molecules like oleylamine were removed. CFTS nanoparticles were also synthesized using a liquid flux method (**Figure 2.2.2.3**). These nanoparticles also exhibited band gaps of the order of 1.3 eV.

Figure 2.2.2.2 (a) TEM image of CFTS NCs (B) U-V Vis absorption spectrum of CFTS NCs[28]

Figure 2.2.2.3 SEM image of CFTS nanoparticles synthesized in different solvents (ethyleneglycol (EG), Triethylenetetramine (TETA) , and TETA-EG)[29]

2.2.3 Applications of CFTS in photovoltaics

2.2.3.1 Photoelectrochemical cells (PEC)

Figure 2.2.3.1.1 Photocurrent vs Potential plot of CFTS NCs in 0.5 M H₂SO₄ under 100 mW/cm² illumination[26]

PECs were fabricated using the nanocrystals on ITO substrates. After this the substrate was annealed in air at 350 C to remove the ligands in order to improve the electrical conductivity. It was observed that there is a photocurrent onset at -0.1 V (**figure 2.2.3.1.1**). The increase in photocurrent at more negative potentials indicates that CFTS is a p-type semiconductor. The inset in the **Figure 2.2.3.1.1** shows the photocurrent vs time plot where it was observed that the photocurrent rises steeply upon illumination and decreases sharply back to its dark current

upon switching off the light illumination. Photocurrents in the range of 11-13 $\mu\text{A}/\text{cm}^2$ were observed with good stability.

2.2.3.2 Counter electrode in Dye-Sensitized solar cells (DSSC)

Figure 2.2.3.2.1 (A) Current density – Voltage curves of CFTS NPs used as counter electrode (B) cyclic voltammetry curves of CFTS and Pt in iodine/iodide electrolyte [30]

CFTS NPs have been employed as a counter electrode in DSSC with iodine/iodide as the electrolyte. The commonly used counter electrode for the regeneration of iodine /iodide electrolyte is Platinum (Pt) due to its high electrocatalytic activity with iodine/iodide electrolyte system. However the high cost associated with the scarcity of Pt poses a significant drawback in the large scale production of DSSCs[31]. Therefore there is a need for the development of low cost, earth abundant and industrially scalable counter electrodes for DSSCs. CFTS NPs as a counter electrode in DSSC exhibited efficiencies of 5.6 % in comparison to 7.1 % Pt based DSSC (**Figure 2.2.3.2.1**). Cyclic voltammetry curves of CFTS and Pt were

similar to each other in terms of the shape and current densities showing that CFTS exhibited similar catalytic activity as Pt in iodine /iodide redox couple.

2.3 $\text{Cu}_2\text{MnSnS}_4$

$\text{Cu}_2\text{MnSnS}_4$ (CMTS) is another possible candidate for investigating earth abundant photovoltaic materials. CMTS exhibits a tetragonal stannite structure (**Figure 2.3.1**) with $I4_2m$ space group symmetry. Its crystal structure is very similar to CFTS except for the replacement of Fe by Mn. Most of the reports on CMTS have primarily focussed on its magnetic properties (antiferromagnetism and ferroelectricity) [32, 33]. There are very few reports regarding its optical and electrical properties.

Figure 2.3.1 Crystal structure of $\text{Cu}_2\text{MnSnS}_4$ [32]

Figure 2.3.2 (A) TEM images of CMTS nanocrystals by hot injection method (B) I-V curves of CMTS nanocrystals in dark and light[34].

CMTS nanocrystals have been synthesized recently by hot injection method (**Figure 2.3.2(A)**) in order to investigate its optical and electrical properties [34, 35]. These CMTS nanocrystals exhibited a band gap of around 1.3 eV ideally suited for photovoltaic applications. **Figure 2.3.2 (B)** shows the I-V curves of CMTS nanocrystals in dark and light. There is a significant difference in the I-V curves in dark and light and indicating the generation of photocarriers upon light illumination. These optical and electrical properties are promising for investigating CMTS as an absorber in thin film solar cells.

Chapter 3. Experimental Section

3.1 Spray Pyrolysis of C(F,M)TS thin films

$\text{Cu}_2(\text{Fe,Mn})\text{SnS}_4$ thin films were prepared by spray pyrolysis (Schematic shown in **Figure 3.1**). The precursor solutions used were $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1M), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1M), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1M) and Thiourea (1M) with DI water as the solvent. These precursors were taken in stoichiometric composition of $\text{Cu}_2(\text{Fe,Mn})\text{SnS}_4$ and sprayed onto soda lime glass substrates on a hot plate at a temperature of 330 °C.

Figure 3.1 Schematic of Spray pyrolysis setup

3.2 Sulphurization of sprayed C(F,M)TS thin films

The as-sprayed films were annealed in sulphur ambient in a tube furnace at a temperature of 400 °C, 500 °C and 600 °C for 30 mins. The C(F,M)TS thin films were placed at the centre of the furnace where the temperature was maintained at

either 400 °C , 500 °C and 600°C and a sulphur powder (25 mg) was placed in a boat at a lower temperature zone of the furnace (200 °C) in Ar atmosphere.

Figure 3.2 Schematic of sulphurisation of $\text{Cu}_2(\text{Fe,Mn})\text{SnS}_4$ thin film set-up

3.3 Field Emission Scanning Electron Microscopy (FESEM)

Surface morphology of the films followed by sulfurization was imaged by FESEM (JEOL, JSM-7600F, 5kV). Thin (10nm) Pt is de-positied on the films before imaging. Energy dispersive x-ray spectrum of the film was also obtained by Oxford EDX detector attached to FESEM.

3.4 Atomic Force Microscopy (AFM)

AFM images were obtained using a commercially available Asylum Research MFP3D using the tapping mode to investigate the surface morphology and roughness of the thin films.

3.5 X-Ray Diffraction

Structural characterization of CFTS thin films was investigated by X-ray diffraction (XRD) Bruker D8 Advance. XRD spectrum was recorded in the 2θ range of 20° - 60° using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$)

3.6 Raman spectroscopy

Micro Raman spectroscopy was performed using a Renishaw system 2000 (excitation wavelength 514 nm and laser spot size 2 μm).

3.7 Absorption spectroscopy

Absorption spectrum was obtained using a UV-Vis spectrophotometer (Shimadzu UV-3600). The band gap was measured from the Tauc plots obtained from the UV-Vis spectrum.

3.8 Hall Measurements

Electrical properties of C(F,M)TS thin films (Resistivity, carrier density and carrier mobility) were estimated using a MMR technologies variable temperature hall measurement system in a four-probe configuration. The C(F,M)TS films were deposited on glass substrate and the hall measurements were carried out at atmosphere pressure at room temperature (302 K). 4 square electrodes (1.6 mm x 1.6 mm) of aluminium were thermally evaporated in square geometry onto the CFTS films.

3.10 Transient Photocurrent Measurements

Transient photocurrent studies were conducted using mode-locked Ti: Sapphire laser seeded Ti: Sapphire regenerative amplifier (Spectra physics, Mai Tai-Spitfire Ace). laser pulses were at 800 wavelengths (100-fs duration, and 1000-Hz repetition rate), which were exposed onto the photoconductor devices with a circular spot diameter of ~ 10 mm. Optical neutral density filters were employed to control the laser pulse energy (1 W power was used for these measurements). A laser power meter was used to measure the average power of the laser pulses. The laser pulse temporal profiles and transient photocurrents were monitored with the 50-ohm-terminated, 400-MHz-bandwidth digital oscilloscope.

3.11 Fabrication of Dye sensitized solar cells with Pt and $\text{Cu}_2\text{FeSnS}_4$ as a counter electrode

Briefly, the FTO glass (2.2mm thickness, 14 Ω/sq , Pilkington) used as current collector was first cleaned, then immersed into a 40 mM aqueous TiCl_4 solution at 70 °C for 30 min and rinsed with water and ethanol. 10 μm -thick transparent TiO_2 layers (Dyesol 18NR-T, average nanoparticle size: 20 nm) were screen-printed on the FTO glass plates (mesh count is 90T mesh/cm, active areas are 0.16 cm^2). After drying at 125 °C, 5 μm -thick scattering TiO_2 layers (Dyesol WER2-O paste, average nanoparticle size: 150-250 nm) were superimposed by screen-printing. The electrodes coated with the TiO_2 pastes were gradually annealed under air at 125°C for 10 min, 325 °C for 5 min, at 375 °C for 5 min, and at 450 °C for 15 min, and finally, at 500 °C for 15 min. The TiO_2 films which were again treated with 40 mM TiCl_4 solution for 30 min at 70 °C, were rinsed with DI water and ethanol and annealed at 500 °C for 30 min. After cooling to room temperature, the TiO_2 photoanodes of optimum devices were made by immersing into 0.3 mM N719 dye solution in a mixture of acetonitrile (ACN) and tert-butyl alcohol (TBA) (volume ratio 1:1) for 15 h. The dye sensitized TiO_2 photoanode and the Pt-coated FTO glass counter electrode were sandwiched together using a 25 μm -thick transparent Surlyn film (Meltonix 1170-25, Solaronix). The electrolyte was injected through the hole at the back of the counter electrode via vacuum backfilling. The electrolyte employed was a solution of containing 1.0 mM 1,3-dimethylimidazolium iodide (DMII), 50 mM LiI, 30 mM I_2 , 0.5 mM tert-butylpyridine, and 0.1 mM guanidinium thiocyanate (GNCS) in the mixed solvent of acetonitrile and valeronitrile (v/v, 85/15). Finally, the hole was sealed using 25 μm -thick surlyn and a cover glass (0.1 mm thickness) to avoid leakage of the electrolyte.

