Cu$_2$ZnSnS$_4$ Nanoparticulate Thin Films and Their Solar Cell Characteristics

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by
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The programme was administrated by The IITB-Monash Research Academy (Year 2016)
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Abstract

Thin film technology for solar cells has emerged as the most promising alternative since it can beat the absorption limit of crystalline silicon solar cells and has also an ideal band gap as compared to silicon. However, current thin films are based on rare and toxic elements such as cadmium and indium. Therefore, during the past 5-7 years, there has been a sudden increase in the interest to develop Cu$_2$ZnSnS$_4$ (CZTS) thin films (based on all non-toxic abundant elements) to facilitate the increasing demand for the electricity and its production. CZTS demonstrate a high optical absorption coefficient ($10^4$ cm$^{-1}$), a suitable band gap (1.4-1.6 eV) and a high electrical conductivity, making it an ideal material for solar energy conversion applications.

The aim of this study is to fabricate and characterize CZTS thin films and evaluate their solar cell performance. In this work, CZTS thin films were grown using two different processes such as electrodeposition and chemical synthesis approach. The first objective is to fabricate high quality quaternary CZTS thin films by single step electro deposition method followed by sulfurization at 550°C. For this, we systematically studied the role of deposition potential over compositional, structural and optical properties of the CZTS films. We discuss the nucleation and growth mechanism of the CZTS thin film and propose an optimum deposition potential of -1.4 V vs. Ag/AgCl to achieve an ideal composition, uniform growth (void free) with tunable optical properties. Using the chrono-amperometric data and the Scharifker and Hill model we found that the nucleation mechanism for CZTS thin film is instantaneous. Optical properties demonstrated the optimum band gap of 1.5 eV for kesterite CZTS films prepared from a precursor electrodeposited at -1.4 V vs. Ag/AgCl. CZTS thin films deposited at optimum potential and assembled into the solar cell structure demonstrated an efficiency of 5.0%. The work also includes the synthesis of size controlled kesterite phase CZTS nanoparticles. The nanoparticle size has been controlled from 2-8 (± 0.5) nm by a simple control of amine-to-precursor molar ratio. We demonstrate the synthesis of as much as 20 gm of quaternary chalcogenide nanoparticles powder in a single reaction, without a size-sorting process. The fabricated devices exhibit efficiencies ranging from 3.6% to 4.5% depending on the CZTS particles average diameter. Comparison of EQE data suggests that
our current is mainly restricted by the collection losses. Further, we have incorporated the extrinsic impurities such as Fe and Mn (to replace Zn) or Se (to replace S) into CZTS in order to control secondary phase formation, micro structural and band gap variation of CZTS. It is demonstrated that the crystal structure, band gap, and photo response of CZTS thin films are affected by substitution of anion/cations. The absorption characteristics show the earth abundant compound Cu₂MnSnS₄/Se₄ (M=Zn, Mn and Fe) band gaps are in the range of 1.0 to 1.5 eV with high optical absorption coefficients (~10⁴ cm⁻¹) in the visible region. The efficiency of CZTS solar cell is enhanced significantly from 4.5% to 7.6% with selenium doping. The variation of device performance may be ascribed to the changes in the microstructure and band gap. A further improvement in the power conversion efficiency was achieved by embedding the silica nanoparticles (150 nm) into the CZTS absorber layer; we studied the effect of silica particles depth in the CZTS absorber layer on optical absorption and solar cell performance theoretically and experimentally as well. We fabricated the CZTS solar cells with 150 nm sized silica nanoparticles at the top, middle and bottom of the absorber layer for light-trapping. The best optical absorption and electrical efficiency (η=5.3%) is observed for particles placed at the middle-level of the absorber layer; this is 18% more than that of the reference cell (η=4.5%). Particles placed on the top lead to higher optical absorption but lower conversion efficiency compared to particles at the bottom.

**Keywords:** Cu₂ZnSnS₄ (CZTS) thin films; Single-step electrodeposition; Nanoparticles; Kesterites; Stannites; Sulfurization; Thin film solar cell; J-V and EQE measurements.
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AM1.5G</td>
<td>Air Mass 1.5 Global</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
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<td>AZO</td>
<td>Aluminium doped zinc oxide</td>
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<tr>
<td>C</td>
<td>Carbon</td>
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<td>Conduction band</td>
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<td>CdS</td>
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<tr>
<td>CIGS</td>
<td>Copper indium gallium sulfide</td>
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<td>CTS</td>
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Chapter 1

Introduction and Literature Review

1.1 Introduction

The growing consumption of electricity across the world has resulted in a demand-and-supply gap. This gap cannot be supported by conventional resources. Therefore, it is necessary to develop renewable-energy–based technologies. To meet the increasing demands, the alternative technologies for energy conversion (solar cells and fuel cells) and storage (super capacitors) are being researched intensively. The most promising and potential alternative renewable energy source is the solar energy. However, the electricity from present solar cell technologies is more expensive than the conventional sources and has not yet reached the grid level. Currently, efficient and low-cost solar cell fabrication is among the most critical issues in the photovoltaic industry [1]. The present photovoltaic industry is based on silicon technology. However, silicon is an indirect band gap semiconductor and a thick
silicon absorber layer is required to absorb a larger amount of incident light, which makes the photovoltaic devices economically costlier [2, 3]. In order to make solar energy a major source for electricity, technology needs to be cost-effective when compared to other sources of electricity. Non-silicon based thin film technologies has emerged as the most promising alternative for solar cells since it has an ideal band gap and can beat the absorption limit of crystalline silicon solar cells. Various thin films such as CIGS (Cu(InGa)Se$_2$), cadmium telluride (CdTe), copper tin sulfide (Cu$_2$SnS$_3$) and cadmium sulfide (CdS), show reasonably good efficiencies, and are part of commercial solar cell devices [4–8]. CIGS solar cells have reached an efficiency of 21% [8], which is close to the bulk-crystalline Si solar cells (25.6%) [9]. However, these thin films are based on rare and toxic elements such as cadmium and indium. Therefore, further research is essential to develop new earth-abundant, environment-friendly, and low-cost materials for solar cells.

During the past five to seven years, there has been a sudden increase in the interest to develop Cu$_2$ZnSnS$_4$ (CZTS: Copper zinc tin sulfide) thin films (based on all abundant and non-toxic elements) in order to facilitate the increasing demand for the electricity and its production. CZTS has a suitable band gap (1.4-1.6 eV), and demonstrates a high optical absorption coefficient ($10^4$ cm$^{-1}$) which makes it an ideal material for solar energy conversion applications [10-13]. CZTS thin films are expected to have theoretical efficiencies of 30%; lab efficiencies have already reached as high as 9.1% [14]. Various hurdles, from the perspective of the material and the device, have to be overcome in order to make the CZTS technology competitive in commercial solar cell modules. CZTS is still not understood well enough in the aspects of defects, material properties, and doping. The main challenge in CZTS fabrication is to obtain a single phase, because this single phase exists in a very narrow region of the phase diagram [15]. During CZTS fabrication, it is very important to avoid secondary phases such as Cu$_2$SnS$_3$, Cu$_2$S, SnS$_2$ and ZnS, which is plausible with a control of temperature and the stoichiometry of the precursors. These secondary phases actually act as recombination centers and charge collection barriers, thereby, suppressing the performance of the device [15]. The aim of this study is to fabricate and characterize single phase CZTS thin films and evaluate their solar cell performance. Non-vacuum and solution based techniques
have been adopted to achieve CZTS precursor films. Furthermore, we focused on the fabrication of large-area devices using the nanoparticle ink approach.

1.2 Thin Film Photovoltaics

The market for thin-film photovoltaics (PV) has been growing rapidly since the past 10 years. The most pressing issues in the photovoltaic industry are efficiency and their higher fabrication cost. These issues are also the main obstacles to popularizing them for general household use. The issue of cost could be solved by replacing silicon wafers with thin films of compound semiconductors.

The main advantage of thin-film solar cells is that they require only a small amount of absorber materials (micron level to lesser thicknesses) and, hence, offer a very competitive cost. Also, in thin-film solar cells, the absorber material is a direct band gap semiconductor and can be directly deposited onto the low-cost substrates by physical and chemical methods. Moreover, it is also possible to tune the band gap by changing the material composition such that it absorbs a larger portion of the solar spectrum [16]. Another advantage of thin-film solar cells is that they enable monolithic integration. This means that the cells in a module can be directly connected in a series during the fabrication of the cells; the series connection does not need any individual processing steps, which saves the money and time. Since thin-film solar cell technology can compete with crystalline silicon solar cells, the proportion of thin-film module production is growing as a portion of the complete solar cell technology spectrum.

1.2.1 Device Structure

Conventional thin-film solar cell technology relies on a single p–n junction with a high absorption coefficient semiconducting absorber material [14]. This absorber layer is squeezed between the two contact layers. Other layers are also required along with the absorber layer in order to passivate the boundaries between the layers; otherwise, the interfaces of these layers will act as recombination centers. A single p-n junction thin-film solar cell broadly comprises a p-type absorber layer and an n-type layer, which creates the p-n junction.
Two types of designs, known as the “substrate” and the “superstrate,” are feasible in thin-film solar cell technologies. The advantage of substrate configuration is that any type of substrate that is flexible, transparent, or opaque can be used since light passes through the cell before hitting the substrate. However, in the case of a superstrate configuration, the substrate should be transparent because light hits the substrate before being absorbed by the cell. The configuration of the substrate yields the highest efficiency due to favorable processing conditions. Figure 1.1 shows the schematic diagram of the structure of CZTS thin-film solar cells. Most of the thin film solar cells have similar device structure, whereas the difference in the absorber material.

![Figure 1.1 Schematic cartoon design of a typical CZTS solar cell structure. Diagram shows various layers of a CZTS thin film solar cell. Mo and Ni/Al are metal contact pads.](image)

A solar cell consists of several different layers, which can be deposited by different methods. On the substrate, back contact with good electrical conductivity, suitable work function, and stability against corrosion and oxidation is required. Recently, alternative metal back contacts have been explored and molybdenum has proven to be suitable for industrial production purposes. A half-micrometer–thick Mo layer is deposited on glass substrate by the metal sputtering system. On top of the back contact, the p-type CZTS absorber layer, with thicknesses that range from 1–2 μm, is deposited. CZTS layers can be grown by various deposition methods [10–15]. The grain size and morphology of CZTS depends on the deposition process, which ultimately influences the efficiency of the device. The absorber
layer is often followed by a thin buffer layer. It can have several functions, for example, the improvement of lattice-matching between the absorber and the n-type layer on the top pushes the p-n junction into the p-type CZTS [17, 18]. Moving the p-n junction into the absorber layer and away from the physical material interface reduces the interface recombination [17, 18]. However, cadmium sulfide (CdS) is the most commonly used buffer layer for CZTS and CIGS solar cells. CdS is generally deposited using chemical bath deposition (CBD) [19]. The buffer layer is then covered by a thick n-type layer (i-ZnO) that is nearly 100 nm. This is done to construct the p-n-junction, while they are not allowed to absorb too much of the incoming light. This layer is mainly a transparent conducting oxide (TCO), also known as the “window layer”. In case of CZTS, this is done with heavily Al-doped ZnO (ZnO:Al/AZO), with a band gap of ~3.3 eV [20]; the heavy doping provides the required conductivity. AZO of a thickness of around 300–500 nm is deposited by the sputtering process.

1.2.2 Solar Cell Basics

Figure 1.2 shows the energy-level diagram of a p-n junction solar cell at equilibrium. When an electron of the absorber layer absorbs photons with an energy that is equal to the band gap energy, the electrons move to the conduction band and leave holes in the valence band. If their recombination is prohibited, they reach the junction at which they are separated by an electric field. Photons with an energy that is less than the band gap energy cannot be absorbed and are considered to be a loss because they are unable to create electron and hole pairs [21]. Photons with higher energy are also absorbed. However, a portion of the energy of these photons is lost as heat [21].

The characteristics of a solar cell p-n junction are similar to a p-n junction diode; the electrical circuit shown in Figure 1.3 is frequently used as a simplified model of the solar cell structural design [15]. Equivalent circuit models describe the entire I-V curve of a solar cell. A basic equivalent circuit model in common use is the single diode model, which is derived for a single solar cell from physical principles; the single diode model is represented by the circuit shown in Figure 1.3. At non-equilibrium conditions (under illumination) the incoming light creates electron and hole pairs [15, 21]. The electrons in the p-type and the holes in the n-type material drifts to other side and are available as external current.
The equation for the illuminated diode is [15]:

\[ j(V_{ex}) = -(j_R(C) + j_R(V)) \left( e^{V_{ex}/k_BT} - 1 \right) - j_R(solar) \quad (1.1) \]

where \( j(V_{ex}) \) is the current in the diode for the voltage \( V_{ex} \); \( j_R(C) \) is the reverse current from the conduction band; \( j_R(V) \) is the reverse current from the valence band; \( j_R(solar) \) is the current density under illumination without voltage; \( V_{ex} \) is the applied voltage; \( k_B \) is the Boltzmann constant; and \( T \) is the temperature.

Figure 1.2 Schematic view of a solar cell p-n junction energy band diagram to indicate the charge separation and flow in a solar cell. This cartoon view also shows the energy loss in a p-n junction solar cell due to unabsorbed light, and excess energy loss as heat.

Equation (1.1) is not applicable to real solar cells, because a real solar cell has series and shunt resistances. The sources of series resistance (\( R_S \)) are the resistances of the bulk of the material, the interface between different layers of the cell, the semiconductor-metal contact, and the metal-metal contact. The shunt resistance (\( R_{SH} \)) occurs because of the short circuit in the p-n junction due to the presence of defects [15]. For ideal cells, \( R_S \) should be zero and \( R_{SH} \) should be infinity [15]. \( R_{SH} \) and \( R_S \) are calculated from the inverse slope of the I-V curve near zero and at the point at which it becomes linear, respectively [15].
The equivalent circuit diagram of a solar cell contains a current source, one diode and two resistors: one in series and one in parallel. The series resistance represents the ohmic losses in solar cell because solar cell is not a perfect conductor. The parallel resistance is a cause of recombination of charge carriers or leakage current between the terminals.

1.3 Current Trends in Thin Film Photovoltaics

The selection of the material for thin-film solar cells is important and needs to possess the following characteristics: The primary characteristic of the material is a suitable band gap with a high absorption coefficient [2]. Almost all photons should be absorbed by a layer that is only a few micrometers thick. A band gap of 1.0–1.6 eV is suitable for the absorption of all the photons in the visible range and to reach sufficient efficiency, according to theoretical calculations [2]. Nevertheless, a number of materials fulfill these characteristics. The most popular solar cell material is amorphous silicon. Silicon belongs to the group IV elements. However, silicon technology is expensive and needs a lot of materials, as discussed in the introduction. Non-silicon thin films are promising alternatives to low-cost solar cell materials. The alternative materials for silicon can be prepared by iso-electronic substitution (also known as cross-substitution) of silicon (group IV) with other suitable group elements (Figure 1.4). Following the cross-substitution principle, the group IV atoms (silicon) can be substituted by an equal number of cations and anions of group III and V or II, and VI, respectively, in order to obtain binary compounds. Common examples of binary compounds are GaAs and CdTe. Further, ternary compound semiconductors can be formed by substituting half of the elements of group II with the elements of group-I and the remaining half with the group III elements. A common example of such a ternary compound
A semiconductor is CuInS$_2$, CuInSe$_2$. Furthermore, with a partial replacement of indium by gallium, a quaternary copper indium gallium selenide (CuInGaSe$_2$) compound is achieved. Several other substitutions are also possible, for example, the replacing of half of the group III element with a group II element, and the other half with a group IV element. Substitution of In/Ga with Zn and Sn in CIGS compound leads to CZTS (Cu$_2$ZnSnS$_4$) (Figure 1.4).

**Figure 1.4** Tree diagram showing cross substitutions starting from silicon. A tree of compound semiconductors that are obtained by cross-substitution of elements by the elements of the groups from the higher and lower group numbers [15].

However, all substituted compounds are not practicable for solar cell applications. Substituted compounds need to fulfill other important conditions such as availability, the ability to exhibit a photovoltaic effect, producibility at an industrial scale, cost-effectiveness, and environment friendliness (for example, low toxicity) [15]. In the light of this, only a few materials such as amorphous silicon (a-Si), cadmium telluride (CdTe), and copper indium gallium sulfide or selenide (CIGS), are actually useful for solar cell applications and ready for the extensive market [15]. However, some of the elements that comprise the chemistry of these films (for example, Te, In, and Ga) are toxic and not earth-abundant, which ultimately leads to a serious restrictions in their application in the mass production of solar cells [7]. In order to address these problems in the current thin-film solar cell materials, further research is required in order to develop alternative solar cell materials. Therefore, during the past five to
seven years, there has been a sudden increase in the interest to develop thin films based on all abundant and toxic free elements to facilitate the increasing demand for the electricity and its production. Alternatively, CZTS (Cu$_2$ZnSnS$_4$) thin films have emerged as excellent prospect materials for photovoltaic device applications. CZTS compounds are earth-abundant and composed of nontoxic elements; further, these compounds demonstrate a high optical absorption coefficient (10$^4$ cm$^{-1}$), a suitable band gap (1.4–1.6 eV), and high electrical conductivity, making them an ideal material for solar-energy–conversion applications [10-13].