3.12 Cyclic voltammetry and Electrochemical Impedance Spectroscopy of CFTS counter electrode

Photocurrent density - photovoltage (J-V) characteristics were measured under an illumination of AM 1.5 (100 mW cm^{-2}) using a solar simulator (San-Ei Electric, XEC-301S) equipped with a 450 W xenon lamp which was coupled with an Agilent semiconductor parameter analyzer (4155C). The power of the simulated light was calibrated to 100 mW/cm^2 by using a silicon reference cell (Fraunhofer) and monitored using a power meter throughout the testing. A black mask (6 mm x 6 mm) was used in the subsequent photovoltaic studies to avoid the effects of diffusive light on cell performance. Impedance spectroscopy (IS) was measured with an Autolab 302 at different DC bias potentials under the region of interest under dark conditions. The applied voltage perturbation had AC amplitude of 20 mV (rms) with a frequency from 1 MHz to 1 Hz. The spectra were fitted using Z-View software. To investigate the catalytic activities of the prepared counter electrodes, cyclic voltammetry (CV) was performed in a three electrode system (Pt mesh, SCE as counter and reference electrodes respectively) with electrolyte described in the DSSC fabrication.

3.13 Fabrication of thin film solar cells

Firstly, CdS buffer layer was deposited on prepared CZTS/Mo/SLG at 80°C for 10 min using chemical bath deposition (CBD). The solution of CBD consisted of deionized H_2O (140 mL), NH_4OH (28~30%, 20 mL), 0.15 M CdSO_4 (20 mL, AR) and 0.75 M thiourea (20 mL, AR). Next, 50 nm i-ZnO followed by 500 nm ZnO:Al layer were deposited by RF and DC magnetron sputtering. Finally Silver ink was printed on Al:ZnO layer to form top contact fingers via shadow mask.

3.14 Characterization of thin film solar cells

A solar simulator (VS-0852) was utilized to measure the J-V characteristics of solar cells under the simulated AM 1.5 100 mW cm^{-2} illumination using a Keithley Source (2612A) meter and IV tester software package. The solar simulator was equipped with a 500 W xenon lamp and the light intensity was calibrated using Si reference solar cell (Fraunhofer). Incident photon to current efficiency (IPCE) spectra was measured with a spectral resolution of 1 nm. 5 nm using a PVE300 photovoltaic device characterization system (Bentham) equipped with a xenon/quartz lamp.

Chapter 4. Results and Discussion

4.1 Earth Abundant $\text{Cu}_2\text{FeSnS}_4$ (CFTS) thin films by spray pyrolysis

A. Crystal structure, Electrical and Optical properties of Earth Abundant CFTS thin films

The CFTS thin films were prepared by spray pyrolysis at a substrate temperature of 330°C. The XRD pattern of the as sprayed films did not show any peaks indicating that the films were either amorphous or CFTS phase were not formed (**Figure 4.1.1**). TGA analysis was performed on the precursor metal chlorides and thio urea to study the film growth after spray pyrolysis (**Figure 4.1.2**). The precursor metal chlorides and thiourea were mixed together and then were heated from 50 °C to 400 °C in air and the weight loss was monitored. The weight loss of 50 % was estimated at 330 °C. However for the formation of CFTS, there should be a weight loss of 70 % (by taking into account the molecular weight of metal chlorides + Thio urea and molecular weight of $\text{Cu}_2\text{FeSnS}_4$). This clearly shows that either the CFTS phase is not fully formed or binary sulphides were formed. Therefore sulphurization was performed to complete the reaction and improve the crystallinity. The films were annealed in sulphur vapour in a tube furnace at different temperatures (400°C (CFTS4), 500°C (CFTS5) and 600°C (CFTS6)). The as sprayed films were brown in colour and the films turned black in colour after sulphurization. The thickness of the films after sulphurization was found to 400 ± 50 nm using surface profilometry. After the films were deposited by spray pyrolysis, they were annealed in sulphur vapour in a tube furnace at different temperatures (400°C (CFTS4), 500°C (CFTS5) and 600°C (CFTS6)). The as

sprayed films were brown in colour and the films turned black in colour after sulphurization.

Figure 4.1.1. XRD of as sprayed CFTS thin films (before sulphurization).

Figure 4.1.2. TGA curves for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + Thiourea performed in air.

Figure 4.1.3 (A), (B) and (C) shows the SEM images of CFTS4, CFTS5 and CFTS6 respectively. From the SEM images, it was observed that the grain size increased with increasing temperature. Similar trend was also observed in $\text{Cu}_2\text{ZnSnS}_4$ with increasing sulphurization temperature[36]. **Figure 4.1.3** (D), (E) and (F) shows the 3-D plots of tapping mode AFM images. The surface roughness increased with increasing temperatures (CFTS4 , CFTS5 and CFTS6 were ~ 72 nm , 103 nm and 123 nm respectively). The AFM images further elucidate the grain growth with increasing sulphurizing temperatures.

Figure 4.1.3. SEM images of (A) CFTS4 and (B) CFTS5 and (C) CFTS6 showing the surface morphology. 3-D AFM tapping mode images of (D) CFTS4 and (E) CFTS5 and (F) CFTS6 showing the surface morphology.

Figure 4.1.4 shows the XRD patterns of CFTS4 , CFTS5 and CFTS6. The peaks marked with black squares in **Figure 4.1.4** in CFTS4, CFTS5 and CFTS6 samples can be indexed to $\text{Cu}_2\text{FeSnS}_4$ thus confirming the presence of CFTS[27].

Figure 4.1.4 X-Ray Diffraction pattern of CFTS4, CFTS5 and CFTS6 indicating the presence of CFTS phase

Peaks corresponding to $\text{Cu}_2\text{Sn}_3\text{S}_7$ (CTS) was observed and marked by the magenta squares in **Figure 4.1.4**[37]. A peak corresponding to Cu_2S was observed only for CFTS4 sample. With increasing sulphurization temperature the intensities of CTS peaks decreased in comparison to CFTS peaks.

However XRD is not a very conclusive technique for distinguishing the various CTS phases as the diffraction peaks overlap for the different phases of CTS. Raman spectroscopy can help to distinguish the various CTS phases. **Figure 4.1.5** shows

the Raman spectra of CFTS4, CFTS5 and CFTS6 thin films. For the CFTS4 sample, Raman peaks at 285, 319 and 373 cm^{-1} was observed. The peaks at 285 and 319 can be attributed to $\text{Cu}_2\text{FeSnS}_4$ and the peak at 373 cm^{-1} is attributed to $\text{Cu}_2\text{Sn}_3\text{S}_7$. For the CFTS5 sample, Raman peaks corresponding to CFTS phase was observed as showed in the **Figure 4.1.5** [38, 39]. The main feature of these spectra is the peak at 319 cm^{-1} . This peak corresponds to the strongest asymmetry vibration of a pure anion mode of the sulphur atom around the Sn metal[40].

Figure 4.1.5. Raman spectra of CFTS4, CFTS5 and CFTS6 showing the presence of CFTS

The CFTS6 sample also exhibited the Raman modes associated with $\text{Cu}_2\text{FeSnS}_4$ (labelled in **Figure 4.1.5**). The interesting feature to notice about the CFTS5 and CFTS6 Raman spectra was that the intensity of the 373 cm^{-1} was very low in

comparison to the CFTS4 indicating that less CTS phase was present in CFTS5 and CFTS6. Therefore both Raman and XRD data confirm that the amount of CFTS increases as the sulfurization temperature increases from 400 to 600 °C. It could be due to that during sulfurization, CTS is formed first followed by the diffusion of Fe inside CTS lattice. As the Fe diffusion is faster at higher temperature, it resulted in higher amount of CFTS phase as the temperature increases [37]. The thickness of the films after sulphurization was found to 400 ± 50 nm using surface profilometry. The elemental composition was estimated from EDX measurements (**Figure 4.1.6**) as CFTS4 – $\text{Cu}_{1.71}\text{Fe}_{0.72}\text{Sn}_{0.78}\text{S}_4$ CFTS5 – $\text{Cu}_{1.88}\text{Fe}_{0.73}\text{Sn}_{0.63}\text{S}_4$ and CFTS6 – $\text{Cu}_{1.87}\text{Fe}_{0.85}\text{Sn}_{1.02}\text{S}_4$. All the samples were Cu poor and CFTS6 was found to be close to the stoichiometric composition.

Sample	Cu-Fe-Sn-S ratio
CFTS4	Cu = 4.2 Fe = 1.78 Sn = 1.91 S = 9.78
CFTS5	Cu = 4.36 Fe = 1.68 Sn = 1.47 S = 9.27
CFTS6	Cu = 6.18 Fe = 2.8 Sn = 3.37 S = 13.1

Figure 4.1.6. Elemental composition estimated from EDX results.

Figure 4.1.7. Carrier density and Mobility of CFTS4, CFTS5 and CFTS6 obtained from hall measurements.

The electrical charge transport properties of the CFTS4, CFTS5 and CFTS6 estimated from hall measurements were shown in **Figure 4.1.7** (Raw data shown in Appendix A). The majority carriers in all the films were holes which show that the films were p-type. CFTS6(11.66 cm²/V.s) films had the highest mobility as compared to CFTS4 (3.04 cm²/V.s) and CFTS5 (2.51 cm²/V.s). The carrier density of CFTS5 and CFTS6 were of the same order (10¹⁴) and that of CFTS4 was of the order of 10¹⁶. The higher carrier density of CFTS4 could be attributed to the higher amount of CTS phase as some CTS phase like Cu₂SnS₃ were reported to possess metallic electrical characteristic [41]. The carrier mobilities of CFTS are comparable with CZTS (6-12 cm²/V.s) suggesting that CFTS could be a potential absorber layer in thin film solar cells [42].

Figure 4.1.8 Current vs Time plots of CFTS5 thin films at an applied bias of 5 V.

Photoconductivity of CFTS5 thin films were investigated in a 2-probe configuration with Al electrodes in vacuum with a white lamp source at an applied bias of 5 V. The CFTS5 did not exhibit any photoconductivity in air. CFTS thin films don't exhibit photoconductivity in air probably due to the adsorption of oxygen in air which creates a depletion layer by capturing free electrons on the surface[43]. The influence of surface oxygen photochemistry on the photoconductivity of metal sulphides have been reported in literature.[44] But in vacuum, CFTS5 exhibited a persistent photoconductivity behavior (**Figure 4.1.8**). Even after switching off the light source, the current did not decay back to its dark state value but it slowly reached the dark current after 600 s. The reason for the low photocurrent in vacuum is due to the severe potential fluctuations and trap states in CFTS. This is evidenced by the Persistent photoconductivity behavior of CFTS. Persistent photoconductivity could be due to random local potential fluctuations that results in electron – hole pair separation before recombination occurs[45]. It could also be due to deep lying traps in the semiconductor that capture the free electrons

and then reemit resulting in increased conductivity even after switching off the light source[46]

Figure 4.1.9 $(\alpha h\nu)^2$ vs $h\nu$ plots of CFTS4 ,CFTS5 and CFTS6 for band gap estimation

As CFTS is a potential absorber layer in thin film solar cells, the band gap is an important property for practical applications. The band gap was estimated using the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ and by extrapolating the linear region of the $(\alpha h\nu)^2$ vs $h\nu$ plots and from the intercept on the $h\nu$ axis[47]. **Figure 4.1.9** shows the $(\alpha h\nu)^2$ vs $h\nu$ plots of CFTS4, CFTS5 and CFTS6 to estimate the band gap of these thin films. The optical band gaps of CFTS4, CFTS5 and CFTS6 are ~ 1.65, 1.54 and 1.46 eV which was similar those reported in literature[27]. These band gaps suggest that CFTS is a potential solar cell absorber material.

B. Application of CFTS thin films in Dye Sensitized Solar cells as a counter electrode

Currently in dye-sensitized solar cells (DSSCs) the ideal counter electrode is Pt owing to its good catalytic activity in iodine/iodide electrolyte[48]. For a material to be considered as a candidate for counter electrode in DSSCs, it needs to exhibit good catalytic activity in iodine/iodide electrolyte. However Pt is expensive and therefore there is a need to develop low cost alternatives to Pt. DSSCs were fabricated using CFTS thin films as a counter electrode to investigate whether CFTS can be a suitable replacement of Pt in DSSCs. DSSC with CFTS6 as counter electrode was not investigated as the FTO substrates melted in the high sulphurization temperatures. **Figure 4.1.10** shows the J-V curves of DSSCs fabricated using CFTS4, CFTS5 and Pt as counter electrode. It is evident from the DSSC performance (Inset of **Figure 4.1.10**) that CFTS5 (8.03%) exhibited good conversion efficiency which is better than a Pt counter electrode (7.57 %). The conversion efficiency of the CFTS4 device (6.78%) was lower than that of Pt counter electrode. This could be due to the presence of the secondary phase like Cu₂S and Cu-Sn-S phases (observed in XRD) which have been shown to have poor catalytic activity in Iodine/Iodide electrolyte[30, 49]. The conversion efficiency exhibited by the CFTS5 device suggests that CFTS can be a viable candidate for replacement of Pt in DSSCs. The conversion efficiencies of spray deposited CFTS5 films (8.03 %) as a counter electrode were also much higher in comparison to CFTS nanoparticles reported in literature (5.9 %)[30]. It is possible that the surface stabilizer on the as synthesized nanoparticles impedes charge transfer, unlike our sprayed CFTS which does not contain any carbonous impurity. It is evident from J-V curves that main improvement in the CFTS5 counter electrode was the fill factor and marginal improvement in V_{oc} (30mV). The CFTS5 device was tested after 3 days to investigate its stability. It exhibited a power conversion

efficiency of 6.11 % (**Figure 4.1.11**).To understand the reason behind the improved power conversion efficiency of CFTS5 counter electrodes, the cyclic voltammetry and impedance spectroscopy studies were conducted and discussed in the following sections.

Figure 4.1.10 Current density (J) – Voltage (V) plots of DSSCs fabricated using Pt and CFTS4 and CFTS5 (error bars indicated)

Figure 4.1.11 J-V curve of CFTS5 counter electrode tested after 3 days.

Figure 4.1.12 (A) C-V curves of CFTS5 and Pt in iodine/iodide electrolyte **(B)** Nyquist plots of symmetric cells (CFTS5 and Pt) measured at a bias of 0.5 V

Figure 4.1.12 (A) shows the cyclic voltammetry curves of the CFTS5 and Pt performed in a 3-electrode system in iodine/iodide electrolyte. The CFTS5 exhibits the typical redox peaks observed when Pt was employed as a working electrode[50]. The cathodic peaks observed in the range of 0.5 V to -0.3 V vs SCE correspond to reduction reactions (1) and (2) shown below[51].

The C-V curves indicate that both the CFTS5 exhibit good catalytic activity in iodine/iodide electrolyte. However in the C-V curve of CFTS5 it was observed that the reduction peak corresponding to (2) has shifted to negative potentials in comparison to Pt which may indicate that the CFTS5 can easily reduce the oxidized electrolyte species and regenerated at the counter electrode[52]. Therefore it is concluded that the good catalytic activity of the CFTS5 in iodine/iodide electrolyte leads to higher conversion efficiency.

To understand the electrochemical characteristics of the CFTS counter electrode Electrochemical Impedance Spectroscopy was performed on symmetric cells. The

high frequency region of the Nyquist plot provides information regarding the R_{ct} (charge transfer resistance) and the double layer capacitance (C_{μ})[53]. The fitting of the measured spectra to a well-established transmission line model[54] allows the calculation of R_{ct} and C_{μ} (see **Figure 4.1.12(B)**). The R_{ct} of Pt and CFTS5 are 7.3 and 21.84 ohm.cm² respectively. The efficiency of CFTS5 was higher than that of Pt despite a having a higher R_{ct} than Pt. However R_{ct} is not the only deciding factor for the counter electrode performance. The double layer capacitance can also provide on the catalytic activity of the counter electrode. The C_{μ} for CFTS5 (6.1×10^{-4} F/cm²) was higher than that of Pt (2.9×10^{-5} F/cm²) which corresponds to higher surface area and hence higher catalytic activity[55]. Therefore based on the C-V curves and EIS studies the improved performance of the CFTS5 DSSC is attributed to the superior catalytic activity of the CFTS5 in iodine/iodide electrolyte.

4.2 Earth Abundant $\text{Cu}_2\text{MnSnS}_4$ (CMTS) thin films by spray pyrolysis

A. Crystal Structure , Electrical and Optical properties of CMTS thin films

Thin films of CMTS were prepared by spray pyrolysis followed by sulphurization at 500 °C. **Figure 4.2.1** shows the SEM images of CMTS thin films sulphurized at 500 °C. Small grains of 200-400 nm can be observed after sulphurization. **Figure 4.2.2 (A)** shows the Raman spectrum of CMTS thin films. A sharp and intense peak at around 328 cm^{-1} can be observed. This mode can be attributed to the A1 mode[40]. This is a signature raman peak for $\text{Cu}_2\text{MnSnS}_4$ thus confirming the formation of $\text{Cu}_2\text{MnSnS}_4$. **Figure 4.2.2 (B)** shows the XRD pattern of CMTS thin films. The peaks shown in **figure 4.2.2** can be indexed to the zinc blende structure of $\text{Cu}_2\text{MnSnS}_4$ [35] further confirming the presence of $\text{Cu}_2\text{MnSnS}_4$. However there are is a CTS peak also observed from the XRD spectrum indicating that a small quantity of CTS is present. This indicates that a sulphurization temperature of 500 C was not sufficient to eliminate all the secondary phases. Therefore sulphurization temperatures higher than 500 C are required for the elimination of the secondary phases.

Figure 4.2.1 SEM images of CMTS thin films after sulphurization

Figure 4.2.2 (A) Raman spectrum and **(B)** XRD pattern of CMTS thin films.

Figure 4.2.3 (A) Tauc plot used to estimate band gap of CMTS **(B)** lists the electrical properties of CMTS obtained from hall measurements

In order evaluate whether CMTS can be a viable candidate as an absorber in solar cells, the band gap must be estimated. UV-Vis absorption spectroscopy was performed to determine the band gap from the Tauc plot (**Figure 4.2.3(A)**). The band gap was found to be around 1.58 eV which is ideally suited for photovoltaic application. Hall measurements were performed on CMTS thin films to estimate

the majority carrier type and other electrical properties such as carrier density and carrier mobility. The CMTS thin films exhibited p-type conductivity which is ideal for using it as an absorber in thin film solar cells. The carrier mobility was ~ 3 and carrier density of the order of 10^{16} (Raw data shown in Appendix A).