1.4 Basic Properties of Cu$_2$ZnSnS$_4$

CZTS (Cu$_2$ZnSnS$_4$) is the quaternary chalcogenide compound semiconductor [4]. As mentioned before, CZTS belongs to the I$_2$–II–IV–VI$_4$ group, which is obtained by replacing one half of indium by zinc and the other half by tin in a CuInS$_2$ ternary compound. According to the theory, CZTS can exist in three types of crystal structures: kesterite (space group $I\bar{4}$), stannite (space group $I\bar{4}2m$), and primitive mixed CuAu (PMCA) (space group $P\bar{4}2m$), as shown in Figure 1.5 [22]. The kesterite-type CZTS is derived from CuInS$_2$ (CIS), while stannite and PMCA are derived from a CuAu-like structure [22]. The only difference between kesterite and stannite is the distribution of Cu and Zn atoms within the unit cell, while Sn atoms occupy the same position in both structures; these structures are also tetragonal with a c$\sim$2a ratio [22]. The PMCA structure has c$\sim$a, which can be considered to be a combination of two kesterite and stannite unit cells [22]. However, this structure has not been observed experimentally [22]. Kesterite and stannite structures are closely related, but show a different cation distribution, which leads to two different space groups [22]. The kesterite structure of CZTS was found to be thermodynamically more stable when compared to the stannite phase [23]. The lattice constants for CZTS are a=0.54 nm and c=1.09 nm [22]. Unfortunately, the complete determination of the phase is challenging due to their structural similarity [24]. Standard X-ray diffraction cannot distinguish between these two phases due to the similar peak positions of the two phases [24]. A synchrotron light or neutron source is required to distinguish between the two phases and identify the secondary phases [24].
Figure 1.5 Crystal structures of the (a) kesterite type, (b) stannite type, and (c) primitive mixed CuAu (PMCA) type of Cu$_2$ZnSnS$_4$ [22].

Due to the larger number of elements in CZTS in comparison with binary and ternary compounds, a wide range of defects is created on the basis of growth conditions and stoichiometry variations [15, 25, and 26]. The majority of defects are antisites, vacancies, or interstitials. They can be located at shallow or deep levels within the band gap, and their concentration depends on their own formation energy [26]. These defects show donor or acceptor behavior, and act as traps or recombination centers, which affect the optoelectronic properties of the material [26]. It has been reported that Cu-poor and Zn-rich CZTS shows higher efficiency when compared to stoichiometric CZTS [27]. The Cu-poor and Zn-rich conditions suppress the $(\text{Cu}_3)_\text{Sn}$ and $\text{Sn}_\text{Zn}$ defects, respectively, during the growth [26, 27]. It has also been reported that Se (or Na) doping in CZTS enhances the electrical conductivity, mobility, and solar cell power-conversion efficiency [28, 29]. Chen et al. presume that charge-compensated defect complexes are easy to form in CZTSSe [30]. They may passivate the deep donor levels which improves the quality of CZTSSe and, thus, the solar cell efficiency. The Se (or Na) doping also facilitates enhanced grain growth and hence reduction of potential barriers at grain boundaries [28, 29].

Fabrication of high-quality, large-area films with an ideal stoichiometry and a controlled phase remains a key challenge in the improvement of the performance of CZTS
devices. A large number of elements in CZTS create difficulties in achieving a single phase and an ideal stoichiometry of the chemical composition throughout the film. During the synthesis of CZTS, the formation of secondary phases, which have non-stoichiometric compositions such as Cu$_2$SnS$_3$, Cu$_2$S, SnS$_2$, and ZnS is frequently observed along with the CZTS phase [12, 13]. These secondary phases act as recombination centers and charge collection barriers that suppress the performance of the cell [15].

**Figure 1.6** Crystal structure ternary phase diagram of CZTS. A fraction of 50% sulfur is assumed. In the different regions indicated in the phase diagram, the secondary phases that appear next to CZTS are presented. In the middle, (marked with an asterisk) only the pure CZTS phase is obtained. Red arrows indicate lines of constant Zn, Sn, or Cu ratios, respectively, which, in this case, have been chosen for the ratios that mean stoichiometry [15].

The type and quantity of minor phases vary with both, the Cu, Zn, and Sn concentration and the growth technique that is employed. The phase representation of CZTS is quite complex and would require a four-dimensional diagram. This problem can be simplified by considering a ternary phase diagram and assuming a perfect balance between sulfur and metals. The ternary phase diagram was developed by Scragg et al. [30] and
Olekseyuk et al. [31]. The ternary phase diagram is shown in Figure 1.6. This phase diagram is valid in equilibrium at 400 °C. Depending on the system composition, different secondary phases are expected and are shown in Figure 1.6, in the corresponding regions of the phase diagram. Cu₅S compounds can be expected for Cu-rich compositions and for Sn-and Zn-poor stoichiometry. A very narrow stability region at the center of the diagram (asterisk) shows a Cu₂ZnSnS₄ single phase. Stoichiometry variations out of this region lead to the formation of additional secondary phases. In this last region, Cu-Sn-S ternary phases are also expected. No stable ternary compound is expected to form between ZnS and SnS₂ or between ZnS and Cu₂S. ZnS is expected as a single phase (alongside CZTS) for Zn-rich composition. For Cu-poor or Sn-rich samples, a second quaternary compound, Cu₂ZnSn₃S₈, is also expected from the reaction between SnS₂ and CZTS at 700 °C [31].

1.5 Fabrication Status of Cu₂ZnSnS₄ Material

CZTS thin films have been deposited by various deposition processes such as sol-gel, chemical, electrochemical methods, spray pyrolysis, pulsed laser deposition, and sputtering or thermal deposition [32–38]. All these deposition methods can be summarized and divided into categories: physical (vacuum based) and chemical methods (non vacuum based).

1.5.1 Physical Methods (Vacuum Based Deposition Techniques)

Physical deposition methods such as sputtering, evaporation, and pulsed laser deposition mainly involve the deposition of CZTS on substrates under certain temperatures and low pressure by using constituent metals or binary chalcogenide material targets. The advantages of these techniques are the easy control of stoichiometry and the homogeneity of the films. For example, sputtering deposition is a popular physical vapor-deposition method. Various types of sputtering methods such as DC, RF, hybrid, and reactive magnetron sputtering have been used to deposit CZTS thin films [39-41]. The sputter deposition method is meritorious in comparison to other physical (vacuum based) techniques. The method provides good control over the stoichiometry of elements, acquires high density films, is contamination free, and utilizes raw materials to the fullest extent. This method is suitable for the preparation of a large-area film with a high degree of uniformity. At present, this is one of
the most promising methods for the deposition of quaternary compound thin films. Fernandes et al. deposited the CZTS thin films by DC magnetron sputtering [39] and studied the influence of the metallic stacking order on the quality of the final CZTS thin films. They reported that the Zn/Sn/Cu (top) stack yields a better quality when compared to other stacking orders. Chalapathy et al. also fabricated the CZTS thin films with DC magnetron sputtering and reported a power-conversion efficiency of 4.59% [40]. They investigated the effect of temperature on the phase of the final CZTS films, and obtained a single phase and the best solar cell efficiency of CZTS prepared at temperatures higher than 560 °C. Katagiri’s group reported conversion efficiencies of 5.74% for CZTS thin-film–based solar cells [41]. The CZTS absorbers layers were deposited by an RF magnetron co-sputtering process using SnS, Cu, and ZnS targets. After deposition, they performed sulfurization of the precursor layers at 580 °C for 3 hr [41]. After this report, the same group has reported an improved solar cell efficiency of 6.7% [42]. They found that soaking these CZTS films in deionized water prior to the deposition of the CdS buffer layer helped to improve the performance of the solar cell [42]. This enhancement is attributed to the removal of the metal oxide layer from the surface of the CZTS. Recently, Toyota Central Research and Development Laboratories reported a power-conversion efficiency of 9.1% for CZTS-based solar cells [43]. The CZTS absorber layer was deposited by the RF magnetron sputtering method by using Cu, Sn, and ZnS as the target elements. To date, this is the best efficiency obtained from CZTS solar cells using the sputtering process [43].

The electron beam evaporation method results in good-quality thin films when compared to other physical deposition methods. This method is suitable for the deposition of materials that have high melting points with high-purity thin films. In recent times, the deposition of CZTS thin films with electron beam evaporation has been extensively studied at the laboratory scale [44-48]. It has been reported that the morphology of the film’s surface, the phase, and the optical properties of CZTS thin films are better. Katagiri et al. first reported the evaporation of CZTS thin films in 1997 [44]. After deposition, they sulfurized the metal stacks of Zn/Sn/Cu (top) at 500 °C for 1–3 h under an N\textsubscript{2} and H\textsubscript{2}S (5 %) atmosphere. The precursor layers that were deposited with a substrate temperature at 150 °C show an efficiency of 0.66%. Later, they reported an improvement in efficiency [45], from 0.66% to
2.62%, by varying the substrate and annealing temperatures. Kobayashi et al. adopted a similar deposition approach but changed the metal stacking order to Zn/Cu/Sn (top) and reported an improved efficiency of 4.53% [46]. Similarly, Wang et al. employed a thermal co-evaporation method in which Cu, Zn, Sn, and sulfur were deposited onto a Mo-coated glass substrate [47]. A sequential annealing process was carried out at 540 °C for 5 minutes in a sulfur atmosphere. Finally, they obtained a power-conversion efficiency of 6.8%. They found that dominant surface recombination is the main reason for the acquired limited power-conversion efficiency of the cell. Using similar deposition techniques, Shin et al. have fabricated CZTS-based solar cells that show an efficiency of 8.4 % (V_\text{OC} = 665 \text{ mV}, J_\text{SC} = 19.5 \text{ mA/cm}^2, \text{FF} = 66.8 \%) , which is the best efficiency reported so far for CZTS solar cells [48].

In comparison to other deposition processes, the pulsed laser deposition process is facile and facilitates thin-film deposition with ideal stoichiometry by controlling the target composition. This process is mainly suitable for deposition of metal oxide thin films. In addition, it results in high quality thin films at low temperatures. In 2007, Moriya et al. reported pulsed laser deposition (PLD) of CZTS thin films [38]. In their deposition process, a KrF pulsed laser with a wavelength of 248 nm was used to ablate a sintered CZTS target. The substrate was kept at room temperature during the deposition process. The deposited films were sulfurized at 300–500 °C in an N\textsubscript{2} atmosphere. Solar cells fabricated from the sample annealed at 500 °C showed an efficiency of 1.74 %.

1.5.2 Chemical Methods

Solution-based techniques have attracted great attention due to their potential for low-cost and large-area deposition. The microstructure and composition of the film can be efficiently controlled by using solution-based techniques. Various solution-based techniques have been explored in CZTS thin-film deposition, such as sol-gel, hydrothermal, spray pyrolysis, solvo thermal, thermolysis, and hot-injection methods [49, 55, and 60]. Fabrication of CZTS thin films directly from the precursors is most attractive, because the chemical composition can be easily controlled by tailoring the precursor chemical composition. In 2014, Park et al. reported the preparation of CZTS thin films [49]. They used metal chlorides
precursors and thiourea as the sulfur source. The CZTS precursor thin films were also fabricated by spin coating of precursor inks, followed by pre-annealing at various temperatures, and sulfurization at 550 °C for 30 min [49]. The CZTS solar cell that is fabricated with a 350 °C pre-annealed sample shows a conversion efficiency of 5.29%.

There are some reports on the deposition of CZTS by the spray pyrolysis technique [50–55]. The first report on CZTS spray pyrolysis was from Nakayama et al. in 1996 [50]. The CZTS thin films were deposited by spraying a solution that contained CuCl₂, ZnCl₂, SnCl₄, and thiourea dissolved in water and ethanol onto a glass substrate that was heated to 280–360 °C [50]. Stoichiometric CZTS thin films were obtained by annealing the as-deposited thin films at 550 °C in an Ar-H₂S atmosphere. The Cu₂S phase was found in Cu-rich films, while the Cu₂SnS₃ phase was found in Zn-poor films. By using a spray pyrolysis process, Rajeshmon et al. studied the effect of various tin precursors on the properties of CZTS thin films [55]. They used SnCl₄ and SnCl₂ precursors and found that the crystal quality and grain size were better for SnCl₄-based CZTS films. However, both precursors yielded the kesterite phase of CZTS. They fabricated solar cells with a superstrate configuration from the SnCl₄-based CZTS thin films. They found that the efficiencies of the solar cells can be improved from 0.38 % to 1.5 % by doping the In₂S₃ buffer layer with indium [56].

The electrodeposition of CZTS thin films can be summarized and divided into two categories: sequential deposition of metal layers (Cu/Zn/Sn) and single-step deposition of precursors, followed by the process of sulfurization. Scragg et al. first reported the development of CZTS thin films by using a sequential electrodeposition approach [57]. They deposited Cu/Sn/Zn (top) metal stacks on a Mo substrate and annealed the substrate at 550 °C for 2 h in a sulfur atmosphere. They observed the secondary phase of SnS₂. Solar cells fabricated from such films showed 0.8% efficiencies. The low efficiency is due to the voids near the interface of the CZTS and Mo, and the formation of the secondary phase due to zinc deficiency. Finally, the group optimized the sequential stack to Cu/Sn/Cu/Zn (top) and annealing conditions, which then showed an efficiency of 3.2% [58]. The IBM group reported an efficiency of 7.3% with a sequentially electrodeposited CZTS absorber layer [59]. They developed a three step method: i) sequential electrodeposition of Cu/Zn/Sn or Cu/Sn/Zn
stacks; ii) annealing of the stacks at a low temperature (210–350 °C) under an N$_2$ atmosphere in order to produce homogeneous alloys; and iii) annealing of these well-mixed CuZn and CuSn alloys at 550–590 °C in a sulfur atmosphere for 5–15 min to allow the formation of CZTS [59]. They found various secondary phases such as Cu$_2$S, SnS and Cu$_2$SnS$_3$ in the films when the sulfurization temperature falls below 580 °C. Above 580 °C, ZnS and Cu$_2$SnS$_3$ reacted and formed the CZTS. Solar cells that were fabricated from the CZTS thin films that were sulfurized at 585 °C for 12 min showed efficiencies of 7.3%. To date, this is highest efficiency for pure CZTS-based solar cells that are prepared using the sequential electrodeposition technique [59]. These studies reveal that electrodeposition is a potential method for the production of large scale, low-cost CZTS films. However, further optimization is required to obtain single phase CZTS films.

Single bath electrodeposition of CZTS thin films was first introduced by Ennaoui et al. [60]. They deposited Cu-Zn-Sn precursor layers on a Mo-coated soda lime glass substrate from an alkaline electrolyte bath that contained Cu (II), Zn (II), and Sn (IV) metal salts. The precursor layers were annealed at 550 °C in Ar-H$_2$S (5 %) atmosphere for 2h in order to achieve CZTS film. Solar cells that were fabricated from CZTS films with Cu/(Zn + Sn) = 0.97 and Zn/Sn = 1.08 showed an efficiency of 3.4 % [60]. Using a similar single-step electrodeposition process, Araki et al. [61] reported CZTS-based thin films solar cells with an efficiency of 3.16 %. The sulfurization of the precursor layers was performed at a higher temperature (600 °C) than that which was reported by Ennaoui et al. (550 °C) [60] for the same amount of time (2 h). The sample that was annealed at 600 °C yielded the best solar cells. Recently, Chen et al. reported the fabrication of CZTS solar cells through the use of the single bath electrodeposition technique [62]. They used reline electrolyte instead of aqueous electrolyte. Solar cells were fabricated from the films, and an efficiency of 3.87% was achieved.

CZTS nanoparticle-based approaches start with a phase-controlled synthesis of nanoparticles and finish with the deposition of the resultant nanoparticle inks, followed by post-treatment of the films [63]. CZTS nanoparticle synthesis requires only general organic solvents and precursor salts. CZTS nanoparticle-based approaches have the potential to
control phase formation, and this is the only approach that enables phase formation prior to the deposition of the film [63]. Nanoparticle-based solar cells can be divided into two categories: one that uses little or no heat treatment during device fabrication, and the other that requires a high-temperature heat treatment during device fabrication [63]. Generally, nanoparticle devices that are processed at a low temperature show poor performance due to smaller-sized particles that create a large concentration of interfaces in the film. Recently, high-efficiency multinary chalcogenide nanoparticle-based solar cells have been fabricated [4, 59]. They achieved high efficiency through the high-temperature annealing of the as-deposited films. This high-temperature heat treatment facilitates the enhancement of grain growth, from nanometer to micron sizes, when carried out in a sulfur or selenium atmosphere [59]. Moreover, it helps to reduce the presence of surface defects and grain boundaries, and contributes to the formation of a favorable conduction pathway for photo-generated carriers; this enables an impressive improvement of every photovoltaic parameter.