Figure 4.2.4. Current vs Time plots of CMTS thin films under light illumination (On and Off)

To investigate the photoconductivity of CMTS thin films, current versus time curves under light illumination was performed in a 2- probe configuration with aluminum electrodes. In contrast to CFTS, CMTS did exhibit photoconductivity in air (**Figure 4.2.4**). There was also an absence of persistent photoconductivity behavior unlike CFTS. The rise in photocurrent upon light illumination was fast and as was the photocurrent decay. These indicate that CMTS might be more promising for solar absorber applications than CFTS. Transient photocurrent measurements using an ultrafast laser with 800 nm wavelength was performed to

estimate the photoconductivity decay (**Figure 4.2.5**) . The decay was fitted with an exponential function and the decay time was estimated around $1.2\ \mu\text{s}$ which is quite promising and hence suggesting that CMTS could be a potential solar absorber material.

Figure 4.2.5. Transient photocurrent decay curve of CMTS thin films.

B. CMTS as an absorber in Thin Film Solar cells

As the optical properties of CMTS is suitable for solar cells (as deduced from the transient photocurrent and photoconductivity I-V measurements), Thin film solar cells were fabricated using CMTS as the absorber. The device configurations used for fabricating CZTS type solar cells were used (**Figure 4.2.6**). To fabricate absorber thin films, the as-sprayed thin films were sulphurized and selenized to improve the crystallinity and increase the grain size in the thin films. Selenization of CMTS thin films were performed in order to provide for band gap tunability in the solar cells by the incorporation of selenium. Selenium incorporation usually decreases the band gap and this provides for variable band gap solar absorbers.

Figure 4.2.6 Device architecture of CZTS solar cells.[56]

The sulphurization and selenization temperatures were increased to 540 °C to avoid the formation of CTS phase. **Figure 4.2.7** shows the XRD patterns of the CMTS and CMTSSe thin films after sulphurization and selenization. In **Figure 4.2.7** the diffraction reflections could be indexed in a tetragonal cell with the space group $I-42m$ with the reflections corresponding to the (112), (200), (220) and

(312) planes observed and an enhancement of the (112) plane suggestive of a preferred crystallite orientation for CMTS (red curve). The lattice parameters for CMTS ($a = 5.492 \text{ \AA}$ (1), $c = 10.824 \text{ \AA}$ (3) and cell volume = $326.5 \text{ \AA}^3$ (3)) estimated are in close agreement with the reported values in literature.[57] Similarly in **Figure 4.2.7**, for CMTSSe (blue curve) was also indexed with the space group $I42m$ and the reflections corresponding to the (112, (220) and (312) planes were observed. The preferred crystallite orientation in CMTSSe is also along the (112) plane. The lattice parameters for CMTSSe are ($a = 5.59 \text{ \AA}$ (1), $c = 11.04 \text{ \AA}$ (3)). It is evident that the length of the a axis and c axis has increased in comparison to CMTS. Hence a shift in the reflection positions of the CMTSSe towards lower 2θ due to the substitution of S^{2-} ($IR = 1.84 \text{ \AA}$) of the larger Se^{2-} ions ($IR = 1.98$)[58]. As expected, the cell volume ($357.6 \text{ \AA}^3$ (3)) of CMTSSe was also larger. The crystallite size was estimated using the Scherrer formula and the Williamson- Hall approach and it was found that the crystallite size of CMTS ($\sim 30 \text{ nm}$) was smaller than the CMTSSe (57 nm).[59] **Figure 4.2.8** (A) shows the Raman spectrum of CMTS thin films. One strong peak at 327 cm^{-1} and a shoulder peak at 343 cm^{-1} was observed in the spectrum. The peak at 327 cm^{-1} corresponds to the A_1 vibration mode and is consistent with those observed in literature and the shoulder peak at 343 cm^{-1} was also observed in Cu_2MnSnS_4 . [40]. This further confirms the presence of CMTS phase in addition to the XRD pattern and shows the absence of any impurity phases.

Figure 4.2.7 XRD patterns of CMTS and CMTSSe thin films after sulphurization and selenization respectively. A shift was observed in the diffraction peaks upon incorporation of Se into CMTS

Figure 4.2.8 shows the Raman spectrum of CMTSSe and it is characterized by 2 prominent peaks. Due to the partial replacement of Sulphur atoms by Se atoms, the frequency of the A1 mode has been shifted to lower frequencies due to the higher atomic mass of Se.[60] Also from XRD analysis it was observed that the cell volume of CMTSSe was larger than CMTS, thus indicating that the bond-stretching force is lower in CMTSSe. Therefore a combination of higher atomic mass of Se and the decreased bond-stretching force results in the shifting of A1 modes towards lower frequencies. **Figure 4.2.8** (C) and (D) shows the cross sectional image of the CMTS and CMTSSe thin films after sulphurization and selenization. It is evident from the SEM image that the grain size is larger in CMTSSe in comparison to CMTS as selenization has been shown to improve grain size.[61]

Figure 4.2.8. Raman spectrum of **(A)** CMTS and **(B)** CMTSSe. Cross sectional SEM images of **(C)** CMTS **(D)** CMTSSe

Figure 4.2.9. EDX spectrum of **(A)** CMTS and **(B)** CMTSSe showing the presence of the metals (Cu, Mn, Sn) and S, Se

CMTS Device	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	Eff(%)
Average and standard deviation	225±12.01	2.04±0.155	0.34±0.008	0.16±0.22

Table 4.2.1 showing the average and standard deviation of CMTS devices

CMTS _{Se} Device	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	Eff(%)
Average and standard deviation	44 ± 10	4.66 ±0.33	0.27±0.005	0.05±0.018

Table 4.2.2. showing the average and standard deviation of CMTS_{Se} devices

EDX spectrum shows the presence of all the metals (Cu,Mn,Sn) for both CMTS and CMTS_{Se} (**Figure 4.2.9**). **Figure 4.2.10** shows the J-V curve of the CMTS and CMTS_{Se} thin film solar cells under AM1.5 illumination. The best CMTS device exhibits a conversion efficiency of 0.19% which is higher than the best CMTS_{Se} (0.07%). **Table 4.2.1 and 4.2.2** shows the average conversion efficiency obtained for CMTS device (0.16 %) and CMTS_{Se} device (0.05%) with error bars included. The standard deviation of these devices has been obtained from 4 different devices for analysis.

Figure 4.2.10. J-V curves of CMTS and CMTSSe champion device under AM1.5 1 sun illumination

Figure 4.2.11 shows the cross section of the CMTS device. The V_{oc} of CMTS device (236mV) was much higher in comparison to the CMTSSe device (52 mV). However the J_{sc} of CMTS (2.22 mA/cm²) was lower than CMTSSe (5.1 mA/cm²). In order to comprehend the J_{sc} trends, the quantum efficiency curves of the CMTS and CMTSSe device was investigated. **Figure 4.2.12** (A) and (B) shows the external quantum efficiency vs wavelength plots for the 2 devices. From the $[E \times \ln(1-EQE)]^2$ vs E plots the band gaps were wavelength plots for the 2 devices. From the $[E \times \ln(1-EQE)]^2$ vs E plots the band gaps were calculated and it was that the CMTS (1.60 eV) had a higher band gap than CMTSSe (1.47 eV). This could account for the increased J_{sc} of the CMTSSe device. For the CMTS device, the EQE curves show a

weak response at the red portion of the spectrum ($\lambda > 600$ nm) which indicates a low collection efficiency. This is could be due to high recombination losses in the bulk and depletion region that limits the minority carrier lifetime.[19]

Figure 4.2.11. Cross section of the CMTS device.

Figure 4.2.12 IPCE curves of (A) CMTS and (B) CMTSSe solar cells (Inset shows the band gap estimate from $E \cdot \ln(1-EQE)^2$ vs E plots)

A similar trend was observed for CMTS_{Se} device. However in CMTS_{Se} device the onset of the EQE curve was shifted to higher wavelength (red shift) in comparison to CMTS device due to its lower band gap. To understand the quality of the *p-n* junction, we extract the diode parameters (n , J_0 , R_s , G_s) of the light and dark J-V curves of the CMTS and CMTS_{Se} (**Figure 4.2.13** and **Table 4.2.3**). The detailed device parameters including the four diode parameters (ideality factor n , reverse saturation current J_0 , series resistance R_s , and shunt conductance G_s) are presented in Table 4.2.3 obtained using the Lambert-W fitting method[62]. It is evident from the dark curves that the CMTS_{Se} had a nearly ohmic behavior and exhibited a poorer rectification than the CMTS dark J-V curves. Overall both devices show very high dark shunt conductance G_s which could be due to very high carrier density absorber or electrical shunt due to film non-uniformity. Furthermore G_s becomes more severe (higher) under light condition which indicates voltage-dependent-collection-efficiency problem i.e. current collection that increases with more negative bias [63]. This suggests a very short collection length (approximately equal to the sum depletion width and minority carrier diffusion length), which again suggests a high carrier density in the absorber. Such high carrier density will lead to very short *p-n* junction depletion width and very short minority carrier lifetime.

Figure 4.2.13. J-V curves (Dark and Light) (A) CMTS (B) CMTS_{Se}

Device	Eff (%)	FF (%)	Voc (mV)	Jsc $\mu\text{A}/\text{cm}^2$	Eg (eV)	Voc,def (V)	n	J0 (A/cm^2)	Rs ($\Omega\cdot\text{cm}^2$)	Gs (mS/cm^2)
CMTS	0.19	35.4	236	2.22	1.6	1.364	1.76 (1.88)	5.38e-6 (1.03e-6)	14.6 (17.6)	6.12 (2.53)
CMTSSe	0.07	27.2	52	5.1	1.47	1.418	1.830 (1.66)	7.87E-04 (3.56e-4)	1.113 (2.8)	79.4 (41.4)

Table 4.2.3. Device characteristics of the CMTS and CMTSSe including the diode parameters: ideality factor n , reverse saturation current J_0 , series resistance R_s , and shunt conductance G_s , extracted using Lambert-W fitting method [62]. The parameters in parantheses are from dark J-V curves.