Research on CZTS nanoparticles has progressed tremendously in the past couple of years. Steinhagen et al. [64] reported, for the first time, the synthesis of CZTS nanoparticles in 2009. They adopted a one-pot technique in which all the precursors (Cu, Zn, Sn metal salts, and elemental sulfur) and oleylamine were mixed at room temperature and then heated to 280 °C in order to allow the formation of CZTS nanoparticles. In the same year, Guo et al. [65] also reported the synthesis of CZTS nanoparticles using a hot-injection approach in which Cu, Zn, Sn metal salts, and elemental sulfur were used as precursors, whereas, oleylamine was used as both a solvent and surfactant. The CZTS thin films were deposited by drop-casting of the CZTS nanoparticle ink onto a Mo-coated soda lime glass substrate, after which they were successively annealed between 400 and 500 °C in a selenium atmosphere for 20 min. The sample annealed at 500 °C yielded the best solar cells, with conversion efficiencies of 0.8%. Soon thereafter, they optimized the chemical composition and thin film deposition process of CZTS and achieved an efficiency of 7.2% [28]. Recently, CZTSSe has reached a record efficiency of 9.85% through a nanoparticle-based approach; this was achieved by optimizing the CZTS nanoparticle ink and film engineering [70]. The improved performance is due to the high-quality kesterite phase of CZTS crystallites that were synthesized in controlled experimental conditions. This technique provides high-quality and large-area films, an easy
fabrication process, and long-term device stability, and will surely become a promising platform for next-generation solar cell fabrication [63].

1.6 Challenges in Cu$_2$ZnSnS$_4$ Research

From the perspective of the material development and the device design, various hurdles have to be overcome in order to make the CZTS technology competitive in commercial solar cell modules. CZTS is still not understood well enough from the perspective of defects, crystal structure, and doping. The main challenge in CZTS fabrication is the obtaining of a single phase, since this single phase exists in a very narrow region of the phase diagram (Figure 1.5) [15]. Also, during CZTS fabrication, it is very important to control secondary phases such as Cu$_2$SnS$_3$, Cu$_2$S, SnS$_2$ and ZnS while maintaining the temperature and the stoichiometry of the precursors [15].

The nature of the doping in CZTS is still a big debated. However, it is assumed that some of the defects contribute the p-type nature of the CZTS [66, 67]. It has also been reported that Na doping yields higher carrier concentrations in the CZTS. Sodium may develop from the glass substrate that is generally used in device processing [68]. CZTS band gap can be tuned by composition variation [16]. Optimum absorption conditions can be adjusted by tailoring the band gap. Moreover, the film morphology, grain boundaries, voids, and compactness also have significant impact on the efficiency of the solar cell [14]. A large grain size implies fewer grain boundaries, which leads to a larger mean free path for the electrons and, hence, reduces the recombination rate of photo-generated charge carriers [70]. On the other hand, the presence of voids reduces the active cell area, while the pinholes shunt the performance of the device [15]. Therefore, films with a large grain size are required for fabrication of high-efficiency solar cells. Consequently, the ability to control the stoichiometry as well as the morphology of CZTS thin films is crucial to the performance of solar cell devices.

CZTS solar cells use the same cell structure as CIGS. CIGS is already commercialized but CZTS is still at the research level, and needs to show a minimum power-conversion efficiency of 15% for commercialization. In order to push the efficiency values further, from
the present 11.1% to the theoretical limit of 30%, a number of issues have to be solved [71]. It has been observed that there is a difference in the efficiencies of cells from research and solar modules from regular production [72]. The reasons for this efficiency difference are the active area and the parasitic absorption in the transparent conducting window layer. The rest of the differences can be reduced by optimizing the module production process to improve the uniformity and material properties across large areas. The CZTS solar cell contains a CdS buffer layer, followed by a non-doped ZnO layer. However, since Cd is toxic and not earth-abundant, it is preferable to use alternative suitable and abundant materials [17]. The suitability of the new buffer layer material partly depends on the nature of the interface. The interface between the CZTS and the buffer layer should not block the electrons; otherwise, the efficiency decreases drastically [17]. The other important interface is the back contact (Molybdenum). When a layer of a Cu, Zn, and Sn precursor is sulfurized (selenization), the sulfur reacts with the Mo layer underneath and forms MoS$_2$ layer at the interface of Mo and CZTS [73, 74]. This critically affects the performance of the device. It has been claimed that MoS$_2$ (MoSe$_2$) assists in the formation of an Ohmic contact when its thickness is less than a few hundred nanometers [75]. Excessive thicknesses have been shown to adversely influence the performance of solar cells [75]. Shin and Scragg et al. studied the temperature-dependent kinetics of the formation of the MoS$_2$ (MoSe$_2$) layer between Mo and CZTS films [73, 75]. They reported that the formation of a thick MoS$_2$ (MoSe$_2$) layer is a serious problem and that a sufficient S (Se) partial pressure during annealing is needed in order to prevent the formation of defects deep in the band gap. They deposited a thin layer of a titanium nitride (TiN) diffusion barrier between CZTSe and Mo, due to which the formation of MoS$_2$ (MoSe$_2$) was greatly suppressed, leading to a power-conversion efficiency of 8.9% [73]. Hence, interface optimization is found to be an important factor in better device performance. Finally, the long-term stability of CZTS under heat, light, and moisture needs to be addressed in order to make CZTS technology competitive in commercial solar cell modules.

1.7 The Objectives of this Thesis

Achieving an appropriate crystal phase and controlled stoichiometry during synthesis is still a big challenge, as has been discussed in the section above. The aim of this study is to
fabricate and characterize CZTS thin films and evaluate their solar cell performance. Non-vacuum and solution based techniques have been adopted to achieve CZTS precursor films. The nanoparticle approach offers a convenient method for the formation of quaternary chalcogenide nanoparticles with a desired stoichiometry and phase. These techniques enable a cheaper method for the fabrication of low-cost and large area photovoltaic films when compared to vacuum-based techniques. Furthermore, we focused on the fabrication of large area devices using nanoparticles ink approach.

The specific objectives of present investigation are:

- The fabrication of CZTS thin-film solar cells using a single-step electrodeposition process with an aim to obtain the kesterite phase of CZTS.
- Solution-based facile synthesis of size-controlled CZTS nanoparticles, and the fabrication of a solar cell device thereof.
- To study the influence of anion/cation substitution on the structural, optical, and electrical transport and photovoltaic performance of CZTS solar cells.
- To investigate the effect of silica nanoparticles embodiment in the CZTS active layer which acts as light scattering centers. We aim to study, theoretically and experimentally, the role of the silica particle in the absorber layer on optical absorption and solar cell performance parameters.

1.8 The Structure of this Report

This report consists of four experimental chapters. Each chapter begins with the motivation and discusses the relevant literature that is used in the experimental work. After the experimental section, the results are presented and discussed with the help of existing literature and finally conclusions are drawn.

Chapter 1 of this report outlines various types of thin-film solar cells with current trends in thin-film technologies. This chapter covers the basic properties of the CZTS material and its various fabrication processes. This chapter also discusses the present challenges of high efficiency solar cells in CZTS research.
Chapter 2 focuses on the fabrication of high-quality CZTS thin films by single bath electrodeposition. We investigated the role of the deposition potential in the compositional, structural, and optical properties of CZTS films. This work demonstrates the optimization of single bath deposition for CZTS films in a reproducible manner, and the fabrication of a solar cell. Finally, the electrical performance of a solar cell is discussed.

Chapter 3 demonstrates a simple and economic approach to synthesizing size-controlled single phase quaternary CZTS nanoparticles by a simple control of the amine-toPrecursor molar ratio. A scalable, binder free ink was prepared with toluene as the dispersal solvent. Instead of hydrazine treatment, we have performed multiple heat treatments in order to remove surfactants from the surface of the nanoparticles, thereby facilitating the improvement of the conductivity of the films. Finally, the results of the CZTS nanoparticle solar cells were discussed with the help of various device characterizations.

Chapter 4 deals with the influence of anion/cation substitution on the structural, optical, electrical transport, and photovoltaic performances of the CZTS device.

Chapter 5 of the thesis deals with the improvement of solar cell efficiency by the embedding of silica nanoparticles in the absorber layer.

Chapter 6 draws important conclusions and summarizes the results from these studies. Based on the results from this work, some recommendations for future CZTS research are presented.

1.9 References


[62] Hao Chen, Qinyan Ye, Xulin He, Jingjing Ding, Yongzheng Zhang, Junfeng Han, Jiang Liu, Cheng Liao, Jun Mei and W. Lau, Electrodeposited CZTS solar cells from Reline electrolyte, Green Chem. 16 (2014) 3841.


Chapter 2

Cu$_2$ZnSnS$_4$ Single-bath Electrodeposition: Toward the Kesterite Phase for Improved Photovoltaic Performance

2.1 Motivation

In general, Cu$_2$ZnSnS$_4$ (CZTS) is grown by two-step process in which metal stacks are first deposited onto the substrate, which is followed by sulfurization [1, 2]. Sequential deposition of metal layers (Cu/Zn/Sn) or co-deposition of all the metal stacks is a more common practice [2]. Various deposition processes such as sol-gel, chemical and electrochemical methods, spray pyrolysis, pulsed laser deposition, and sputtering or thermal deposition have been adopted to deposit the metal (Cu, Zn and Sn) layers [3-9]. Among these methods, the single bath electrochemical process offers a convenient method for the deposition of all the elements together at an optimum deposition potential, which can
potentially lead to precise control over the stoichiometry of the CZTS film [10]. Pawar et al. initiated the single bath electrodeposition process of CZTS thin films deposited at -1.05 V vs. SCE, by using a complexing agent to reduce the reduction potential for all the metals [1, 11]. Araki et al. also reported single bath electrodeposition of CZTS thin films [12]. However, they used -1.20 V vs. Ag/AgCl deposition potential, which has shown to be Zn-rich and S-poor, relative to the stoichiometry [12]. Although various successful attempts to deposit CZTS with a single bath are reported, issues such as cracks, pinholes, the phase quality, and the stoichiometry of the film are addressed inadequately.

In the single bath deposition process, the deposition potential is an important parameter, which controls the quality of the film with appropriate stoichiometry. Despite this, a clear correlation between the deposition potential and the quality of the crystal (crystal structure and stoichiometry) of CZTS films is not available in the literature. Hence, we investigate the role of the deposition potential in the compositional, structural, and optical properties of CZTS films. This work demonstrates the optimization of single bath deposition for CZTS films in a reproducible manner. Finally, CZTS thin films deposited at optimum potential were then assembled into the solar cells and have tested their device performance.

2.2 Experimental Section

2.2.1 Electrodeposition of Cu₂ZnSnS₄ Thin Films

All chemicals were purchased from Sigma-Aldrich and were used without any further purification. The electrodeposition bath was prepared by dissolving the CZTS precursors of 0.02 mol/L CuSO₄, 0.01 mol/L ZnSO₄, 0.02 mol/L SnCl₂, 0.2 mol/L tri-sodium citrate, 0.01 mol/L tartaric acid, and 0.01 mol/L Na₂SO₄ in deionized water. The tri-sodium citrate was added as complexing agent for the precursors. The pH of the electrolyte solution was maintained in the range of 4.0–5.0 for the deposition of the CZTS films. Before the deposition, fluorine doped tin oxide (FTO), molybdenum (Mo)-coated glass substrates (2 cm × 2 cm) were cleaned by ultrasonication in a soap solution (detergent + deionized water),
acetone and isopropyl alcohol, respectively, and finally in deionized water for 10 min each, followed by drying under a nitrogen flow for 5 min. Further, a 2 cm × 2 cm active area of the FTO-coated cleaned glass electrode was immersed in an electrodeposition bath in order to synthesize CZTS films at fixed potentials for 3 min. at room temperature.

CZTS is a complex metal system with varied reduction potentials of Cu (-1.1 V), Zn (-1.3 V), and Sn (-0.6 V) with respect to the Ag/AgCl reference electrode [13]. Therefore, an optimum potential window is measured by cyclic voltammetry (CV) in the Cu-Zn-Sn-S precursor solution with complexing agent (Figure 2.1), at a scan rate of 25 mV/sec.

**Figure 2.1** A cyclic voltammetry plot of the aqueous electrolyte used for Cu-Zn-Sn-S deposition on FTO glass electrodes. The scan rate was 25 mV s⁻¹.

The CV plot shows a sharp rise in the cathodic current from the beginning of the scan, followed by a plateau region. The sharp rise in the cathodic current could be due to the metallic deposition of copper and tin. The first reduction peak is observed at -1.0 V vs. Ag/AgCl. Therefore, we have chosen a minimum -1.0 V vs. Ag/AgCl potential for chronoamperometric deposition. At more negative potentials (> -1.4 V vs. Ag/AgCl), the current reaches the maximum which indicates that the H₂ evolution reaction (visible bubble formation). Similarly, anodic peaks are also observed in the anodic scan due to the stripping (dissolution) of the metals [13]. Reduction potential assignment is an important task because
the electrolyte contains multiple reduction species, all of which need to be reduced at a given potential. Hence, the compositional, structural and optical properties of the CZTS films deposited at fixed potentials of -1.0, -1.2, -1.4, -1.6, -1.8, and -2.0 V vs. Ag/AgCl were examined.

2.2.2 The Sulfurization Process

After deposition, the films were washed copiously with deionized water and dried at room temperature for 2 hr. Further, the films were sulfurized with sulfur powder heated at 550 °C for 30 minutes with continuous argon flow in a tubular furnace. The sulfurization conditions were maintained for all samples, and the residual sulfur was removed by dipping the film in isopropyl alcohol for 2 min.

2.2.3 Solar Cell Assembly and Processing

The fabrication of a thin-film solar cell is complex and involves numerous independent processing steps. Figure 2.2 shows the schematic of a CZTS heterojunction solar cell that contains various layers of materials.

![Figure 2.2 Schematic diagram of the CZTS thin-film solar cell.](image)

The device stack consisted of glass/ Mo (600 nm)/ Absorber (800 nm)/ CdS (50 nm)/ i-ZnO (100 nm)/ Al: ZnO (300 nm)/Ni/Al (contact). The various processing steps and
experimental details include the cleaning of substrates, back-contact deposition (Mo), the absorber layer, the CdS buffer layer deposition, the n-type layer (ZnO), the window layer (Al:ZnO) and front metal contact (Al) deposition. These processing steps also require optimization in order to attain high-power conversion efficiencies.

We used soda lime glass substrates with dimensions of 2 cm × 2 cm to deposit all the layers. Surface contamination of glass leads to poor adhesion and non-uniform deposition of films, which ultimately affects the performance of the device. In order to achieve a high level of cleanliness, the glass substrates (2 cm × 2 cm) were cleaned by ultrasonication in a soap solution (detergent + deionized water), acetone, and isopropyl alcohol, respectively, and finally in deionized water for 10 min each followed by drying under a nitrogen flow for 5 min. Then, they were immediately loaded into the metal sputtering system for Mo deposition. The device-fabrication process starts with the deposition of the Mo back contact. Mo is preferred as a back contact over CuInGaSe₂ (CIGS) and CZTS solar cells due to its high thermal stability; it also inhibits the interfacial reactions with the absorber layer. The structure and properties vary with the deposition parameters. Hence, we have optimized the Mo deposition parameters in order to achieve good adhesion and electrical conductivity. A Mo layer that was approximately 500–600 nm-thick was deposited onto the glass substrate.

After Mo deposition, an 800 nm-thick CZTS absorber layer was deposited by single bath electrodeposition process, as discussed in the sections above. Then, a 50 nm-thick CdS buffer layer was deposited by chemical bath deposition that contained 0.015M CdCl₂, 6mL NH₄OH, 0.37M (NH₄)₂SC in an aqueous solution (30 mL deionized water) at 80 °C for 5 min. The solution was continuously stirred in order to mix the solution and the bath temperature was kept constant at 80 °C. After deposition, the films were washed copiously with deionized water and dried under nitrogen gas; they were then annealed at 320 °C for 30 min. Further, highly resistive intrinsic ZnO (n-type layer) was deposited on CdS by dielectric sputtering, and Al-doped ZnO (AZO) was deposited on intrinsic ZnO by metal sputtering. At the top, Al top contacts were deposited by the thermal evaporation system. Finally, the total area (1.44
cm$^2$) of all the devices was defined by mechanical scribing of the samples. A summary of all the deposition parameters are listed in Table (2.1).

**Table 2.1:** Summary of the sputtering conditions used during the deposition of Mo, i-ZnO and AZO.

<table>
<thead>
<tr>
<th>Deposition conditions</th>
<th>Mo</th>
<th>i-ZnO</th>
<th>AZO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>40</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Pressure (mbar)</td>
<td>$2.7 \times 10^{-3}$</td>
<td>$2 \times 10^{-3}$</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>RF power (W)</td>
<td>200</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Argon flow (SCCM)</td>
<td>75</td>
<td>50</td>
<td>75</td>
</tr>
</tbody>
</table>

### 2.2.4 Characterization Techniques

Electrodeposition experiments were performed using a potentiostat/galvanostat (Metrohm Instruments-302 N) at room temperature. A conventional three-electrode cell configuration was employed; it included an FTO/Mo coated glass that had an area of 3×3 cm$^2$ as a working electrode, a platinum wire as the counter, and Ag/AgCl as the reference electrode. The electrodeposited CZTS films were characterized using X-ray diffraction spectrum (XRD) (Xpert PANalytic X-ray diffractometer) with Cu Kα radiation ($\lambda$ = 1.54 Å), Raman scattering (Lab RAM HR 800 Micro laser Raman system in back scattering geometry using the 514.5 nm line of Ar$^+$-laser as an excitation source), field emission gun scanning electron microscope (FEGSEM) (JEOL JSM-7600F FEG-Scanning Electron Microscope operated at 15 kV) and energy-dispersive X-ray analysis (EDX) characterization techniques. The chemical composition and valence states of the constituent elements were analyzed by X-ray photoelectron spectroscopy (Thermo VG Scientific MultiLab, ESCA Probe) using Al K$_\alpha$ ($h\nu = 1486.6$ eV) as the exciting source for identification of oxidation state.

The optical properties of CZTS films were measured by UV-visible absorption and transmittance spectroscopy (Lambda 950-Perkin Elmer). The Mott–Schottky analysis was
performed by using a three-electrode electrochemical cell that contained platinum as the counter electrode, Ag/AgCl as a reference electrode, and an FTO substrate as a working electrode in an aqueous redox electrolyte of 1M NaOH and 0.1 M Na$_2$SO$_4$. The electrolyte pH was adjusted to 5.0. For the Mott–Schottky analysis, impedance measurements were performed for selected DC bias potentials (-0.2 to 1.0 V versus Ag/AgCl) in the frequency range of 0.01 Hz to 100 KHz. The amplitude of the sinusoidal signal was 10 mV RMS, and all the parameters (V$_{FB}$, N$_A$ and W) were estimated to be at 1 KHz frequency [14]. The photovoltaic (PV) characteristics of the fabricated devices were measured using a Keithley 2400 source meter and a Newport solar simulator (model number 91160) with an illumination of AM 1.5 G. External quantum efficiency (E QE) measurements were carried out by a double source illumination system (Xenon lamp, QTH lamp). All measurements were performed at room temperature.

2.3 Results and Discussion

2.3.1 Role of Deposition Potential

2.3.1.1 Mixed Phase to Single Phase Control of Cu$_2$ZnSnS$_4$

X-Ray diffraction measurements are done to investigate the alloy formation before and sulfurization. Figure 2.3a shows the XRD patterns of precursor films that are deposited at different deposition potentials before sulfurization. XRD patterns show that at positive potentials (< -1.4 V vs. Ag/AgCl), elemental Cu, Sn and an alloy of Cu$_6$Sn$_5$ are present, but Zn is scarce. At more negative potentials (> -1.4 V vs. Ag/AgCl), elemental Cu, Zn, Sn and alloys of Cu$_2$SnS$_3$, ZnS, Cu$_6$Sn$_5$ and CuZn$_2$ are formed, as indexed in Figure 2.3b.
Figure 2.3 (a) XRD spectra of as-deposited CZTS samples grown at different potentials, as indicated; and (b) XRD patterns for possible secondary phases labeled with respect to standard ICDD cards.

Figure 2.4a compares the XRD patterns of CZTS samples deposited at different deposition potentials after sulfurization. The XRD patterns show the major characteristic peaks of (112), (220) and (132) planes, which correspond to the kesterite structure of CZTS and correlate well with the ICDD value of kesterite CZTS (ICDD No: 00-026-0575). The crystal phase of the films, the growth orientation, the lattice parameters, and the lattice strain are estimated using XRD data. It was found that the film prepared from a precursor electrodeposited at -1.4 V vs. Ag/AgCl has the perfect kesterite phase of CZTS. We observe a variation in the peak intensities and FWHM of the (112) peak at 28.44° after sulfurization, with respect to the deposition potential. At -1.4 V vs. Ag/AgCl, the (112) (2θ = 28.44°) peak becomes relatively more intense with less FWHM when compared to all other samples, as mentioned in Table (2.2); this indicates that the film has a good crystalline quality [10]. Table (2.2) shows the lattice parameters, and the crystallite size of the films, which is calculated using the Scherer formula [15]. We found a uniform preferential growth orientation along (112) for all the characterized samples.
Figure 2.4 (a) XRD spectra of sulfurized CZTS samples grown at different potentials, as indicated; (b) the Williamson–Hall plot for analysis of strain and crystallite sizes; and (c) the lattice strain versus deposition voltage obtained from the Williamson–Hall analysis.

A slight variation in the lattice parameter was observed for the samples deposited at the potential -1.4V vs. Ag/AgCl. This variation can be attributed to the tetragonal distortion (a change in c/2a ratio) that is common in the chalcopyrite crystal structure of CZTS samples [15, 16]. For the tetragonal kesterite phase, the c/2a ratio has been reported to be larger than the unity using neutron diffraction studies of powder samples [17]. However, in non-stoichiometric films, the ratio is observed to be slightly lower than unity, which can be attributed to the presence of the residual strain that is induced by the secondary phases. Further, lattice strain and crystallite sizes are measured using the Williamson–Hall analysis (Figure 2.4b), which is an effective method for calculating the crystallite size and lattice strain from the peak-broadening mechanism [15]. A positive slope indicates a compressive lattice strain, while a negative slope indicates tensile strain [16].
Table 2.2: Lattice parameters calculated from the dominant (112) and (220) XRD peaks of CZTS samples that were grown at different voltages.

<table>
<thead>
<tr>
<th>Voltage (V vs. Ag/AgCl)</th>
<th>Peak position (degree)</th>
<th>Index of plane</th>
<th>Inter planar distance (Å)</th>
<th>FWHM of (112) plane (degree)</th>
<th>Lattice parameter (Å)</th>
<th>(Crystallite size ±2) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.0</td>
<td>28.45</td>
<td>(112)</td>
<td>3.13</td>
<td>0.23</td>
<td>a = 5.42, c = 10.87</td>
<td>36</td>
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<tr>
<td></td>
<td>47.35</td>
<td>(220)</td>
<td>1.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.2</td>
<td>28.47</td>
<td>(112)</td>
<td>3.13</td>
<td>0.20</td>
<td>a = 5.42, c = 10.86</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>47.37</td>
<td>(220)</td>
<td>1.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.4</td>
<td>28.44</td>
<td>(112)</td>
<td>3.12</td>
<td>0.19</td>
<td>a = 5.41, c = 10.83</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>47.37</td>
<td>(220)</td>
<td>1.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.6</td>
<td>28.44</td>
<td>(112)</td>
<td>3.11</td>
<td>0.26</td>
<td>a = 5.40, c = 10.79</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>32.68</td>
<td>(220)</td>
<td>1.91</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>-1.8</td>
<td>28.54</td>
<td>(112)</td>
<td>3.11</td>
<td>0.20</td>
<td>a = 5.40, c = 10.78</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>32.68</td>
<td>(220)</td>
<td>1.91</td>
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</tbody>
</table>

Table (2.3) presents the nature of the strain in films based on the nature of the plots, the crystallite size, and the lattice strain. Figure 2.4c shows the variation in the lattice strain of different films deposited at various potentials. It can be observed that the stoichiometric film deposited at -1.4 V vs. Ag/AgCl has a smaller lattice strain \(2.52 \times 10^{-4}\) compared to the non-stoichiometric films \(7.54 \times 10^{-4}\). A high lattice strain is typically attributed to the presence of secondary phases. However, in non-stoichiometric films, we observed a large magnitude of lattice strain in the range of \(5 \times 10^{-4}\) to \(7 \times 10^{-4}\). These secondary phases (defects) induce the strain in the lattice.
Table 2.3: Summary of crystallite size determined from the Debye–Scherer formula and Williamson–Hall analysis.

<table>
<thead>
<tr>
<th>Voltage (V vs. Ag/AgCl)</th>
<th>Crystallite size (nm) from Scherer formula</th>
<th>Strain type</th>
<th>Crystallite size (nm) from W-H plot</th>
<th>(Micro-strain±0.21) × 10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.0</td>
<td>36</td>
<td>Compressive</td>
<td>39</td>
<td>7.54</td>
</tr>
<tr>
<td>-1.2</td>
<td>40</td>
<td>Compressive</td>
<td>49</td>
<td>5.23</td>
</tr>
<tr>
<td>-1.4</td>
<td>80</td>
<td>Compressive</td>
<td>85</td>
<td>2.52</td>
</tr>
<tr>
<td>-1.6</td>
<td>54</td>
<td>Compressive</td>
<td>68</td>
<td>1.23</td>
</tr>
<tr>
<td>-1.8</td>
<td>53</td>
<td>Tensile</td>
<td>34</td>
<td>4.00</td>
</tr>
</tbody>
</table>

It is understood that XRD characterization is not an ideal tool for phase analysis of the CZTS due to the identical peak positions of two phases (kesterite and stannite); it is also not ideal for some of the secondary phases [17]. Therefore, we employed Raman spectroscopy for the phase analysis of all CZTS samples after sulfurization [17]. At positive potentials (-1.0 V and -1.2 V vs. Ag/AgCl), we observed a tetragonal Cu₂SnS₃ phase (297 cm⁻¹) and a cubic Cu₂SnS₃ phase (356 cm⁻¹) due to zinc deficiency. The major peaks at 288, 338, 350, 370 cm⁻¹ for samples deposited at -1.4 V vs. Ag/AgCl, and -1.6 V vs. Ag/AgCl correspond to the CZTS kesterite phase (Figure 2.5). The most intense Raman peaks were observed at 288 and 338 cm⁻¹, which corresponds to the A₁ phonon mode of the kesterite structure (sulfur atom vibration) and is in good agreement with the literature [17-19]. In addition, a strong and sharp peak at 338 cm⁻¹ is also an indicator of CZTS that has good crystalline quality [19]. Thus, the Raman spectrum confirms a good-quality crystal phase that is prepared at -1.4 V vs. Ag/AgCl, and -1.6 V vs. Ag/AgCl.
2.3.1.2 Compositional and Morphological Analysis

In order to identify the elemental composition of the sulfurized CZTS samples, we recorded XPS spectra of all the samples. Figure 2.6 shows a high-resolution XPS analysis of four constituent elements of CZTS films, namely, Cu 2p, Zn 2p, Sn 3d, and sulfur 2p. The CZTS samples deposited at -1.4 and -1.6 V vs. Ag/AgCl show a Cu 2p\(^{3/2}\) peak at 932.6 eV, which matches with the reported value [10]. However, there is a blue shift for the positive potential (-1.0 V & -1.2 V vs. Ag/AgCl)-deposited films and a red shift for the negative-deposited film (-1.8 V vs. Ag/AgCl). The blue and red shift of the Cu 2p\(^{3/2}\) peak is due to a deficiency in Zn but abundance in the Sn structure, which is further confirmed from EDX analysis. In contrast to -1.4 V deposited samples (which show good stoichiometry), the intensity of the copper 2p peak is low for the samples deposited at -1.2 and -1.8 V vs. Ag/AgCl. The peak positions and peak separation (19.8 eV) between Cu 2p\(^{3/2}\) and Cu 2p\(^{1/2}\) indicates the presence of a Cu (+1) state [10].
Figure 2.6 The XPS spectra of sulfurized CZTS samples, deposited at different voltages: (a) core-level spectra for Cu 2p states; (b) core-level spectra for Zn 2p states; (c) core-level spectra for Sn 3d states; and (d) core-level spectra for S 2p states.

A similar trend in peak shift is observed in XPS data of all the elements due to deficiency of zinc. The peak separation of 23 eV between Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ indicates a Zn (+2) state. Figure 2.6c shows Sn 3d XPS peaks for all the samples. The peak separation 8.5 eV, observed between Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$, indicates the Sn (+4) state [10]. Figure 2.6d shows the S 2p peaks for all the samples. The sulfur 2p peaks located at 162.0 and 162.7 eV in the spectra consist of sulfide 2p$_{3/2}$ and 2p$_{1/2}$ peaks, which indicates that sulfur is present in the sulfide (-2) state in the CZTS film [10]. Secondary phases of the tetragonal Cu$_2$SnS$_3$ phase and cubic Cu$_2$SnS$_3$ phases were observed at other than -1.4 V and -1.6 V vs. Ag/AgCl films, and became Sn-rich and zinc-deficient, which was also confirmed from the Raman
measurements. These peak positions match well with the Cu$_2$SnS$_3$ phase [20]. XPS data also confirms that -1.4 V vs. Ag/AgCl is an appropriate potential for an idealized composition.

The stoichiometry of the constituent elements before and after sulfurization is identified using EDX presented in Figure 2.7. At more positive potentials (< -1.4 V vs. Ag/AgCl,) the four components are not deposited with appropriate ratios (that is, close to stoichiometric proportion) on the substrate. Interestingly, sulfur is also present in the pre-treated samples at a low atomic percentage (below 15 at. wt %) when compared to the ideal stoichiometry (50 at. wt %). The low sulfur content might be due to a negative charge of sulfur ions; it is deposited only because of attraction from the local positive charges of copper, tin and zinc [13]. At -1.4 V vs. Ag/AgCl, the composition is proportionate to the stoichiometry, except for that of sulfur (which is lower than 15 atomic wt %).

The EDX composition of CZTS thin films deposited at various potentials (Figure 2.7a) shows that the concentration of zinc and sulfur increases with the deposition potential. The concentration of sulfur has a strong influence on the mechanical properties of the films [21]. A higher sulfur concentration makes the film powdery, unstable and non-useful for further thermal treatment [21]. At potentials greater than -1.6 V vs. Ag/AgCl, the CZTS films are powdery and do not bind strongly to the substrate, causing it to fall off during rinsing/cleaning. Moreover, at more negative potentials (> -1.4 V vs. Ag/AgCl), water decomposes and produces hydrogen gas bubbles; it is possible that the bubbles also interfere with the adhesion of the film [14]. As-deposited films EDX measurements indicate that the four components were not deposited with appropriate ratios on the substrate. In order to obtain appropriate stoichiometry and phase, the films need sulfurization at 550 °C after deposition. Figure 2.7b shows the variation of the atomic percentages of the constituent elements after sulfurization. It reveals that the CZTS samples prepared from a precursor that was electrodeposited at positive potentials (-1.0 V & -1.2 V vs. Ag/AgCl) demonstrates zinc deficiency associated with secondary phases such as Cu$_2$SnS$_3$ and SnS$_2$. This observation is also consistent with the Raman spectroscopy analysis presented in Figure 2.5. From EDX
analysis, it is found that the stoichiometry of the films achievable at -1.4 V vs. Ag/AgCl is in agreement with the results of XPS and Raman scattering.

Figure 2.7 (a) EDX compositions variation plot of as-deposited CZTS samples deposited at various potentials; and (b) EDX composition variation plot of sulfurized CZTS samples deposited at various potentials.

The thickness of the films measured before and after sulfurization using cross-sectional SEM images and profilometry is presented in Table (2.4). Before sulfurization, the film thickness increases for samples deposited at positive potentials (≤ -1.4 V vs. Ag/AgCl), which is due to favorable deposition of zinc. At more negative potentials (> -1.4 V vs. Ag/AgCl), the films are unstable (due to hydrogen gas bubble formation) and powdery (due to extra sulfur) and fall off during rinsing/cleaning [14, 21]. After cleaning, the thickness of the film is found to be lesser when compared to the films deposited at positive potentials. Moreover, after sulfurization of the precursor films, an increase in the thickness of the film is observed due to sulfur diffusion as well as due to the grain growth of CZTS films.
Table 2.4: Measured film thickness of pre-sulfurized and after-sulfurized CZTS thin films by cross-sectional SEM and profilometry.

<table>
<thead>
<tr>
<th>Voltage (V vs. Ag/AgCl)</th>
<th>Film thickness (± 0.1µm) (Pre-sulfurization) (Cross sectional SEM)</th>
<th>Film thickness (± 0.1µm) (After-sulfurization) (Cross sectional SEM)</th>
<th>Film thickness (± 0.1µm) (Pre-sulfurization) (Profilometry)</th>
<th>Film thickness (± 0.1µm) (After-sulfurization) (Profilometry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.0</td>
<td>1.0</td>
<td>1.1</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>-1.2</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>-1.4</td>
<td>1.5</td>
<td>1.7</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>-1.6</td>
<td>1.4</td>
<td>1.6</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>-1.8</td>
<td>1.3</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>

In addition to the composition of sulfurized CZTS samples, film-surface morphology and cross-sectional analysis are also crucial in evaluating the uniformity of the film and the size of the grain. As discussed earlier, film uniformity, a high grain size, and minimal defects are essential in enhancing the performance of the solar cell. Figure 2.8a shows the SEM image of the sulfurized CZTS samples that are deposited at an optimum voltage (-1.4 V vs. Ag/AgCl), which indicates a compact arrangement of CZTS micro crystals without any pinholes and other structural defects such as cracks. Figure 2.8b shows the cross-sectional view of the CZTS thin film with a uniform film thickness of (1.7 ± 0.1) µm. Secondary phases are frequently observed in the electrodeposited CZTS samples [22]. In order to confirm homogeneous composition formation along the thickness and the length, we prepared a cross section of the deposited sample of -1.4 V vs. Ag/AgCl by cutting the film into slices at the center and recording the EDX line scan. Figure 2.8c and d shows that the concentrations of copper, zinc, tin and sulfur stay constant within the accuracy of the measurement. Almost all four components have homogeneous compositions along the thickness as well as along the length.
Figure 2.8 (a) SEM surface morphology of the sulfurized CZTS sample deposited at -1.4 V vs. Ag/AgCl; (b) SEM cross section of the sulfurized CZTS sample prepared from a precursor that was electrodeposited at -1.4 V vs. Ag/AgCl; (c) EDX line scan taken across the thickness; and (d) EDX line scan taken across horizontally.