Figure 4.2.14. (A) IQE spectra of CMTS device (inset shows the $d(\text{IQE})/d(\lambda)$ used to estimate the band gap (B) absorption coefficient (obtained from $-\ln(1-\text{IQE})$) vs energy plots at below band gap excitation

The bandgap-voltage offset (V_{oc} deficit) can provide useful information regarding the electronic quality of the solar cell absorber.[64] The bandgap-voltage offset of CMTS (1.36 eV) was marginally lower than CMTSSe (1.41 eV) which shows that the recombination losses (due to deep defects and interfaces) was probably lower in CMTS.[65] Defect passivation and grain growth strategies such as doping with Na

could reduce the recombination in CMTS and hence increasing the conversion efficiency of CMTS.[66] **Figure 4.2.14** (A) shows the internal quantum efficiency curves (IQE) for CMTS device after taking into account the reflection of the device. Using the IQE curve a derivative of IQE w.r.t. wavelength was plotted and a band gap of 1.62 eV was obtained from the inflection point (inset of **Figure 4.2.14** (A)). This is in close agreement with the band gap values obtained from $[E \times \ln(1 - EQE)]^2$ vs E plots. The decay of the IQE curve below the band gap could shine light upon the electrostatic potential fluctuations in the absorber. Electrostatic potential fluctuations in a semiconductor are very important particularly when considering its application in photovoltaics.[4] From the model developed by Shklovskii and Efros [67], the absorption coefficient below the band gap for photon energies close to the band gap, could be related by the following equation

$$\alpha \propto \exp\left(\frac{-2}{5\sqrt{\pi}} \frac{E_g - \hbar\omega}{\gamma/2}\right) \quad \text{..... (1)}$$

Where E_g is the band gap, $\hbar\omega$ is the photon energy and γ is the amplitude of potential fluctuations. Since the IQE curve is determined by the absorption coefficient and the collection efficiency in the solar cell, the absorption coefficient can be obtained from the IQE curve using the following relationship

$$\alpha \propto -\ln(1 - IQE(\hbar\omega)) \quad \text{..... (2)}$$

which is derived from using a small IQE approximation ($IQE < 0.3$). [4, 68] Upon plotting the absorption coefficient versus photon energy and fitting it with equation (2), the amplitude of potential fluctuations (γ) can be obtained and for CMTS it was found to be around 80 meV (**Figure 4.2.14** (B)). This was higher in comparison to CZTSSe (56.4 meV) and CIGSSe (35.5 meV).[4] Therefore the fundamental understanding the nature of defects and the defects that cause potential fluctuations is needed which could result in improving the conversion efficiencies of CMTS in the future.

The conversion efficiencies of CMTS solar cells are very promising and could open up new possibilities in earth abundant thin film photovoltaics. The most promising among the earth abundant thin film solar cell are CZTS and the first report on its efficiency was 0.66 % by Katagiri et al in 1997. [69] Currently the record efficiencies for CZTS solar cells stands at 12.6 % in 2014. CMTS has similar band gaps with CZTS and conversion efficiencies as high as 28 % is theoretically possible based on the Shockley-Queisser limit. By optimizing the buffer layers and the electrical properties of the absorber layer (by tuning carrier density and mobility), efficiencies of the current CMTS solar cells could be further improved and this will be investigated in the future. The maximum V_{oc} which could be obtained from CMTS after taking into account the thermodynamic and entropic loss is ~ 400 mV below the band gap.[70, 71] For the band gap of CMTS (1.6 eV), the maximum J_{sc} that could be obtained is ~ 25 mA/cm² and assuming a loss of 20 % from the CMTS device, a J_{sc} of 20 mA/cm² could be obtained. By taking into account a reasonable FF of 65 %, a practical conversion efficiency of 15.6 % could be obtained.

Chapter 5. Conclusion

Solar cells fabricated using earth abundant materials exhibit the best potential to develop terawatt photovoltaics. In this thesis, C(F,M)TS thin films were synthesized by a simple solution processed spray pyrolysis technique (an aqueous and ambient technique). For CFTS thin films, the sulphurization temperatures were varied from 400-600 °C to investigate the formation of the CFTS phase. It was observed that at 600 °C, the CFTS phase was formed with minimal CTS secondary phase impurity. Also the crystallinity of CFTS thin films synthesized at 600 °C was much higher than those synthesized at lower temperatures. It could be due to that during sulfurization, CTS is formed first followed by the diffusion of Fe inside CTS lattice. As the Fe diffusion is faster at higher temperature, it resulted in higher amount of CFTS phase as the temperature increases. The electrical properties of CFTS4, CFTS5 and CFTS6 were studied using hall measurements to estimate its carrier density and carrier mobility. CFTS4 and CFTS5 (10^{16} cm^{-3}) exhibited higher carrier density than CFTS6 (10^{14} cm^{-3}) due to the presence of CTS phase. All the films exhibited p-type conductivity thus indicating that they can be employed as an absorber in thin film solar cells. The band gaps of CFTS were in the range of 1.45-1.65 eV further indicating the potential for use as an absorber in photovoltaics. Upon investigation of its photoconductivity, it was observed that CFTS exhibited persistent photocurrent behavior due to random local potential fluctuations and deep lying traps in the semiconductor. However CFTS did not exhibit photoconductivity in air. Dye Sensitized Solar Cells (DSSC) were fabricated with CFTS thin film as a photocathode in iodine/iodide electrolyte, exhibits good power conversion efficiency of 8.03 % indicating that CFTS would be a promising cheaper alternative to replace Pt as a counter electrode in DSSCs. Based on the C-V curves and EIS studies the improved performance of the CFTS DSSC is attributed to the superior catalytic activity of the CFTS5 in iodine/iodide electrolyte.

CMTS thin films were also prepared by spray pyrolysis followed by sulphurization. The thin films exhibited p-type conductivity with a carrier density of $\sim 10^{16} \text{ cm}^{-3}$ and carrier mobility $\sim 3 \text{ cm}^2/\text{V.s}$. Band gaps estimated from absorption spectroscopy were $\sim 1.6 \text{ eV}$ indicating that this could be used in thin film solar cells. The photocurrent vs time plots in air revealed that the CMTS thin films exhibited photoconductivity. Transient photocurrent measurements were performed to estimate the photoconductivity decay which was found to be $1.2 \mu\text{s}$. These results indicate that there is more potential for CMTS to be employed as an absorber in thin film solar cells rather than CFTS. Subsequently thin film solar cells were fabricated using CMTS as an absorber. CMTS_{Se} were also synthesized as selenized CMTS films provide the opportunity of tuning the band gap of CMTS. XRD and Raman analysis confirmed the expansion of the lattice of CMTS due to the incorporation of Se. As the ionic radii of Se is larger than S, there is an increase in the unit cell area due to the incorporation of Se. Thin film solar cells were fabricated using CMTS and CMTS_{Se} as an absorber in the CZTS device architecture. CMTS exhibited a higher conversion efficiency of 0.19 % which was higher than that obtained from CMTS_{Se} device (0.07%). The band gap was calculated from EQE measurements for CMTS (1.6 eV) and CMTS_{Se} (1.47 eV). Although J_{sc} was higher in CMTS_{Se} device due to its lower band gap, CMTS exhibited a higher overall conversion efficiency due to its lower shunt conductance and larger V_{oc} . Through analyses of the device characteristics we identify a key problem of very high carrier density in the CMTS absorber that leads to short collection length, low V_{oc} , low quantum efficiency at long wavelength and high shunt conductance that quench the fill factor. The V_{oc} deficit of CMTS was marginally lower than CMTS_{Se} device thus indicating lesser recombination in CMTS. The amplitude of the potential fluctuations in CMTS thin films solar cells was estimated to be $\sim 80 \text{ meV}$ which was higher than that of CZTS or CIGS solar cells. Therefore the fundamental understanding of the nature of defects and the defects that cause potential fluctuations is needed which could result in improving

the conversion efficiencies of CMTS in the future. CMTS solar cells show great potential for development of earth abundant thin film photovoltaics as a practical conversion efficiency of $\sim 16\%$ could be achieved.

Chapter 6. Future Works

6.1 Controlling the optical and electrical properties of C(F,M)TS by doping

In order to develop high efficiency solar harvesting devices with CFTS and CMTS , the carrier lifetime must be increased significantly. For this to happen the recombination in these films must be reduced. Doping with sodium (Na) can increase the carrier lifetime and this has been observed in CZTS solar cells[72]. Recently the role of Sodium doping in CZTS has been studied and it was observed that sodium significantly decreases the non-radiative recombination in CZTS[73]. CZTS thin films with different grain sizes exhibited similar radiative and non-radiative recombination dynamics when sodium was present. Increasing the carrier lifetime and reducing non-radiative recombination in C(F,M)TS thin films would present a significant leap in developing C(F,M)TS as an absorber in thin film solar cells. Antimony doping can help in grain growth and can provide improved solar cell performance as observed in CIGS solar cells. Na could be incorporated by using NaCl during the spraying process for C(F,M)TS. For Antimony doping, Antimony Sulphide will be used as a dopant C(F,M)TS. Upon doping with Sb and Na, the grain size could be improved and recombination could be reduced and this could lead to improved electrical and optical properties, thus providing a route to increase the power conversion efficiencies of C(F,M)TS solar cells.