2.3.1.3 Nucleation and Growth Mechanism

A schematic view of nucleation and the growth mechanism is presented in Figure 2.9. Current transient curves are recorded during the electrochemical deposition (Figure 2.10a) in order to study the influence of the applied potential on the nucleation and growth of the film. The shape of the transient curves indicates the stages of nucleation and the growth of the films. The current transient plot (Figure 2.9) shows three regions. Region (I) represents the initial stage just before the application of the potential, when a liquid boundary film is layered adjacent to the solid substrate and the bulk solution, as represented in the illustration. In region (II), the current density increases rapidly due to the nucleation of metals and an
increase in the density of nuclei. During this stage, the transport of electro active species to
the nuclei formed on the surface occurs through hemispherical diffusion zones developed
around each nucleus [23]. Further, with an increase in time, the radius of the hemispherical
diffusion zones increases due to the growth. This causes a drop in the current density due to a
decrease of the mass flux that moves to the electrode surface (region (II)). In region (III), we
observed a stabilization plateau at a lower current density, which indicates saturated growth.
At higher potentials, the current density increases rapidly, and the nucleation rate depends
significantly on the applied potential [23]. At positive potentials (< -1.4 V vs. Ag/AgCl), we
observed the formation of Sn-rich films because zinc is not reduced properly; at more
negative potentials (> -1.4 V vs. Ag/AgCl,) we observed poor sulfur composition.

Figure 2.9 Schematic representation of CZTS nucleation and growth phenomena involved at
various stages. Region (I) represents the initial stage that is just before the application of the
potential. Region (II) shows the nucleation and the growth stage. Region (III) represents the
growth saturation.
The possible growth model can be realized by plotting $i$ vs $t^{1/2}$ from current transient plots (Figure 2.10b inset), which reveals a mass transport of the electro active species [23]. Therefore, the Scharifker and Hill model can be applied to understand the growth mechanism, which can have two types of nucleation modes: instantaneous nucleation (Eq. (2.1)) and progressive nucleation (Eq. (2.2)) [23]. Our experimental data fitting matches well with instantaneous nucleation (Figure 2.10b) in which all the reaction sites of the surface are activated simultaneously and the number of nuclei growing on the surface are saturated at the initial deposition stage.

Figure 2.10 (a) Current–time (potentiostatic) transients for the nucleation and growth of CZTS films on FTO electrodes recorded at various formation potentials; and (b) Normalized $(i/i_{\text{max}})^2$ vs. $(t/t_{\text{max}})$ plots obtained from the current–time transients (inset shows the $i$ vs $t^{1/2}$ plot).

The models for instantaneous and progressive nucleation are given by Equations (2.1) and (2.2), respectively [23];

$$\left( \frac{i}{i_{\text{max}}} \right)^2 = \frac{1.9542}{t/t_{\text{max}}} \left[ e^{-1.2564} - \exp \left( -1.2564 \left( \frac{t}{t_{\text{max}}} \right) \right) \right]^2 \quad (2.1)$$
\[
\left( \frac{i}{i_{\text{max}}} \right)^2 = \frac{1.2254}{\left( \frac{t}{t_{\text{max}}} \right)^{\frac{2}{3}}} \left( 1 - \exp \left[ -2.3367 \left( \frac{t}{t_{\text{max}}} \right)^2 \right] \right)^2
\]

where \( i_{\text{max}} \) and \( t_{\text{max}} \) are current and time coordinates of the peak, respectively.

### 2.3.1.4 Band gap Control of Cu\(_2\)ZnSnS\(_4\)

A high absorption coefficient and an optimal direct band gap of 1.5 eV of the CZTS absorber film are among the most basic requirements of the high-performance solar cell. Consequently, we next characterize the UV-visible absorption and transmittance spectra of CZTS thin films using the UV-visible spectrometer in the wavelength range of 400–1200 nm (Figure 2.11a). The optical band gap of the thin films are calculated from the absorption and transmittance data. In agreement with the values reported in the literature, we observed an optical band gap of 1.5 eV for the stoichiometric CZTS film. The optical absorption coefficient \( (\alpha) \) was calculated from the transmittance data using the following formula [24].

\[
\alpha = \frac{1}{t} \ln \left[ \frac{1}{T} \right]
\]

where “\( t \)” is the film thickness and \( T \) is the transmittance. In this work, the CZTS film thickness that was estimated after sulfurization is presented in Table (2.4). The absorption coefficient of the CZTS thin films after sulfurization is of the order of \( 10^4 \) cm\(^{-1} \) in the visible region. Figure 2.11b shows the variation in the band gap with the deposition potential. The observed variation in the band gap can be attributed to the presence of secondary phases. Some secondary phases such as cubic Cu\(_2\)SnS\(_3\) and tetragonal Cu\(_2\)SnS\(_3\) have a low band gap (\( \sim 1.15 \) eV) when compared to CZTS (1.5 eV). However, Cu\(_2\)S has a higher band gap (1.8 eV) [13]. The optical band gap and the absorption measurements confirm that kesterite CZTS has possible utility as a solar cell.
Figure 2.11 (a) UV-visible transmittance spectra of sulfurized CZTS thin films grown at different potentials; and (b) variation of the band gap with the deposition potential. The inset shows the absorption coefficient in comparison with the deposition voltage.

2.3.2 Electrochemical Mott–Schottky Measurements

The Mott–Schottky model has been used to determine the carrier type, carrier concentration, flat-band voltage, and depletion width. Electrochemical impedance measurements were carried out at different dc potentials (-0.2 V to 1.0 V vs. Ag/AgCl) in order to determine the film capacitance. Figure 2.12 shows the Mott–Schottky plots (1/C² vs V plot) at a frequency of 1 KHz. The frequency of 1 KHz is chosen because, at a higher frequency range, capacitance measurements become erroneous due to the contribution of the surface or interface states [14]. Also, the imaginary part of the impedance becomes smaller, and other measurement errors such as the parasitic impedance of the cell become significant at higher frequencies. So, an optimized frequency (1 KHz) is used in order to get the appropriate capacitance values and to completely exclude the contribution of the surface state. Figure 2.12 shows capacitance values of up to -0.2 V vs. Ag/AgCl cathodic potential. It should be mentioned that at more negative potentials (> -0.2 V vs. Ag/AgCl,) a slight deviation from the straight line behavior was observed, which might be due to the etching of
the film in the electrolyte solution (not shown in the Figure 2.12). The carrier concentration is calculated from the slope of the $1/C^2$ vs $V$ plot using the following equation [14, 25].

$$N_A = \left[ \frac{2}{\varepsilon_0 \varepsilon_r \varepsilon_0} \int \frac{d(1/C^2)}{dV} \right]^{-1} \quad \text{(2.4)}$$

In Eq. (2.4) $\varepsilon_r$ is the dielectric constant of the CZTS film, $\varepsilon_0$ is the permittivity of the free space ($8.85 \times 10^{-14}$ F/cm) and $e_0$ is the electric charge ($1.6 \times 10^{-19}$ C). The dielectric constant of CZTS (6.7) is chosen for calculations [26]. The extrapolated intercept on the X-axis gives the flat-band voltage ($V_{FB}$). The obtained carrier concentration in prepared films is $N_A=10^{17}$ cm$^{-3}$ with a flat-band potential of $V_{FB}=0.71$ V. The flat-band potential is useful in estimating the position of the valence band and the conduction band edges of a semiconductor at the interface of the electrode (CZTS in this case) and the electrolyte [25]. A negative slope indicates the p-type nature of the films. Carrier density is an order higher in comparison with Tanaka et al. ($10^{16}$ cm$^{-3}$) and lowers with Katagiri et al. ($10^{19}$ cm$^{-3}$) [27, 28]. The absence of secondary phases (defects) at -1.4 V vs. Ag/AgCl films leads to a higher carrier concentration when compared to all other deposition potentials.

The thickness of the space charge region was estimated from the following equation [29].

$$W = \left[ \frac{2 \varepsilon_r \varepsilon_0 (V_{FB} - V)}{\varepsilon_0 N_a} \right]^{\frac{1}{2}} \quad \text{(2.5)}$$

The thickness of the space charge region was estimated to be 0.2 μm at -0.2 V vs. the Ag/AgCl potential. This wider space charge region is good for separation of the charge carriers. The gradient of the Mott–Schottky curve did not change significantly, indicating that the composition of the film is uniform throughout its depth [30]. The Mott–Schottky results also confirm that the quality of the crystal developed in this study is good because the films show a higher carrier concentration ($10^{17}$ cm$^{-3}$) as well as a wider space charge region.
Figure 2.12 Mott–Schottky plots for the sulfurized CZTS thin films grown at different potentials on FTO-coated glass. The inset shows the Mott-Schottky plot for sulfurized CZTS sample grown at -1.4 V vs. Ag/AgCl.

2.3.3 Device Characterizations

2.3.3.1 J-V Characteristics

Figure 2.13a shows the cross-sectional SEM image of the as-fabricated solar cell. The device consists of well-faceted large-grain crystallites without any noticeable voids in the CZTS absorber layer. The grain size of the CZTS absorber layer is about 400 nm-1.0 μm. The MoS$_2$ layer is not visible at the contact between CZTS and Mo in the cross-sectional SEM image; this might be due to the similar appearance between Mo and MoS$_2$. Figure 2.13b shows the J–V characteristics of the electrodeposited CZTS thin film solar cell under AM 1.5G illumination. The device shows that a power-conversion efficiency of 5.0 % is achieved.
on the basis of the active area of 1.44 cm$^2$. Table (2.5) shows the summary of the solar cell electrical parameters that are derived from the JV data. The short-circuit current density of 17.8 mA/cm$^2$ with an open-circuit voltage of 485 mV and a fill factor of 58% have been obtained from the solar cell JV data. The shunt resistance ($R_{SH}$) and series resistance ($R_S$) are calculated from the inverse slope of the JV curve near zero and where it becomes linear, respectively (Table (2.5)). The calculated series resistance ($R_S$) is 5 Ω-cm$^2$, and the shunt resistances ($R_{SH}$) are 510 Ω-cm$^2$. For an ideal solar cell, $R_S$ should be zero and $R_{SH}$ should be infinity. Our solar cell shows a high $R_S$ (5 Ω-cm$^2$) when compared to the high-efficiency CZTS solar cell reported by IBM [31]. The poor interfacial contact (this may be due to high roughness of electrochemically deposited CZTS and other layers), the high series resistance between the layers, and the small $R_{SH}$ implies the presence of shorts across the p-n junction. Therefore, a low $R_S$ indicates that a high current passes through the cell and a high $R_{SH}$ indicates that there are fewer shorts in the cell. It is expected that the device performance will be enhanced by improving the sheet resistance of the Mo layer and by optimizing the thickness of the CZTS absorber layer.

![Figure 2.13](image)

**Figure 2.13** (a) Cross-sectional SEM image of a CZTS thin film solar cell, (b) J-V curve of the electrodeposited CZTS solar cell measured under simulated AM 1.5G solar irradiation.
Table 2.5: The electrical performance parameters of the electrodeposited CZTS solar cell.

<table>
<thead>
<tr>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>$R_S$ (Ω-cm$^2$)</th>
<th>$R_{SH}$ (Ω-cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.8</td>
<td>485</td>
<td>58</td>
<td>5.0 ± 0.1</td>
<td>5</td>
<td>510</td>
</tr>
</tbody>
</table>

2.3.3.2 Quantum Efficiency Measurements

Figure 2.14a shows the wavelength-dependent external quantum efficiency (EQE) curve for the CZTS hetero junction solar cell. The EQE sharply increases from 350 nm and then drops rapidly at 400 nm due to the absorption of the ZnO and AZO layers; it reaches a maximum value of 79% at 540 nm, and then drops slowly at about 800 nm due to the lower absorption coefficient of CZTS at near-band gap wavelengths. From the EQE curve, we conclude that the short circuit current loss is a result of carrier collection efficiency in the range of 550 nm to 760 nm, which may be ascribed to severe backside recombination, short minority charge carrier lifetime, and the inadequate thickness of the absorber layer. The photon energy ($\hbar \nu$) and the optical band gap ($E_g$) are interrelated to the optical absorption coefficient $\alpha$ by applying Tauc’s model, $\alpha \hbar \nu = A (\hbar \nu − E_g)^n$, in which $A$ is a constant and $n$ is $1/2$ for a direct transition [32]. It has been proved from experiments and theoretical electronic band structure calculations that CZTS is a direct band gap semiconductor. Thus, by plotting $(\hbar \nu \times \ln(1 − EQE))^2$ against $\hbar \nu$ (Figure 2.14b), a band gap of 1.51 eV is obtained for the CZTS film, which is also consistent with the band gap estimated from the UV-visible data.
Figure 2.14 (a) EQE curve of the CZTS solar cell, (b) The band gap of the CZTS absorber layer estimated to be 1.51 eV, from a plot of \((h\nu \times \ln(1 - EQE))^2\) vs \(h\nu\).

**2.3.3.3 Photoluminescence and Carrier-Lifetime Measurements**

Figure 2.15a shows the photoluminescence (PL) spectra of CZTS thin film measured at room temperature with a 600 nm excitation wavelength. The PL spectra show the symmetric and sharp peak at 1.5 eV due to the band-to-band transitions of CZTS [33]. In order to understand the carrier lifetime in the CZTS solar cell, we have carried out TRPL spectroscopy. Figure 2.16b shows the TRPL decay curve of the CZTS film was measured at the 380 nm excitation wavelength and emission observed at 800 nm at room temperature. In this case, a double exponential analysis was used to obtain satisfactory \(\chi^2\) values (generally between 0.9 and 1.1) in order to fit the data [34].

\[
I(t) = C_1 e^{-t/\tau_1} + C_2 e^{-t/\tau_2} \tag{2.6}
\]

where \(I(t)\) represents the PL intensity as a function of time, \(\tau_1\) and \(\tau_2\) are decay times, and \(C_1\) and \(C_2\) are coefficients.
Figure 2.15 (a) Photoluminescence spectrum of the CZTS thin film at room temperature; and (b) Time-resolved photoluminescence (TRPL) spectrum of the CZTS solar cell. The solid line (Red) is the fitting curve, as calculated from eq. (2.6).

The calculated carrier lifetimes from these curves are 0.95 ns and 5.2 ns. Bi-exponential decay of TRPL is associated with the complex carrier dynamics and recombination processes. $\tau_1$ is the faster decay time and $\tau_2$ is the slower decay time [31, 34]. The faster decay time ($\tau_1$) is associated to the charge carrier separation time [31, 34]. The slower decay time ($\tau_2$) is related to the minority carrier lifetime in the low injection regime [31, 34]. This minority carrier lifetime is due to various non-radiative, bulk, and interface recombination processes [31, 34]. The charge separation time is 0.95 ns, which was observed in our case because TRPL measurements were carried out for the entire p-n junction instead of for only the CZTS and CdS buffer layers. The low minority carrier lifetime in our case might be the reason for the low open-circuit voltage, the low fill factor, and the low quantum efficiency at longer wavelengths. These lifetimes could be greatly improved by an optimization of grain size.
2.4 Summary

To summarize, we fabricated high-quality crystalline CZTS thin-film solar cells by using a single-step electrodeposition followed by a sulfurization process. XRD and Raman spectra reveal the kesterite crystal structure of the fabricated CZTS samples. UV-vis spectroscopy data shows that the films have a high optical absorption coefficient ($10^4 \text{ cm}^{-1}$) in the visible region and that their optical band gap ranges from 1.1 to 1.8 eV on the basis of the deposition potential. We find that good quality films are obtained at a potential of -1.4 V vs. Ag/AgCl. XPS and EDX data also reveals that the film deposited at -1.4 V vs. Ag/AgCl demonstrates appropriate stoichiometry in the chemical composition and the valance states of the constituent elements when compared to the all other deposition potentials. The analysis of nucleation and the growth mechanism identifies a diffusion-controlled instantaneous nucleation process. Using Mott–Schottky plots, we confirmed the p-type nature of the film and calculated that the charge carrier density is $10^{17} \text{ cm}^{-3}$, the flat-band potential $V_{FB}$ is 0.71 V, and the thickness of the space charge region is 0.2 μm. We have fabricated the solar cells with optimized deposition potential and have tested their device performance. The best processed cell showed an efficiency of 5.0%. The external quantum efficiency (EQE) curve suggested that the CZTS absorber layer had an optical band gap of 1.5 eV, with a device EQE value of more than 79%. The extracted carrier life time (5.2 ns) from the TRPL data clearly demonstrated the reasonable electronic properties of the CZTS thin film. The next logical step is to control grain size/boundaries, roughness, formation of impurity phases, defect density and the like; these are some existing challenges that need to be addressed immediately for an efficient solar-cell design.

2.5 References


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Chapter 3

Size Controlled Quaternary Cu$_2$ZnSnS$_4$ Nanoparticles: Ink Formulation to Device Characterization

3.1 Motivation

The development of low-cost alternatives for the fabrication of thin-film solar cells is essential in order to make solar energy a major source for electricity when compared to other sources of electricity. Most high-efficiency CuInGaSe$_2$ (CIGS) and Cu$_2$ZnSnS$_4$ (CZTS) solar cells are deposited using vacuum-based techniques [1, 2]. However, these vacuum-deposition techniques are very expensive and have issues in fabrication of devices over large areas [3]. Therefore, there is a growing interest in the development of low-cost- and large-area-solution–based techniques. The solution process offers a convenient method for the formation of quaternary chalcogenide nanoparticles with a desired stoichiometry and phase [3]. This technique enables a cheaper method for the fabrication of low-cost photovoltaic films when
compared to vacuum-based techniques [3]. Unfortunately, most of the nanoparticle-synthesis approaches discussed so far involve complex chemistry (solvent and two or more reducing or oxidizing agents, and organic metal precursors) and expensive precursors in the rendering of sub-gram quantities of mono-disperse nanoparticles [4–11]. In all these attempts to synthesize the nanoparticles, issues such as phase purity, stoichiometry, and uniformity of the quaternary chalcogenide nanoparticles have not been addressed systematically. Furthermore, from the industry perspective, a simple, economic, and scalable approach needs to be designed in order to synthesize phase controlled mono-disperse nanoparticles and, hence, their ink.

In this study, we demonstrate a simple and economic approach to synthesize size-controlled quaternary chalcogenide Cu$_2$ZnSnS$_4$ (CZTS) nanoparticles. The size of the nanoparticles has been controlled from 2–8 (± 0.5) nm by a simple control of the amine-to-precursor molar ratio. We demonstrate the synthesis of as much as 20 g of quaternary chalcogenide nanoparticles powder in a single reaction, without a size-sorting process. Furthermore, a scalable, binder-free ink was made with toluene as the dispersal solvent. These inks were coated on Mo-coated glass substrates by a simple knife-coating method. Instead of treatment with hydrazine, we have administered multiple heat treatments to CZTS thin films in order to remove surfactants from the surface of the nanoparticles, facilitating improvement in the conductivity of the films. All structural, optical, and electrical-transport measurements confirm the potential use of these nanoparticles in photovoltaic applications. Therefore, we fabricated solar cells and studied the effect of particle size on device performance.

3.2 Experimental Section

3.2.1 Preparation of Size Controlled Quaternary Cu$_2$ZnSnS$_4$ Nanoparticles

We demonstrate a simple one-step approach for the synthesis of 20.2 g of Cu$_2$ZnSnS$_4$ nanoparticles powder from metal chloride precursors by using a long-chain amine as the solvent, reducing and surface-functionalizing agent. In a typical synthesis of 6 nm-sized Cu$_2$ZnSnS$_4$ nanoparticles, 50 mM of CuCl$_2$, 25 mM ZnCl$_2$, and 25 mM SnCl$_2$ were added to 600 mM of oleylamine (amine-to-precursor molar ratio of 1:6) in a three-necked round-
bottomed flask. The reaction mixture was heated at 120 °C for 30 min. in order to form the metal-amine complex under a nitrogen atmosphere. At this point, 100 mM of sulfur was added to the mixture, which immediately changed the color of the reaction mixture to light brown. Later, the temperature was raised to 220 °C at a rate of 5 °C/min with a further heating of 0.5 h. The obtained nanoparticles were collected from the growth solution by precipitation with acetone, followed by centrifugation and hence re-dispersion in hexane. After several hexane/isopropanol extractions, the final product was dried under vacuum. The size was controlled with a 1:15 (2.5 nm), 1:12 (3.5 nm), 1:9 (5 nm), 1:6 (6 nm), and 1:4 (8 nm) molar ratio of precursor to amine, respectively. A brief illustrated detail of the synthesis procedure is given in Figure 3.1.

![Synthesis Procedure Diagram](image.png)

**Figure 3.1** Schematic flow diagram of amine-functionalized CZTS nanoparticle synthesis. As indicated, after nucleation at 120 °C, the solution changes from blue to brownish, which indicates the formation of the metal-amine complex, and growth at 220 °C leads to a blackish solution due to the initiation of the formation of CZTS. The growth reaction takes 0.5 hrs to finish.

### 3.2.2 Binder-free Ink Formulation and Thin Film Deposition

One of the main challenges in nanocrystal-based solar cells is the making of fine, uniform ink. Conventionally, ink formulation requires organic surfactants or stabilizers, and binders to make fine ink, which are difficult to remove after film processing and result in impurities in the film [12]. Our primary goal was to develop a fine, uniform ink-formulation method with a binder-free single solvent. For ink formulation, the solvent needs to be so
volatile that the films dry rapidly without leaving substantial residues; it also needs to have a functional group to stabilize the ink. This formulation method needs to be cost effective and also be able to deposit uniform films over large areas. In this study, we used toluene as a solvent for ink formulation. The dried CZTS nanoparticles were dispersed in toluene (150 mg/mL) to make nanoparticle ink. The dispersed nanoparticles were ball milled for 12 h in order to form a uniform ink. Moreover, toluene-based ink was found to be stable for many months without precipitation. These inks were deposited onto various substrates (fluorine-doped tin oxide (FTO), soda-lime glass, and molybdenum (Mo)-coated glass) by simple knife-coating (also known as doctor blade method) [11]. Typically, a small amount of the concentrated nanoparticle ink is drop-casted on the edge of a substrate; adhesive tape (scotch tape) is then used as a doctor-blading guide (Figure 3.2). The thickness of the tape determines the initial thickness of the doctor-bladed film. A circular glass rod was used to deposit the films. A second coat of the ink was then applied in a manner similar to the first one to fill the cracks in the first layer, resulting in the final film. The substrate was immediately coated with the CZTS layer, after which was covered with a narrow tube end funnel to prevent fast evaporation of the solvent. Fast evaporation of solvent could create cracks in the film, which is undesirable. Each layer of the nanoparticle films was found to be \( \sim (0.4\pm0.1) \mu\text{m} \) in thickness when measured by the scanning electron microscope (SEM) cross-sectional analysis.

**Figure 3.2** The schematic demonstration of the fabrication of CZTS-based absorber layers using CZTS nanoparticle ink.
3.2.3 Surfactant Removal and Sulfurization Process

After each coating, the thin films were annealed at 360 °C for 30 min with a continuous flow of argon gas in a tubular furnace in order to remove the capping agent (amine, in our case) and to improve the conductivity of the film. This post-deposition heat treatment also helps to densify the film. After the annealing, the films were sulfurized using sulfur powder that was heated at 550 °C for 30 minutes with a continuous flow of argon in a tubular furnace. The residual sulfur was removed by dipping the film in isopropyl alcohol for 2 min.

3.2.4 Solar Cell Assembly and Processing

The device stack consisted of glass/ Mo/ Absorber (700-800 nm)/ CdS (50 nm)/ i-ZnO (100 nm)/ Al: ZnO (300 nm)/ Al (contact). After Mo deposition, an 800 nm thick CZTS absorber layer was deposited by the doctor-blade deposition method followed by sulfurization, as discussed in the sections above. A 50 nm-thick CdS film was deposited by chemical bath deposition using CdSO₄, ammonia, (NH₂)₂SC aqueous solution at 80 °C. Furthermore, intrinsic ZnO was deposited on CdS by dielectric sputtering, and Al-doped ZnO (acts as window layer) was deposited on intrinsic ZnO by metal sputtering. At the top, Al contacts were deposited using thermal evaporation technique. The various processing steps and experimental details of device fabrication have been discussed in the chapter 2. Finally, the total area (1.44 cm²) of all the devices was defined by mechanical scribing of the samples.

3.2.5 Characterization Techniques

The as-prepared nanoparticles were characterized using XpertPANalytic X-ray diffractometer with Cu Kα radiation (λ= 1.54 Å), Raman scattering (Lab RAM HR 800 Micro laser Raman system in back scattering geometry using the 514.5 nm line of Ar⁺-laser as an excitation source), field emission gun scanning electron microscope (FEGSEM) (JEOL JSM-7600F FEG-Scanning Electron Microscope operated at 15 kV) and energy-dispersive X-ray analysis (EDX) characterization techniques. High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained with JEOL JEM 2100F, field emission gun transmission electron microscope
(FEGTEM) at an accelerating voltage of 200kV. The chemical composition and valence states of the constituent elements were analyzed by X-ray photoelectron spectroscopy (Thermo VG Scientific MultiLab, ESCA Probe using Al K$_{α}$ (hv = 1486.6 eV),) which was used as the excitation source for identification of the oxidation state. The optical properties of quaternary chalcogenide nanoparticles were measured by UV-visible absorption and transmittance spectroscopy (Lambda 950-Perkin Elmer).

I-V curves of the thin films have been measured, both in the dark and in illumination using a solar simulator (AM 1.5 G, 100 mW/cm$^2$). The photo voltaic (PV) characteristics of the fabricated devices were performed using a Keithley 2400 source meter and a Newport solar simulator (model number 91160) with AM 1.5 G illumination. External quantum efficiency (EQE) measurements were carried out by a double source illumination system (Xenon lamp, QTH lamp). All measurements were performed at room temperature.

3.3 Results and Discussion

3.3.1 Structural Investigation

X-ray diffraction (XRD) measurements were carried out for the nanoparticles in order to analyze the crystal phase. Figure 3.3 shows the XRD patterns of the CZTS nanoparticles as a function of size. The XRD patterns show major characteristic peaks of (112), (220) and (132) planes, which correspond with the kesterite structure of CZTS and correlates well with the ICDD value of kesterite CZTS (ICDD No: 00-026-0575). We observe a variation in the peak FWHM at 2θ = 28.44°, which is due to the size effect of the nanoparticles [13]. The (112) peak (2θ = 28.44°) broadens and the FWHM of the peak increases with decreasing particle size. The crystallite size was estimated by the FWHM of the (112) peak by using the Debye–Scherrer formula in the range of 2.5 nm to 8 nm, which is in agreement with the HRTEM data [13, 14]. The data shows the shift in the peak position, which might be due to strain in the crystal lattice [15].
Figure 3.3 XRD patterns of different sizes of CZTS nanoparticles. The FWHM of the peaks increases with decreasing particle size.

It is understood that for ternary and quaternary chalcogenide nanoparticles XRD characterization alone cannot confirm their crystal structure due to the same peak positions of two phases (kesterite and stannite) and also for some of the secondary phases such as ZnS and Cu$_2$SnS$_3$ [16]. Therefore, we employed the Raman spectroscopy measurements for the phase analysis of as synthesized and annealed CZTS nanoparticles films. Figure 3.4a shows the Raman spectroscopy data for 8 nm size as synthesized CZTS nanoparticles. The FWHM of Raman peak is larger than those observed in bulk CZTS. Raman data shows the broad peak at 338 cm$^{-1}$ which is assumed to be due to scattering from kesterite CZTS (A$_1$ phonon mode) (Figure 3.4a) [16, 17]. The broadening in Raman spectrum is attributed to the inhomogeneous broadening [18]. The frequency distribution in inhomogeneous broadening can be perfectly interpreted by a Gaussian line shape instead of a Lorentzian line shape [18, 19]. Hence, the experimental data was deconvoluted using peaks of Gaussian distribution to identify the peak locations as shown in Figure 3.4a. A linear background was used to fit the data. The fitted peaks at 288, 338, 350, 370 cm$^{-1}$ correspond to the CZTS kesterite phase [16, 17]. On the other hand, peak broadening could also mask the existence of some secondary phases of Raman peaks such as ZnS and SnS$_2$ [20]. However, we have done the Raman measurements after annealing the films of nanoparticles and the peaks at 288, 338, 350, 370 cm$^{-1}$ were
observed with no noticeable secondary phase peaks of ZnS or SnS$_2$ (Figure 3.4b). Thus, the Raman and XRD results confirm that our nanoparticles are CZTS and other secondary phases are not observed within the detection limit of Raman scattering.

**Figure 3.4** Raman spectra of as synthesized and annealed CZTS thin films. The red line is the sum of the peaks used to deconvolute the experimental spectrum. In (a), as synthesized CZTS nanoparticles show the broad Raman scattering peak at 338 cm$^{-1}$ presumably due to scattering from kesterite CZTS. In (b), annealed (at 550 °C) CZTS nanoparticles thin films shows two most intense Raman peaks at 338 cm$^{-1}$ and 288 cm$^{-1}$ which confirm the CZTS kesterite phase.

### 3.3.2 Morphological and Compositional Analysis

Transmission electron microscopy was performed in order to investigate the size, shape, and the distribution of the as synthesized nanoparticles. Figure 3.5 shows transmission electron microscope images of different sizes of CZTS nanoparticles that were prepared by varying the metal precursor-to-amine molar ratio as 1:15 (2.5 nm), 1:12 (3.5 nm), 1:9 (5 nm), and 1:4 (8 nm). It clearly shows that there is a continuous increase in the size of the nanoparticles upon decreasing the amine concentration. This demonstrates the multifunctional role of the amine, which acts as a solvent as well as a surface-functionalizing agent in controlling the growth of the nanoparticles. In each case, the nanoparticles are spherical and have a standard deviation of particle size distribution of $\sigma \leq 20\%$. The average sizes of the
nanoparticles are 2.5 ± 0.5 nm, 3.5 ± 0.6 nm, 5 ± 0.5 nm, 6 ± 0.5 nm, and 8 ± 0.5 nm, respectively (Figure 3.5a-e). The particle-size distribution becomes large when the precursor-to-amine molar ratio changes from 1:15 to 1:4. The higher content of amine supports diffusion-controlled growth (due to low concentration of growth species,) which assists in the formation of uniform small-sized nanoparticles [21]. At lower amine concentrations, the concentration of the growth species is higher, which supports a faster diffusion and give rise to the production of large-sized nanoparticles [21]. The selected area electron diffraction (SAED) pattern (Figure 3.5f) shows the polycrystalline nature of the sample, and the indexed planes match well with the tetragonal kesterite phase of CZTS (ICDD No: 00-026-0575), which further confirms the phase purity of the nanoparticles. High-resolution TEM (HRTEM) image (inset of Figure 3.5f of single CZTS nanoparticle illustrates the crystal plane with inter planar spacing of 3.12 Å, which corresponds to (112) plane of kesterite phase CZTS.

Figure 3.5 TEM images of CZTS nanoparticles produced with different mole ratios of metal precursor to oleylamine: (a) 1:15 (2.5 ± 0.5 nm), (b) 1:12 (3.5 ± 0.5 nm), (c) 1:9 (5 ± 0.5 nm), (d) 1:6 (6 ± 0.5 nm), (e) 1:4 (8 ± 0.5 nm), (f) SAED pattern of CZTS nanoparticles of 5 nm. The inset shows the HRTEM image of single CZTS nanoparticle.
Figure 3.6a shows the SEM surface morphology of a CZTS nanoparticle thin film after sulfurization. The film shows a compact arrangement of nanoparticles without any pinholes and other structural defects such as cracks. Figure 3.6b shows the EDX spectrum of a CZTS thin film and even distribution of Cu, Zn, Sn, and S across the entire substrate. EDX spectra reveals that the CZTS films are in perfect stoichiometry (Figure 3.6c and 3.6d), which is also confirmed by XPS measurements.

![Figure 3.6](image)

**Figure 3.6** (a) SEM surface morphology of the sulfurized CZTS nanoparticle film, (b) EDX composition mapping of CZTS nanoparticles, (c) EDX spectra of the CZTS nanoparticle film, and (d) atomic percentage of the elements present in the CZTS nanoparticle film.

XPS measurements were performed to ascertain the elemental composition and valence states of the elements that compose CZTS nanoparticles. Appropriate composition and valence state are important to maintain the stoichiometry. Figure 3.7 shows a high resolution XPS analysis of the four constituent elements of copper 2p, zinc 2p, tin 3d, and sulfur 2p. Figure 3.7a shows the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks at 932.3 eV and 952.3 eV, respectively. This peak separation of 20 eV indicates a Cu (I) state [22]. Figure 3.7b shows the Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ peaks located at 1022 eV and 1045 eV, with the splitting of 23 eV indicating the Zn (II) state [22]. The presence of the Sn (IV) state is confirmed from the peak splitting of 8.5 eV.
of the two peaks that are located at 486.2 eV and 494.7 eV, corresponding to Sn3d\(\frac{5}{2}\) and Sn 3d\(\frac{3}{2}\), respectively (Figure 3.7c). The S 2p core-level spectrum consists of 2p\(\frac{3}{2}\) and 2p\(\frac{1}{2}\) peaks at 161.0 eV and 162.1 eV, respectively, which are consistent with the 160–164 eV range expected for S in the sulfide phase (Figure 3.7d) [22].

![Figure 3.7](image)

**Figure 3.7** The XPS spectra of CZTS nanoparticles: (a) core-level spectra for Cu 2p, (b) core-level spectra for Zn 2p, (c) core-level spectra for Sn 3d, and (d) core-level spectra for S 2p.

### 3.3.3 Optical Properties

An optimal direct band gap and a high absorption coefficient are among the most basic requirements of a high-performance solar cell. Therefore, we next characterize the UV-visible absorption spectra of different-sized CZTS nanoparticles (dispersed in toluene) using UV-visible spectrometer in the wavelength range of 300–1000 nm (Figure 3.8a). Absorption data shows the quantum confinement effect for particle sizes below 3.5 nm, which is consistent with the theoretically calculated excitonic Bohr radius of CZTS (3.3 nm) [23]. The optical band gap is calculated from the absorption data using Tauc’s plot (Figure 3.8b). This reveals
that CZTS nanoparticles have band gaps of 1.62, 1.55, 1.51, 1.50, and 1.50 eV. The band gap of CZTS thin film increases with decrease in average particle size due to quantum confinement effect [23].

![Figure 3.8](image_url) (a) Optical absorption spectra of different sized CZTS nanoparticles and (b) Tauc plot for the corresponding absorbance curves. The band gap of CZTS increases with decrease in size of the nanoparticle due to the quantum confinement effect. The particles also show high optical absorption coefficients (~10^4 cm\(^{-1}\)) in the visible region.