Figure 6.1.1.1 Increase in grain size with increasing antimony doping observed in CIGS solar cells[74].

6.2 Investigation of the optical and electrical properties by pump probe spectroscopy

Since CMTS thin films are more promising for solar cell applications than CFTS, it would be important to study the recombination in CMTS thin films. This could be understood from pump probe spectroscopy, an optical technique that elucidates the recombination in semiconductors. As seen from **Figure 6.2.1**, the conversion efficiencies of co evaporated CIGS is better than sputtered CIGS. This is reflected from **Figure 6.2.2** , where the relaxation time for co evaporated CIGS is longer than sputtered CIGS and hence a higher conversion efficiency[75]. This could be used to understand CMTS thin films under different sulphurization and selenization conditions , Antimony and Sodium doping. The relaxation dynamics of CMTS thin films with different sulphurization and selenization and antimony doping conditions will be investigated and the thin film with the longest relaxation time will be used as an absorber layer in thin film solar cells. This will help in developing high efficiency solar cells. Also pump probe spectroscopy can help to understand what are the limitations in CFTS thin films which does not exhibit photoconductivity in air.

Figure 6.2.1. J-V curves of (A) sputtered CIGS (B) Co-evaporated CIGS[75]

Figure 6.2.2 Reflectivity transient of (A) sputtered CIGS (B) Co-evaporated CIGS[75]

List of Publications

1. "Facile Water based Spray Pyrolysis of Earth Abundant $\text{Cu}_2\text{FeSnS}_4$ Thin Films as an Efficient Counter Electrode in Dye-Sensitized Solar Cells"
Rajiv Ramanujam Prabhakar, Nguyen Huu Loc, Mulmudi Hemant Kumar, Pablo Boix, Sun Juan, Rohit Abraham John, Sudip K Batabyal and Lydia Helena Wong
ACS Applied Materials and Interfaces 6, 17661 (2014)
2. "Lead-free halide perovskite solar cells with high photocurrents realised through vacancy modulation"
Mulmudi Hemant Kumar, Sabba Dharani, Wei Lin Leong, Pablo P.Boix, **Rajiv Ramanujam Prabhakar**, Tom Baikie, Chen Shi, Hong Ding, Ramesh Ramamoorthy, Mark Asta, Michael Graetzel, Subodh G. Mhaisalkar, Nripan Mathews.
Advanced Materials 26, 7122 (2014)
3. "Evolution of nanoplate morphology, structure and chemistry during synthesis of pyrite by a hot injection method"
HuGe, Liu Hai, **Rajiv Ramanujam Prabhakar**, Lam Yeng Ming and Thirumany Sritharan
RSC Advances 4, 16489 (2014)
4. "Cobalt Dopant with Deep Redox Potential for Organometal Halide Hybrid Solar Cells"
Teck Ming Koh, Sabba Dharani, Dr. Hairong Li, **Rajiv Ramanujam Prabhakar**, Nripan Mathews ,Andrew C. Grimsdale and Subodh G. Mhaisalkar
ChemSusChem 7, 1909 (2014)

5. "Iron Pyrite (FeS₂) Thin Films Based Counter Electrodes for High Efficiency Dye Sensitized Solar Cells"
*Sudhanshu Shukla, Nguyen Huu Loc, Pablo Boix, Koh Teck Ming , **Rajiv Ramanujam Prabhakar**, Mulmudi Hemant Kumar, Jun Zhang, Shi Chen, Nripan Mathews, Thirumany Sritharan and Qihua Xiong*
ACS Nano 8 , 10597 (2014)

6. Incorporation of Cl in sequentially deposited lead halide perovskite films for highly efficient mesoporous solar cells
*Sabba Dharani, Herlina Arianita Dewi, **Rajiv Ramanujam Prabhakar**, Tom Baikie, Chen Shi, Du Yonghua, Nripan Mathews, Pablo P. Boix, Subodh G. Mhaisalkar*
Nanoscale 6, 13854 (2014)

7. Impact of Anionic Br⁻ Substitution on Open Circuit Voltage in Lead Free Perovskite (CsSnI_{3-x}Br_x) Solar Cells
*Dharani Sabba, Hemant Kumar Mulmudi, **Rajiv Ramanujam Prabhakar**, Thirumal Krishnamoorthy, Tom Baikie, Pablo .P Boix, Subodh.G Mhaisalkar, Nripan Mathews*
Journal of Physical Chemistry C Volume **119** Page **1763**

8. Synthesis of Cu(In,Ga)(S,Se)₂ thin films using an aqueous spray-pyrolysis approach, and their solar cell efficiency of 10.5%
*Mohammed Anower Hossain, Zhang Tianliang, Lee Kian Keat, Li Xianglin, **Rajiv Ramanujam Prabhakar**, Sudip K. Batabyal, Subodh G Mhaisalkar, Lydia Helena Wong*
Journal of Materials Chemistry A DOI: 10.1039/c4ta05783j

Papers Submitted

1. Photovoltaic Effect in Earth Abundant Solution Processed $\text{Cu}_2\text{MnSnS}_4$ and $\text{Cu}_2\text{MnSn}(\text{S,Se})_4$ Thin Films
Rajiv Ramanujam Prabhakar , Su Zhenghua, Zeng Xin , Tom Baikie, Sudhanshu Shukla , Sudip Batabyal , Oki Gunawan and Lydia Helena Wong
Advanced Energy Materials
2. Crystalline tin disulfide as promising anode for lithium-ion battery applications: A performance evaluation with lithium manganese oxide cathode
Apoorva Chaturvedi , Vanchiappan Aravindan , Peng Hu, **Rajiv Ramanujam Prabhakar**, Lydia Helena Wong , Christian Kloc and Madhavi Srinivasan
Chemistry- A European Journal

Patents Filled

1. **Title:** Semiconducting Photovoltaic Materials
Inventors: 1) RajivRamanujam PRABHAKAR; 2) ZENG Xin; 3) Sudip Kumar BATABYAL; 4) WONG Lydia Helena
Singapore Provisional Patent (Filling date 15/01/2015)

References

1. Polizzotti, A., et al., *The state and future prospects of kesterite photovoltaics*. Energy & Environmental Science, 2013. 6(11): p. 3171-3182.
2. Unold, T. and H.W. Schock, *Nonconventional (Non-Silicon-Based) Photovoltaic Materials*. Annual Review of Materials Research, 2011. 41(1): p. 297-321.
3. Lewis, N.S. and D.G. Nocera, *Powering the planet: Chemical challenges in solar energy utilization*. Proceedings of the National Academy of Sciences, 2006. 103(43): p. 15729-15735.
4. Gokmen, T., et al., *Band tailing and efficiency limitation in kesterite solar cells*. Applied Physics Letters, 2013. 103(10): p. -.
5. Xiang, C., et al., *820 mV open-circuit voltages from Cu₂O/CH₃CN junctions*. Energy & Environmental Science, 2011. 4(4): p. 1311-1318.
6. Jeong, S., et al., *An analysis of temperature dependent current–voltage characteristics of Cu₂O–ZnO heterojunction solar cells*. Thin Solid Films, 2011. 519(19): p. 6613-6619.
7. Lee, S.W., et al., *Improved Cu₂O-Based Solar Cells Using Atomic Layer Deposition to Control the Cu Oxidation State at the p-n Junction*. Advanced Energy Materials, 2014: p. n/a-n/a.
8. Devika, M., N.K. Reddy, and K.R. Gunasekhar, *Structural, electrical, and optical properties of as-grown and heat treated ultra-thin SnS films*. Thin Solid Films, 2011. 520(1): p. 628-632.
9. Sinsermsuksakul, P., et al., *Overcoming Efficiency Limitations of SnS-Based Solar Cells*. Advanced Energy Materials, 2014: p. n/a-n/a.
10. Sinsermsuksakul, P., et al., *Enhancing the efficiency of SnS solar cells via band-offset engineering with a zinc oxysulfide buffer layer*. Applied Physics Letters, 2013. 102(5): p. -.
11. Wadia, C., A.P. Alivisatos, and D.M. Kammen, *Materials Availability Expands the Opportunity for Large-Scale Photovoltaics Deployment*. Environmental Science & Technology, 2009. 43(6): p. 2072-2077.
12. Ennaoui, A., et al., *Iron disulfide for solar energy conversion*. Solar Energy Materials and Solar Cells, 1993. 29(4): p. 289-370.
13. Steinhagen, C., et al., *Pyrite Nanocrystal Solar Cells: Promising, or Fool's Gold? The Journal of Physical Chemistry Letters*, 2012. 3(17): p. 2352-2356.