### 3.3.4 Device Characterizations

#### 3.3.4.1 J-V Characteristics

To study the particle size effect on device performance, five different size nanoparticles were used in the absorber layer of solar cells. Figure 3.9 shows the J-V characteristics of the nanoparticle-based CZTS thin-film solar cells for five different particle sizes measured under AM 1.5 G illuminations. Table (3.1) shows the summary of the solar cells electrical parameters that are derived from the J-V data. The fabricated devices exhibit efficiencies ranging from 3.6% to 4.5% depending on the CZTS particles average diameter. From J–V characteristics, we observe that device with 8 nm particle size showed enhanced performance (4.5 %) when compared to other particle sizes. The active area of the device is
1.44 cm². All the electrical parameters of the devices are similar, with the $V_{oc}$ ranging from 480 mV to 500 mV and significant variation in the $R_{SH}$ from 300 - 420 Ω-cm². This significant difference in $R_{SH}$ might be related to porosity and grain size of the films, which might provide shunt paths, and therefore shorting issue might happen. Smaller particles are capped with high content of amine, which creates voids caused by the volatilization of the organic solvent during the annealing process. The poor interfacial contact (this may be due to the high roughness of CZTS and other layers) the high series resistance between the layers and the small $R_{SH}$ implies the presence of shorts across the p-n junction. Therefore, a low $R_S$ indicates that a high current passes through the cell, and a high $R_{SH}$ indicates that there are fewer shorts in the cell. It is expected that the device performance will be enhanced by improving the sheet resistance of the Mo layer and by optimizing the grain size of the CZTS absorber layer.

Figure 3.9 J-V curve of the CZTS nanoparticles solar cell devices as a function of their average diameter measured under AM 1.5G solar illumination.
Table 3.1: Electrical performance parameters of CZTS solar cells as a function of their average diameter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF (%)</th>
<th>$R_S$ (Ω-cm$^2$)</th>
<th>$R_{SH}$ (Ω-cm$^2$)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 nm</td>
<td>15.6</td>
<td>500</td>
<td>58</td>
<td>8</td>
<td>420</td>
<td>4.5±0.1</td>
</tr>
<tr>
<td>6 nm</td>
<td>14.5</td>
<td>493</td>
<td>58</td>
<td>9</td>
<td>418</td>
<td>4.3±0.1</td>
</tr>
<tr>
<td>5 nm</td>
<td>14.1</td>
<td>492</td>
<td>57</td>
<td>9</td>
<td>415</td>
<td>4.0±0.1</td>
</tr>
<tr>
<td>3.5 nm</td>
<td>13.5</td>
<td>491</td>
<td>58</td>
<td>10</td>
<td>390</td>
<td>3.8±0.1</td>
</tr>
<tr>
<td>2.5 nm</td>
<td>13.2</td>
<td>480</td>
<td>56</td>
<td>10</td>
<td>300</td>
<td>3.6±0.1</td>
</tr>
</tbody>
</table>

3.3.4.2 Quantum Efficiency Measurements

Figure 3.10a shows the wavelength-dependent (EQE) curve for different particle size CZTS solar cells. In all the devices, the EQE sharply increases from 350 nm and then drops rapidly at 400 nm due to the absorption of the ZnO and AZO layers; the EQE reaches a maximum value at around 550 nm, and then drops slowly from 560 to 675 nm due to reflection losses and the low diffusion length of absorber layer. The sudden drop of EQE from 690 nm to 900 nm is attributed to rear surface recombination and the lower absorption coefficient of CZTS at near-band gap wavelengths. The EQE of solar cell with CZTS film comprising of 8 nm particles is 80%. The EQE data (Figure 3.10a) suggests that the short circuit current loss is a result of carrier collection efficiency in the range of 550 nm to 760 nm, which may be ascribed to severe backside recombination, short minority charge carrier lifetime, and the inadequate thickness of the absorber layer. An approximate effective collection depth of 700–1000 nm for the minority charge carriers created in the absorber can be concluded from these results. The external quantum efficiency (EQE) curve indicated that the CZTS absorber layer had an optical band gap of 1.50 eV (Figure 3.10b).
Figure 3.10 (a) EQE for CZTS nanoparticles solar cell devices as a function of their average diameter, (b) The band gap of the CZTS absorber layer, which is estimated to be 1.50 eV, from a plot of \((h\nu \times \ln(1 - \text{EQE}))^2\) vs \(h\nu\).

3.3.4.3 Photoluminescence and Carrier-Lifetime Measurements

Figure 3.11a shows the photoluminescence (PL) spectra of the CZTS thin film, which is measured at room temperature with a 600 nm excitation wavelength. The PL spectra show the broad peak centered at 1.5 eV due to the band-to-band transitions of CZTS [24]. In order to understand the carrier lifetime in the CZTS solar cell, we have carried out TRPL spectroscopy. Figure 3.11b shows the TRPL decay curve of the CZTS film, which was measured at the 380 nm excitation wavelength, and the emission observed at 800 nm (Note that the PL spectrum shows a peak at 800 nm) at room temperature. In this case, a double exponential analysis was used to obtain satisfactory \(\chi^2\) values (generally between 0.9 and 1.1) in order to fit the data [25].

\[
I(t) = C_1 e^{-t/\tau_1} + C_2 e^{-t/\tau_2} \quad (3.1)
\]

where \(I(t)\) represents the PL intensity as a function of time, \(\tau_1\) and \(\tau_2\) are decay times, and \(C_1\) and \(C_2\) are coefficients. The calculated carrier lifetimes from these curves are 0.8 ns
and 3.2 ns. Bi-exponential decay of TRPL is associated with the complex carrier dynamics and recombination processes. $\tau_1$ is the faster decay time and $\tau_2$ is the slower decay time [2, 25]. The faster decay time ($\tau_1$) is related to the charge carrier separation time $\nu$. The slower decay time ($\tau_2$) is related to the minority carrier lifetime in the low injection regime [2, 25]. This minority carrier lifetime is due to various non-radiative, bulk, and interface recombination processes [2, 25]. The charge separation time is 0.8 ns, which was observed in our case because TRPL measurements were carried out for the entire p-n junction instead of for only the CZTS and CdS buffer layers. The low minority carrier lifetime in our case might be the reason for the low open-circuit voltage, the low fill factor, and the low quantum efficiency at longer wavelengths. These lifetimes could be greatly improved by an optimization of grain size.

![Figure 3.11](image)

**Figure 3.11** (a) Photoluminescence spectrum of the CZTS thin film at room temperature, (b) Time-resolved photoluminescence spectrum (TRPL) of the CZTS solar cell. The solid red line is the fitting curve, as calculated from eq. (3.1).

### 3.4 Summary

To summarize, we demonstrate a simple synthesis method for the large scale synthesis of size-controlled CZTS nanoparticles. This approach provides better control over particle size that range from 2.5 to 8 nm, by control of the amine-to-precursor molar ratio. XRD and
Raman data confirms the kesterite phase of the CZTS nanoparticles. XPS data further confirms the presence of four constituent elements with appropriate valence states. A low-cost, binder-free single solvent was used to formulate the nanoparticle ink; the films were deposited by the doctor blade method. We have done multiple heat treatments to remove surfactants and to improve the conductivity of the films. XRD spectra reveal the corresponding kesterite phase of the nanoparticles. UV-vis spectroscopy data shows that the films have a high optical absorption coefficient ($10^4$ cm$^{-1}$) in the visible region, and its optical band gap estimated to be 1.51 eV. Hence, we fabricated the solar cells with these nanoparticles and tested their device performance. The fabricated devices show efficiencies ranging from 3.6% to 4.5% depending on the CZTS particles average diameter. The EQE of solar cell with CZTS film comprising of 8 nm particles is 80%. Comparison of EQE data suggests that our current is mainly restricted by collection losses. Hence, we expect better performance by optimizing the thickness of the absorber layer, and by controlling the grain size and the device fabrication process.

3.5 References


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Chapter 4

Quaternary Cu$_2$MSnS$_4$/Se$_4$ (M=Zn, Mn and Fe) Nanoparticles: Influence of Ionic Substitution on Device Performance

4.1 Motivation

The incorporation of extrinsic impurities such as Fe and Mn (to replace Zn) or Se (to replace S) in the wurtizite structure of Cu$_2$ZnSnS$_4$ offers better flexibility and control over the stoichiometry and the crystal phase [1]. The cationic substitution in Cu$_2$MSnS$_4$/Se$_4$ (M=Zn, Mn and Fe) helps in tuning the optoelectronic properties of the quaternary chalcogenides. Typically it may lead to an improvement in the band gap energy from 1.0 eV to 1.5 eV and also suppress the formation of the secondary phase [1]. To date, there are only a few reports on the fabrication of Cu$_2$MSnS$_4$/Se$_4$ (M=Zn, Mn and Fe) nanoparticles based devices [2-8].
Very recently, J. Chu et al. reported the first CFTS solar cell with 0.07% power conversion efficiency [9], wherein, they found that a thickness of 600 nm as absorber might not be sufficient to absorb the light. In addition, Wong and co-workers also demonstrated the fabrication of ‘9% efficiency’ cation substituted CZTS solar cell with Cd substitution [10], wherein, cadmium, a toxic element could be doped up to 4 mol% with an efficiency enhancement factor of two in comparison to pristine CZTS [10]. Also, Chu et al. reported the CMnTS solar cells with 0.49% power conversion efficiency [11]. The poor efficiency of CMnTS (M=Mn) solar cells is attributed to the high interface resistance between CMnTS and CdS layers [11]. As per our knowledge, these are the only few reports on the substitution of anion and cations in CZTS. Therefore, further research is essential to understand the influence of anion/cation substitution on the structural, optical and electrical properties of the absorber films in order to achieve high efficiency solar cells. Sol-gel, hot-injection, spray pyrolysis, solvothermal and hydrothermal synthesis methods have been adopted to synthesize Cu$_2$MSnS$_4$/Se$_4$ (M=Zn, Fe, and Mn) nanoparticles [2-8]. The solution process offers a convenient method for the formation of quaternary chalcogenide nanoparticles that have the desired stoichiometry and phase. This technique enables a cheaper method for the fabrication of low-cost photovoltaic films when compared to vacuum-based techniques. Unfortunately, most of the nanoparticle-synthesis approaches discussed thus far involve complex chemistry (solvent and two or more reducing or oxidizing agents and organic metal precursors) and expensive precursors to render sub-gram quantities of mono-disperse nanoparticles [2–8]. In all these attempts to synthesize the nanoparticles, issues such as phase purity, stoichiometry, and uniformity of the quaternary chalcogenide nanoparticles are not addressed systematically. Furthermore, from the industry perspective, a simple, economic and scalable approach needs to be designed to fabricate mono-disperse nanoparticles and hence their ink.

In this study, we report a simple and economic approach to synthesize quaternary chalcogenide (Cu$_2$MSnS$_4$/Se$_4$, M= Zn, Mn and Fe) nanoparticles. We studied the influence of the incorporation of extrinsic impurities such as Fe and Mn (to replace Zn) or Se (to replace S) on the optical, electrical transport, and photovoltaic device performance of nanoparticle thin films. We demonstrate the synthesis of as much as 20 g of quaternary chalcogenide nanoparticle powder in a single reaction, without a size-sorting process. Furthermore, a
scalable, binder-free ink was made with toluene as the dispersal solvent. These inks were coated on Mo-coated glass substrates by a simple knife-coating method. Instead of hydrazine treatment, we carried out multiple heat treatments in order to remove surfactants from the surface of the nanoparticles, which improved the conductivity of the films. The structural, optical, photo-response and electrical transport measurements confirm the potential use of these nanoparticles in photovoltaic applications. Hence, we have fabricated solar cells, and have tested their efficiency.

4.2 Experimental Section

4.2.1 Cation/Anion Substitution in Cu$_2$ZnSnS$_4$

The synthesis strategy is the same as that for the CZTS nanoparticles that replace different cations (Mn and Fe to replace Zn) and anions (S and Se). In a typical synthesis of quaternary nanoparticles, 50 mM of CuCl$_2$, 25 mM ZnCl$_2$, 25 mM MnCl$_2$, 25 mM FeCl$_2$, and 25 mM SnCl$_2$ were dissolved in 600 mM of oleylamine (amine-to-precursor molar ratio of 1:6) in a three-necked round-bottomed flask. The reaction mixture was heated at 120 °C for 15 min. in order to form the metal-amine complex under a nitrogen atmosphere. At this point, 100 mM of sulfur (selenium powder for CZTSe and CZTSSe) was added into the mixture, which immediately changed the color of the reaction mixture to light brown. Later, the temperature was raised to 220 °C at a rate of 5 °C/min with a further heating for 2 h. The obtained nanoparticles were collected from the growth solution by precipitation with acetone, followed by centrifugation and, hence, re-dispersion in hexane. After several hexane/acetone extractions, the final product was dried under vacuum.

4.2.2 Binder-free Ink Formulation and Thin Film Deposition

As-prepared nanoparticles were dispersed in toluene (150 mg/mL) to make nanoparticle ink. The dispersed nanoparticles were ball milled for 10 h to form a uniform ink. The toluene-
based ink was found to be stable for many months without precipitation. These inks were deposited onto various substrates (fluorine-doped tin oxide (FTO), soda-lime glass, and molybdenum (Mo)-coated glass) by simple knife-coating (also known as doctor blade method) [12]. Typically, a small amount of the concentrated nanoparticle ink is drop-casted on the edge of a substrate; adhesive tape (scotch tape) is then used as a doctor-blading guide. The thickness of the tape determines the initial thickness of the doctor-bladed film. A circular glass rod was used to deposit the films. A second coat of the ink was then applied in a manner similar to the first one to fill the cracks in the first layer, resulting in the final film. The substrate was immediately coated with the CZTS layer, after which was covered with a narrow tube end funnel to prevent fast evaporation of the solvent. Fast evaporation of solvent could create cracks in the film, which is undesirable.

4.2.3 Control of S/Se Ratio in Cu$_2$ZnSnS$_4$

After each coating, the thin films were annealed at 400 ºC for 30 min with a continuous flow of argon (Ar) gas in a tubular furnace in order to remove the capping agent (amine, in this case) and to improve the conductivity. After the annealing, the films were sulfurized (selenized) using sulfur (selenium) powder heated at 550 ºC for 30 minutes with a continuous flow of argon in a tubular furnace. The residual sulfur was removed by dipping the film in isopropyl alcohol for 2 min.

4.2.4 Solar Cell Assembly and Processing

Fabricated the solar cells device stack consist of glass/ Mo/ CMTS/Se (700 nm)/ CdS (50 nm)/ ZnO (100 nm)/ Al: ZnO (300 nm)/Al (contact) (Figure 4.1). After Mo deposition, a 700 nm-thick absorber layer was deposited by the doctor blade deposition method followed by sulfurization, as discussed in the sections above. A 50 nm thick CdS film was deposited by chemical bath deposition. Further intrinsic ZnO was deposited on CdS by dielectric sputtering and Al doped ZnO was deposited on intrinsic ZnO by metal sputtering. On top, Al contacts
were deposited through thermal evaporation system. Finally, the total area (1.44 cm²) of all the devices was defined by mechanical scribing of the samples.

![Diagram](image)

**Figure 4.1** Schematic diagram of CMTS/Se (M=Zn, Fe, Mn) thin-film solar cell.

### 4.2.5 Characterization Techniques

The as-prepared nanoparticles were characterized using XpertPANAlytic X-ray diffractometer with Cu Kα radiation (λ= 1.54 Å), Raman scattering (Lab RAM HR 800 Micro laser Raman system in back scattering geometry using the 514.5 nm line of Ar⁺-laser as an excitation source), field emission gun scanning electron microscope (FEGSEM) (JEOL JSM-7600F FEG-Scanning Electron Microscope operated at 15 kV) and energy-dispersive X-ray analysis (EDX), inductively coupled plasma atomic emission spectroscopy (ICP-AES) characterization techniques. High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained with JEOL JEM 2100F, field emission gun transmission electron microscope (FEGTEM) at an accelerating voltage of 200kV. The chemical composition and valence states of the constituent elements were analyzed by X-ray photoelectron spectroscopy (Thermo VG Scientific MultiLab, ESCA Probe using Al Kα (hv = 1486.6 eV),) which was used as the excitation source for identification of the oxidation state. The optical properties of quaternary chalcogenide
nanoparticles were measured by UV-visible absorption and transmittance spectroscopy (Lambda 950-Perkin Elmer).

The electrical properties (carrier concentration, Hall mobility, and electrical resistivity) were acquired using a Hall Effect measurement system (Model 8404 AC/DC, Lake Shore) with an applied magnetic field intensity of 0.50 T by a four-point probe using van der Pauw geometry. I-V curves of the thin films measured using a solar simulator (AM 1.5 G, 100 mW/cm$^2$). The photo voltaic (PV) characteristics of the fabricated devices were measured using a Keithley 2400 source meter and a Newport solar simulator (model number 91160) with AM 1.5 G illumination. External quantum efficiency (EQE) measurements were carried out by a double source illumination system (Xenon lamp, QTH lamp). All measurements were performed at room temperature.