14. Büker, K., N. Alonso-Vante, and H. Tributsch, *Photovoltaic output limitation of n-FeS₂ (pyrite) Schottky barriers: A temperature-dependent characterization*. Journal of Applied Physics, 1992. 72(12): p. 5721-5728.
15. Katagiri, H., *Cu₂ZnSnS₄ thin film solar cells*. Thin Solid Films, 2005. 480–481(0): p. 426-432.
16. Morales-Acevedo, A., ed. *Solar Cells - Research and Application Perspectives*. 2013, InTech.
17. Wang, W., et al., *Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency*. Advanced Energy Materials, 2013: p. n/a-n/a.
18. Katagiri, H., et al., *Enhanced Conversion Efficiencies of Cu₂ZnSnS₄-Based Thin Film Solar Cells by Using Preferential Etching Technique*. Applied Physics Express, 2008. 1: p. 041201.
19. Ahmed, S., et al., *A High Efficiency Electrodeposited Cu₂ZnSnS₄ Solar Cell*. Advanced Energy Materials, 2012. 2(2): p. 253-259.
20. Guo, Q., et al., *Fabrication of 7.2% Efficient CZTSSe Solar Cells Using CZTS Nanocrystals*. Journal of the American Chemical Society, 2010. 132(49): p. 17384-17386.
21. Rajeshmon, V.G., et al., *Role of precursor solution in controlling the opto-electronic properties of spray pyrolysed Cu₂ZnSnS₄ thin films*. Solar Energy, 2011. 85(2): p. 249-255.
22. Jiang, M., et al., *Cu₂ZnSnS₄ polycrystalline thin films with large densely packed grains prepared by sol-gel method*. Journal of Photonics for Energy, 2011. 1(1): p. 019501-019501-6.
23. Romero, M.J., et al., *Comparative study of the luminescence and intrinsic point defects in the kesterite Cu₂ZnSnS₄ and chalcopyrite Cu(In,Ga)Se₂ thin films used in photovoltaic applications*. Physical Review B, 2011. 84(16): p. 165324.
24. Bernardini, G.P., et al., *EPR and SQUID magnetometry study of Cu₂FeSnS₄ (stannite) and Cu₂ZnSnS₄ (kesterite)*. Physics and Chemistry of Minerals, 2000. 27(7): p. 453-461.
25. Eibschütz, M., E. Hermon, and S. Shtrikman, *Determination of cation valencies in Cu₂₅₇Fe₁₁₉SnS₄ by Mössbauer effect and magnetic susceptibility measurements*. Journal of Physics and Chemistry of Solids, 1967. 28(9): p. 1633-1636.
26. Yan, C., et al., *Synthesis and characterizations of quaternary Cu₂FeSnS₄ nanocrystals*. Chemical Communications, 2012. 48(20): p. 2603-2605.

27. Zhang, X., et al., *Crystal phase-controlled synthesis of Cu₂FeSnS₄ nanocrystals with a band gap of around 1.5 eV*. Chemical Communications, 2012. 48(41): p. 4956-4958.
28. Wu, M. and T. Ma, *Platinum-Free Catalysts as Counter Electrodes in Dye-Sensitized Solar Cells*. ChemSusChem, 2012. 5(8): p. 1343-1357.
29. Zhou, J., et al., *Solar cell material Cu₂FeSnS₄ nanoparticles synthesized via a facile liquid reflux method*. Materials Letters, 2015. 140(0): p. 119-122.
30. Park, J.-Y., et al., *Quaternary semiconductor Cu₂FeSnS₄ nanoparticles as an alternative to Pt catalysts*. RSC Advances, 2013. 3(47): p. 24918-24921.
31. Wu, M., et al., *Economical Pt-Free Catalysts for Counter Electrodes of Dye-Sensitized Solar Cells*. Journal of the American Chemical Society, 2012. 134(7): p. 3419-3428.
32. Fries, T., et al., *Magnetic ordering of the antiferromagnet Cu₂MnSnS₄ from magnetization and neutron-scattering measurements*. Physical Review B, 1997. 56(9): p. 5424-5431.
33. Fukushima, T., K. Yamauchi, and S. Picozzi, *Magnetically induced ferroelectricity in Cu₂MnSnS₄ and Cu₂MnSnSe₄*. Physical Review B, 2010. 82(1): p. 014102.
34. Cui, Y., et al., *A general strategy for synthesis of quaternary semiconductor Cu₂MSnS₄ (M = Co²⁺, Fe²⁺, Ni²⁺, Mn²⁺) nanocrystals*. Journal of Materials Chemistry, 2012. 22(43): p. 23136-23140.
35. Liang, X., et al., *Dilute magnetic semiconductor Cu₂MnSnS₄ nanocrystals with a novel zincblende and wurtzite structure*. RSC Advances, 2012. 2(12): p. 5044-5046.
36. Junhee, H., et al., *Crystallization behaviour of co-sputtered Cu₂ZnSnS₄ precursor prepared by sequential sulfurization processes*. Nanotechnology, 2013. 24(9): p. 095706.
37. Cheng, A.-J., et al., *Imaging and phase identification of Cu₂ZnSnS₄ thin films using confocal Raman spectroscopy*. Journal of Vacuum Science & Technology A, 2011. 29(5): p. -.
38. Rincón, C., et al., *X-ray diffraction, Raman spectrum and magnetic susceptibility of the magnetic semiconductor Cu₂FeSnS₄*. Solid State Communications, 2011. 151(13): p. 947-951.
39. Berg, D.M., et al., *Raman analysis of monoclinic Cu₂SnS₃ thin films*. Applied Physics Letters, 2012. 100(19): p. -.

40. Himmrich, M. and H. Haeuseler, *Far infrared studies on stannite and wurtzstannite type compounds*. Spectrochimica Acta Part A: Molecular Spectroscopy, 1991. 47(7): p. 933-942.
41. Wu, C., et al., *Hexagonal Cu₂SnS₃ with metallic character: Another category of conducting sulfides*. Applied Physics Letters, 2007. 91(14): p. -.
42. Mitzi, D.B., et al., *The path towards a high-performance solution-processed kesterite solar cell*. Solar Energy Materials and Solar Cells, 2011. 95(6): p. 1421-1436.
43. Jie, J.S., et al., *Photoconductive Characteristics of Single-Crystal CdS Nanoribbons*. Nano Letters, 2006. 6(9): p. 1887-1892.
44. Soci, C., et al., *Nanowire Photodetectors*. Journal of Nanoscience and Nanotechnology, 2010. 10(3): p. 1430-1449.
45. Paul, G.S. and P. Agarwal, *Persistent photocurrent and decay studies in CdS nanorods thin films*. Journal of Applied Physics, 2009. 106(10): p. -.
46. González, J.C., et al., *Hopping conduction and persistent photoconductivity in Cu₂ZnSnS₄ thin films*. Journal of Physics D: Applied Physics, 2013. 46(15): p. 155107.
47. Woo, K., Y. Kim, and J. Moon, *A non-toxic, solution-processed, earth abundant absorbing layer for thin-film solar cells*. Energy & Environmental Science, 2012. 5(1): p. 5340-5345.
48. Wang, Q., et al., *Characteristics of High Efficiency Dye-Sensitized Solar Cells†*. The Journal of Physical Chemistry B, 2006. 110(50): p. 25210-25221.
49. Mulmudi, H.K., et al., *Solution processed transition metal sulfides: application as counter electrodes in dye sensitized solar cells (DSCs)*. Physical Chemistry Chemical Physics, 2011. 13(43): p. 19307-19309.
50. Huang, Z., et al., *Application of carbon materials as counter electrodes of dye-sensitized solar cells*. Electrochemistry Communications, 2007. 9(4): p. 596-598.
51. Wu, M., et al., *A novel catalyst of WO₂ nanorod for the counter electrode of dye-sensitized solar cells*. Chemical Communications, 2011. 47(15): p. 4535-4537.
52. Yi, L., et al., *One dimensional CuInS₂-ZnS heterostructured nanomaterials as low-cost and high-performance counter electrodes of dye-sensitized solar cells*. Energy & Environmental Science, 2013. 6(3): p. 835-840.

53. Jiang, Q.W., et al., *Surface-Nitrided Nickel with Bifunctional Structure As Low-Cost Counter Electrode for Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry C, 2010. 114(31): p. 13397-13401.
54. Fabregat-Santiago, F., et al., *Characterization of nanostructured hybrid and organic solar cells by impedance spectroscopy*. Physical chemistry chemical physics : PCCP, 2011. 13(20): p. 9083-118.
55. Li, G.-r., et al., *Carbon Nanotubes with Titanium Nitride as a Low-Cost Counter-Electrode Material for Dye-Sensitized Solar Cells*. Angewandte Chemie International Edition, 2010. 49(21): p. 3653-3656.
56. Delbos, S., *Ksterite thin films for photovoltaics : a review*. EPJ Photovolt., 2012. 3.
57. Lpez-Vergara, F., et al., *Cu₂Mn_{1-x}CoxSnS₄: Novel ksterite type solid solutions*. Journal of Solid State Chemistry, 2013. 198(0): p. 386-391.
58. Shannon, R., *Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides*. Acta Crystallographica Section A, 1976. 32(5): p. 751-767.
59. Williamson, G.K. and W.H. Hall, *X-ray line broadening from fcc aluminium and wolfram*. Acta Metallurgica, 1953. 1(1): p. 22-31.
60. He, J., et al., *Composition dependence of structure and optical properties of Cu₂ZnSn(S,Se)₄ solid solutions: An experimental study*. Journal of Alloys and Compounds, 2012. 511(1): p. 129-132.
61. Woo, K., et al., *Band-gap-graded Cu₂ZnSn(S_{1-x}Se_x)₄ Solar Cells Fabricated by an Ethanol-based, Particulate Precursor Ink Route*. Sci. Rep., 2013. 3.
62. Zhang, C., et al., *A simple and efficient solar cell parameter extraction method from a single current-voltage curve*. Journal of Applied Physics, 2011. 110(6): p. -.
63. Hegedus, S., D. Desai, and C. Thompson, *Voltage dependent photocurrent collection in CdTe/CdS solar cells*. Progress in Photovoltaics: Research and Applications, 2007. 15(7): p. 587-602.
64. King, R.R., et al., *Band gap-voltage offset and energy production in next-generation multijunction solar cells*. Progress in Photovoltaics: Research and Applications, 2011. 19(7): p. 797-812.

65. De Wolf, S., et al., *Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance*. The Journal of Physical Chemistry Letters, 2014. 5(6): p. 1035-1039.
66. Gershon, T., et al., *The Role of Sodium as a Surfactant and Suppressor of Non-Radiative Recombination at Internal Surfaces in Cu₂ZnSnS₄*. Advanced Energy Materials, 2014: p. n/a-n/a.
67. Efros, B.I.S.a.A.L., *Electronic Properties of Doped Semiconductors* 1979, Berlin: Springer Verlag
68. Liu, X.X. and J.R. Sites, *Solar-cell collection efficiency and its variation with voltage*. Journal of Applied Physics, 1994. 75(1): p. 577-581.
69. Katagiri, H., et al., *Preparation and evaluation of Cu₂ZnSnS₄ thin films by sulfurization of E • B evaporated precursors*. Solar Energy Materials and Solar Cells, 1997. 49(1-4): p. 407-414.
70. Green, M.A., et al., *Solar cell efficiency tables (version 39)*. Progress in Photovoltaics: Research and Applications, 2012. 20(1): p. 12-20.
71. Polman, A. and H.A. Atwater, *Photonic design principles for ultrahigh-efficiency photovoltaics*. Nat Mater, 2012. 11(3): p. 174-177.
72. Zhou, H., et al., *Rational Defect Passivation of Cu₂ZnSn(S,Se)₄ Photovoltaics with Solution-Processed Cu₂ZnSnS₄:Na Nanocrystals*. Journal of the American Chemical Society, 2013. 135(43): p. 15998-16001.
73. Gershon, T., et al., *The Role of Sodium as a Surfactant and Suppressor of Non-Radiative Recombination at Internal Surfaces in Cu₂ZnSnS₄*. Advanced Energy Materials, 2015. 5(2): p. n/a-n/a.
74. Yuan, M., et al., *Optimization of CIGS-Based PV Device through Antimony Doping*. Chemistry of Materials, 2009. 22(2): p. 285-287.
75. Chen, S.-C., et al., *Ultrafast carrier dynamics in Cu(In,Ga)Se₂ thin films probed by femtosecond pump-probe spectroscopy*. Optics Express, 2012. 20(12): p. 12675-12681.

Appendix A

Raw Hall data for CFTS and CMTS thin films

Raw Hall data for CFTS4, CFTS5 and CFTS6 thin films.

CFTS4

Data Point #	4			
Variable Field (G)	6004.3			
Process: Four Probes Resistivity Measurement				
Probes Source Meter	12 43	23 14	34 21	41 32
Current 1 (A)	1.93E-07	1.93E-07	1.93E-07	1.93E-07
Voltage 1 (V)	0.13608	0.17726	0.13381	0.17572
Current 2 (A)	-1.93E-07	-1.93E-07	-1.93E-07	-1.93E-07
Voltage 2 (V)	-0.13721	-0.17944	-0.1426	-0.17574
Resistance (Ohm)	707748.4	923638.6	715939.7	910140.9
Ratio	0.7662611	0.77513	0.786625	0.777625
Form Factor	0.9960439	0.996504	0.997048	0.996627
Resistivity (Ohm*cm)	184.1195	185.1295	183.7057	182.7031
Process: Four Probes Hall Measurement				
Probes Source Meter	13 24	24 31	13 24	24 31
Current 1 (A)	1.93E-07	1.93E-07	1.93E-07	1.93E-07
Voltage 1 (V)	0.04726	-0.04126	0.045688	-0.04157
Current 2 (A)	-1.93E-07	-1.93E-07	-1.93E-07	-1.93E-07

Voltage 2 (V)	-0.038349	0.034584	-0.04024	0.035606
Resistance (Ohm)	221721.8	-196418	222476.8	-199860
Field (G)	5990.2		-6018.3	
Temperature (K)	302.94			
Resistivity (Ohm*cm)	183.9144			
Mobility (cm ² /Vs)	3.041394			
Density (cm ⁻³)	1.12E+16			
Hall Coeff. (cm ³ /Coul)	559.3564			
Sheet Number (cm ⁻²)	5.58E+11			
Sheet Res. (Ohm/cm ²)	3678289			
Type of Carriers	holes			

CFTS5

Data Point #	4			
Variable Field (G)	6007.7			
Process: Four Probes Resistivity Measurement				
Probes Source Meter	12 43	23 14	34 21	41 32
Current 1 (A)	1.21E-08	1.21E-08	1.21E-08	1.21E-08
Voltage 1 (V)	0.19895	0.14471	0.19956	0.1545
Current 2 (A)	-1.21E-08	-1.21E-08	-1.21E-08	-1.21E-08
Voltage 2 (V)	-0.20154	-0.15509	-0.2032	-0.15309

Resistance (Ohm)	1.65E+07	1.24E+07	1.66E+07	1.27E+07
Ratio	0.748552	0.744333	0.763737	0.768066
Form Factor	0.995016	0.994749	0.995906	0.99614
Resistivity (Ohm*cm)	3261.279	3270.973	3311.206	3301.401
Process: Four Probes Hall Measurement				
Probes Source Meter	13 24	24 31	13 24	24 31
Current 1 (A)	1.21E-08	1.21E-08	1.21E-08	1.21E-08
Voltage 1 (V)	-0.05121	0.05717	-0.0513	0.056571
Current 2 (A)	-1.21E-08	-1.21E-08	-1.21E-08	-1.21E-08
Voltage 2 (V)	0.045021	-0.04488	0.045211	-0.0448
Resistance (Ohm)	-3975255	4215159	-3986905	4187286
Field (G)	5994.7		-6020.6	
Temperature (K)	302.98			
Resistivity (Ohm*cm)	3286.215			
Mobility (cm ² /Vs)	2.502415			
Density (cm ⁻³)	7.59E+14			

Hall Coeff. (cm ³ /Coul)	8223.473			
Sheet Number (cm ⁻²)	3.80E+10			
Sheet Res. (Ohm/cm ²)	6.57E+07			
Type of Carriers	holes			

CFTS6

Data Point #	3			
Variable Field (G)	4994.3			
Process: Four Probes Resistivity Measurement				
Probes Source Meter	12 43	23 14	34 21	41 32
Current 1 (A)	1.56E-08	1.56E-08	1.56E-08	1.56E-08
Voltage 1 (V)	0.40317	0.36521	0.33737	0.056865
Current 2 (A)	-1.56E-08	-1.56E-08	-1.56E-08	-1.56E-08
Voltage 2 (V)	-0.03701	-0.46298	-0.08337	-0.73772
Resistance (Ohm)	1.41E+07	2.65E+07	1.35E+07	2.55E+07
Ratio	0.531479	0.508012	0.529497	0.553957
Form Factor	0.968049	0.963159	0.967654	0.972301
Resistivity (Ohm*cm)	2675.381	2621.078	2562.456	2615.936
Process: Four Probes Hall Measurement				
Probes Source Meter	13 24	24 31	13 24	24 31
Current 1 (A)	1.56E-08	1.56E-08	1.56E-08	1.56E-08

Voltage 1 (V)	0.32459	-0.29045	0.30517	-0.29075
Current 2 (A)	-1.56E-08	-1.56E-08	-1.56E-08	-1.56E-08
Voltage 2 (V)	-0.09335	0.0769	-0.10571	0.075771
Resistance (Ohm)	1.34E+07	-1.18E+07	1.32E+07	-1.17E+07
Field (G)	5012.3		-4976.3	
Temperature (K)	301.98			
Resistivity (Ohm*cm)	2618.713			
Mobility (cm ² /Vs)	11.44775			
Density (cm ⁻³)	2.08E+14			
Hall Coeff. (cm ³ /Coul)	29978.38			
Sheet Number (cm ⁻²)	6.25E+09			
Sheet Res. (Ohm/cm ²)	8.73E+07			
Type of Carriers	holes			

CMTS – Raw Hall data

Data Point #	3			
Variable Field (G)	5024.6			
Process: Four Probes Resistivity Measurement				
Probes Source Meter	12 43	23 14	34 21	41 32
Current 1 (A)	2.83E-07	2.83E-07	2.83E-07	2.83E-07
Voltage 1 (V)	0.25772	0.27549	0.26763	0.27496

Current 2 (A)	-2.82E-07	-2.82E-07	-2.82E-07	-2.82E-07
Voltage 2 (V)	-0.26187	-0.2531	-0.26203	-0.25405
Resistance (Ohm)	920948.6	936900.6	938930.3	937844.6
Ratio	0.9829737	0.9978383	0.9988437	0.9819842
Form Factor	0.9999998	1	1	0.9999997
Resistivity (Ohm*cm)	126.3066	127.5291	127.5933	126.3708
Process: Four Probes Hall Measurement				
Probes Source Meter	13 24	24 31	13 24	24 31
Current 1 (A)	2.83E-07	2.83E-07	2.83E-07	2.83E-07
Voltage 1 (V)	0.012194	0.0099994	0.011574	0.0095512
Current 2 (A)	-2.82E-07	-2.82E-07	-2.82E-07	-2.82E-07
Voltage 2 (V)	- 0.0051845	0.0032386	- 0.0046249	0.003009
Resistance (Ohm)	30806.93	11986.6	28713.82	11596.56
Field (G)	5030.3		-5018.9	
Temperature (K)	300.92			
Resistivity (Ohm*cm)	126.95			
Mobility (cm ² /Vs)	2.91965			
Density (cm ⁻³)	1.68E+16			

Hall Coeff. (cm ³ /Coul)	370.6494			
Sheet Number (cm ⁻²)	5.05E+11			
Sheet Res. (Ohm/cm ²)	4231665			
Type of Carriers	holes			