4.3 Results and Discussion

4.3.1 Influence of Anion/Cation Substitution in Cu$_2$ZnSnS$_4$

4.3.1.1 Phase Transformation from Kesterite to Zincblende

X-ray diffraction (XRD) measurements were carried with all nanoparticles in order to analyze the crystal phase. Figure 4.2a shows the XRD patterns (along with corresponding ICDD patterns) of Cu$_2$ZnSnS$_4$, Cu$_2$FeSnS$_4$, Cu$_2$MnSnS$_4$, Cu$_2$ZnSnSe$_4$, Cu$_2$ZnSn(S$_{0.5}$Se$_{0.5}$)$_4$ nanoparticles that were prepared at a large-scale. The CZTS sample show major peaks at 28.5, 47.3, and 56.1, 2θ-values, which can be indexed as (112), (220) and (312) planes, corresponding to the kesterite structure (ICDD No: 00-026-0575). The strongest intensity of the (112) peak suggests the favored orientation effect on the structure of the crystal. When there is partial substitution of sulfur with Se atoms the XRD peaks shift to lower 2θ angles. After complete replacement of sulfur with Se, we obtain CZTSe, the XRD peaks of which are appear at lower 2θ angles when compared to both CZTS and CZTSSe. The shifting of the XRD peaks to lower angles implies an increase in lattice parameter values, which is expected,
given the larger atomic radius of Se (atomic radius~ 0.198 nm) in comparison to sulfur (atomic radius~0.184 nm) [13]. When Zn is substituted with Mn, the nanoparticles show a zincblende crystal structure, which matches quite well with the reported literature [4]. CFTS diffraction patterns can be indexed to the zincblende structure, which corresponds similar with the reported literature [14]. The lattice parameters are calculated for all the nanoparticles from the XRD data and presented in Table (4.1). We found that there is an increase in the value of the lattice parameters when partial or total replacement of sulfur with selenium is achieved. According to Salome et al., the (112) peak position of CZTSSe is used to estimate the ratio of S/(S+Se) [15]. The (112) peak position (2θ=27.55°) of CZTSSe lies between the CZTS and CZTSe. The relation between the (112) peak position and the ratio is expressed by the following equation [15]:

\[
\frac{[S]}{[Se+S]} = \frac{x-27.05}{A} \quad \text{(4.1)}
\]

where A is a linear factor and takes the value 1.45, which results from the (112) peak position difference between the CZTS and CZTSe, and x is the CZTSSe peak position. By using this equation the composition ratio is estimated to be 34%, which is close to the EDS results.

**Figure 4.2** The powder XRD patterns of kesterite and zincblende Cu₂MnSnS₄/Se₄ (M=Zn, Mn and Fe) nanoparticles. The substitution of different metals leads to change in lattice volume as indicated by the peak shift toward the lower diffraction angle. (b) Raman spectra of all the sulfurized/selenized nanoparticles thin film samples.
The XRD results of the ternary and quaternary nanoparticles alone cannot confirm their crystal structure; this is because of the same peak positions for two phases (kesterite and stannite) as well as for secondary phases such as ZnS and Cu$_2$SnS$_3$ [16]. Therefore, we applied Raman spectroscopy measurements for the phase analysis of all sulfurized/selenized nanoparticle thin films (Figure 4.2b). The most intense Raman peak in CZTS is observed at 338 cm$^{-1}$, which corresponds to the A$_1$ phonon mode of the kesterite structure of CZTS and agrees well with the literature [17]. The major Raman peak of CZTSe is observed at 196 cm$^{-1}$, which also corresponds to the A$_1$ phonon mode of the kesterite phase [18]. The shift of the A$_1$ vibration mode to lower energies is due to the substitution of S by Se. The CZTSSe shows the peak at 201 cm$^{-1}$, which is located in between the CZTS and CZTSe A$_1$ vibration mode [19].

The mid-location of the CZTSSe peak is ascribed to the change in the lattice vibrations after incorporation of S into the CZTSe lattice structure [20]. The peak shift is consistent with the XRD results. For the CFTS sample, Raman peaks are observed at 285 and 319 cm$^{-1}$. The peaks at 285 cm$^{-1}$ and 319 cm$^{-1}$ can be attributed to Cu$_2$FeSnS$_4$ [21, 22]. The major peak at 319 cm$^{-1}$ is due to the strongest asymmetrical vibration of a pure anion mode of the sulfur atom around the Sn metal [21, 22]. The peak at 285 cm$^{-1}$ corresponds to a pure anion mode around the Cu cation [21, 22]. The CMnTS also shows a strong peak positioned at 328 cm$^{-1}$, which is again attributed to the A$_1$ mode of CMnTS [11]. Thus, the XRD and Raman results confirm that nanoparticles are in requisite phase and secondary phases are not present in as-synthesized samples.

The as-synthesized nanoparticles are capped by the long chain amine groups and organic solvents (toluene) used in the ink formulation also contain carbon atoms. However, organic impurities need to be removed from the films for realistic applications [23]. If a solvent is not removed completely, it will leave carbon residues on the surface of the as-synthesized nanoparticle film. The carbon residues can reduce the surface energy of the particles and hinder the growth of nanoparticle thin films [23]. Thus, for the grain growth to occur, the surface of the nanoparticles needs to be cleaned properly. At high-temperature heat treatment, the solvent evaporates and thus it gets removed from the film. In order to analyze the carbon residues in the as-deposited, annealed and sulfurized CZTS thin films, Raman spectroscopy (Figure 4.3) measurements are performed to estimate the carbon presence in the CZTS films.
qualitatively. The Raman measurements show the peaks positioned at 1350 and 1582 cm\(^{-1}\) in the as-deposited films, which correspond to D and G peaks of graphitic carbon [24]. The intensities of D and G peaks were drastically suppressed after annealing the films at 400 °C in an argon gas atmosphere. After sulfurization, the D and G peaks completely disappear; this indicates that the carbon residues are completely removed from the films. The complete removal of carbon residues might be due to interaction of carbon with sulfur vapor to form CS\(_2\), COS, and H\(_2\)S [25]. Moreover, if rich carbon residues are present in the sample, then more sulfur is required to interact with these carbon residues so as to form a clean surface for the crystal growth [25].

![Figure 4.3](image)

**Figure 4.3** Raman spectra of the CZTS as-deposited, annealed, and sulfurized thin films.

### 4.3.1.2 Morphological and Compositional Analysis

Transmission electron microscopy was performed to investigate the size, shape, and distribution of the as-synthesized particles. The high resolution TEM (HRTEM) image shows the bright fringes with a 3.13 Å lattice spacing (Figure 4.4a). This d-spacing corresponds to the (112) lattice plane of kesterite CZTS (ICDD No: 00-026-0575).

The selected area electron diffraction (SAED) pattern (inset of Figure 4.4a) shows the polycrystalline nature of the sample; the indexed planes match well with the tetragonal
kesterite phase of CZTS (ICDD No: 00-026-0575), which further confirms the phase purity of the nanoparticles. Figure 4.4b–f shows the transmission electron microscope images of all the quaternary chalcogenide nanoparticles that are produced at gram scale (Insets of Figure 4.4). In each case, the nanoparticles are nearly spherical, with a standard deviation of $\sigma \leq 20\%$ in the particle size distribution.

**Figure 4.4** (a) HRTEM and SAED images of CZTS nanoparticles, large-area TEM image of (b) CZTS, (c) CFTS, (d) CMnTS, (e) CZTSe, (f) CZTSSe nanoparticles produced at a large scale, and inset photographs show a particular batch of nanoparticles that were produced at a large scale.

Thermo gravimetric analysis (TGA) of CZTS samples performed under N$_2$ atmosphere up to 1000 °C reveals the presence of a significant proportion of volatile compounds (around 10 wt %) in the CZTS particles (Figure 4.5a). TGA curve of the CZTS nanoparticles shows a well-defined weight loss profile over a temperature range of 240–415 °C, which is attributed to the decomposition of the organic ligands that are attached to the particle surface, such as oleylamine and chemisorbed amine-modified complexes. The early weight loss of approximately 4% can be ascribed to the removal of physically adsorbed water molecules and
trace solvent molecules [26, 27]. In addition to the films’ composition, surface morphology
and cross-sectional analysis are also crucial to evaluate the uniformity and the grain size of
the film. A large grain size with minimal defects and large-area uniformity are necessary for
the improvement of the performance of the solar cell. The as-deposited films show smaller
grains, which is not desirable if the solar cells are to be high in efficiency. Hence the as-deposited thin films should be annealed at higher temperatures in order to achieve appropriate
grain size and crystallinity. Figure 4.5b–f shows the SEM images of surface and cross-
sectional morphologies of all the samples after sulfurization/selenization. The surface
morphologies of the samples show dense and large grains as a result of the post sulfurization/selenization process. The same trend was found in the grain sizes of all the
samples. The highest grain size with densely packed grains was observed in case of the
CZTSe and CZTSSe, while slightly smaller grains are seen in the CZTS, CMnTS, and CFTS
samples. The enhanced grain growth is due to selenium inclusion in CZTS; this has also been
found in most investigations on Se substitution in CZTS [20]. The increased grain size of the
CZTSSe absorber layer decreases the charge carrier recombination at the grain boundaries
[28]. The insets of Figure 4.5 show the cross-sectional SEM images of the nanoparticle thin
films after sulfurization/selenization, with thicknesses varying from 800–900 nm. All films
are uniform and show a compact arrangement of nanoparticles without any voids and other
structural defects such as cracks.

The compositions of all the as-synthesized, annealed and sulfurized nanoparticle films
were determined using energy-dispersive X-ray spectroscopy (EDX), inductively coupled
plasma atomic emission spectroscopy (ICP-AES) and are listed in Table (4.1). The as-
synthesized CZTS, CZTSSe, and CZTSe samples are slightly rich in Zn-content and the ratios
of Sn and Cu are almost stoichiometric. Annealing was carried out in the presence of argon
gas to avoid Sn–S loss. From the kinetic gas theory (Hertz–Knudsen equation), maximum
evaporation rate per area \( A \) in the vacuum can be expressed as [29]:

\[
\frac{1}{A} \frac{dn}{dt} = \frac{P}{\sqrt{2\pi m k_B T}} \quad (4.2)
\]

where \( m \) is the mass of the evaporant particles; \( P \) is the equilibrium vapor pressure of the
evaporating particles at the temperature, \( T \); and \( k_B \) is the Boltzmann constant. This Hertz–
Knudsen equation is valid if the evaporation process is carried out in a vacuum; however, in a gas atmosphere, this approach is not applicable any more [29]. In a gas atmosphere, there are collisions between evaporating particles and the surrounding gas particles and, thus, the evaporation is limited by diffusion and convection in the surrounding gas phase [29]. Hence, the evaporation rate in an inert gas atmosphere is always lower than the vacuum. Even though there might be apprehension about Sn–S loss after heat treatment in vacuum; there is no significant loss of Sn–S in the films after heat treatment in presence of an argon gas atmosphere.

![Figure 4.5](image)

**Figure 4.5** (a) TGA curve of the as-synthesized CZTS nanoparticles. TGA indicates that the content of the oleylamine ligands on the CZTS nanoparticles’ surfaces is about 10 wt%. SEM surface morphologies of the sulfurized/selenized (b) CZTS, (c) CFTS, (d) CMnTS, (e) CZTSe, and (f) CZTSSe nanoparticles film on the Mo/glass substrate. The inset shows the corresponding SEM cross sections of the sulfurized/selenized nanoparticle film on the Mo-coated glass substrate.
Table 4.1: Compositional analysis and lattice parameters of all the nanoparticles.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Precursor Ratio</th>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before annealing</td>
<td>After annealing</td>
</tr>
<tr>
<td></td>
<td></td>
<td>:3.9</td>
<td>:3.1</td>
</tr>
<tr>
<td>CZTS</td>
<td>ICP</td>
<td>1.9:1.1:1.1 :4</td>
<td>1.9:1.0:0.8 :3.1</td>
</tr>
<tr>
<td></td>
<td>EDX</td>
<td>1.8:1.2:1.0 :4</td>
<td>1.9:1.1:0.9 :3.4</td>
</tr>
<tr>
<td>CZTSSe</td>
<td>ICP</td>
<td>2.1:1.0:1.0 :2.3:2.4</td>
<td>1.9:1.0:1.1 :2.3:2.2</td>
</tr>
<tr>
<td></td>
<td>EDX</td>
<td>2.0:1.1:1.1 :2.5:2.5</td>
<td>2.0:1.1:1.0 :2.2:2.3</td>
</tr>
<tr>
<td>CZTSe</td>
<td>ICP</td>
<td>1.8:1.1:1.2 :3.5</td>
<td>2.0:1.0:0.8 :2.8</td>
</tr>
<tr>
<td></td>
<td>EDX</td>
<td>1.9:1.2:1.1 :3.2</td>
<td>1.9:1.1:0.9 :3.0</td>
</tr>
<tr>
<td>CMnTS</td>
<td>ICP</td>
<td>2.0:1.1:1.0 :4.1</td>
<td>2.0:1.0:0.9 :3.4</td>
</tr>
<tr>
<td></td>
<td>EDX</td>
<td>2.0:1.2:1.1 :4.0</td>
<td>1.9:1.1:0.9 :3.6</td>
</tr>
<tr>
<td>CFTS</td>
<td>ICP</td>
<td>1.8:1.1:1.0 :4.1</td>
<td>1.9:1.1:0.8 :3.9</td>
</tr>
<tr>
<td></td>
<td>EDX</td>
<td>2.0:1.2:1.1 :4.0</td>
<td>1.9:1.2:0.9 :3.8</td>
</tr>
</tbody>
</table>

4.3.1.3 Band gap Control

An optimal direct band gap and high absorption coefficient is among the most basic requirements for a high performance solar cell. We characterize the UV-visible absorption spectra of quaternary chalcogenide nanoparticles (dispersed in toluene) using UV-visible spectrometer in the wavelength range of 300-1200 nm (Figure 4.6a). The optical band gap of the Cu$_2$MSnS$_4$ (M= Zn, Fe, Mn) nanoparticles is calculated using Tauc’s plot (Figure 4.6b). Figure 4.6a shows the absorption spectra of Cu$_2$ZnSnS$_4$, Cu$_2$FeSnS$_4$, Cu$_2$MnSnS$_4$, Cu$_2$ZnSnS$_4$, Cu$_2$FeSnS$_4$, Cu$_2$MnSnS$_4$,
Cu$_2$ZnSnSe$_4$, Cu$_2$ZnSn(S$_{0.5}$Se$_{0.5}$)$_4$ and the corresponding band gap of 1.51, 1.46, 1.28, 1.04, and 1.24 eV, respectively. These band gap values are similar to those reported in the literature [14, 5, 30–32]. The estimated band gap of CZTSSe is 1.24 eV, which is larger than that of CZTSe and less than that of CZTS. The band gap estimation by using Tauc’s plot for CZTSe family is usually not reliable due to the presence of mid gap states and the band gap strongly depends upon the composition of the films [32–33].

According to reference [32], the band gap of CZTSSe can be estimated by the following equation:

$$E_g(x) = xE_g(CZTS) + (1 - x)E_g(CZTSe) - bx(1 - x) \quad (4.3)$$

where $x$ is the composition ratio of sulfur and selenium, and $b$ is the specific compositional independent optical bowing constant that describes the degree of nonlinearity in the band gap. According to theoretical calculations, the $b$ value for the CZTSSe sample is 0.1 eV [15]. Thus, the calculated band gap is 1.25 eV, which is very close to the experimental value. As-prepared nanoparticles show absorption in the whole visible range. In addition, CFTS spectra show a broad band that extends from approximately 400 nm to 600 nm. The absorbance band centred at 502 nm represents the excitonic band of CFTS [6]. The absorption coefficients of all the thin film samples were calculated from the UV-visible transmittance data at 600 nm (inset of Figure 4.6b). The optical-absorption coefficient ($\alpha$) was calculated from the transmittance data using the following equation [34]:

$$\alpha = \frac{1}{t} \ln \left[ \frac{1}{T} \right] \quad (4.4)$$

where $t'$ is the film thickness, and $T$ is the transmittance. Almost all samples show an absorption coefficient of an order ($\approx 10^4$ cm$^{-1}$) in the visible region, which is similar to theoretical estimation and plenty of experimental observations [34].
Figure 4.6 (a) Optical-absorption spectra of all the nanoparticles as labeled on the figure, (b) Tauc’s plot of various quaternary chalcogenide nanoparticles. The inset shows the absorption coefficient variations plot of various quaternary chalcogenide nanoparticles, which was calculated using Eqn. (4.4). The substitution of different anion/cations in CZTS leads to a change in the band gap energy, from 1.5 eV to 1.04 eV, with high optical-absorption coefficients (~$10^4$ cm$^{-1}$) in the visible region.

4.3.1.4 Electrical Properties

In order to investigate the potential of the quaternary chalcogenide nanoparticles as an active layer in photovoltaic applications, we have studied the photo-conductivity of the nanoparticle thin films. In order to measure the photo response, we used FTO as the back contact and silver (Ag) as the top contact (Figure 4.7a). Current-voltage (I–V) curves of the thin films were measured, both in the dark and under illumination using a solar simulator (AM 1.5G, 100 mW/cm$^2$). A current increment (by an order of 32%) is observed under illumination for all the samples, as shown in Figure 4.7b. The higher current shows an effective charge transfer characteristic, which confirms that the capping agent was removed from the nanoparticles surface [35]. The dark current for samples varies in the sequence CZTSSe > CZTSe > CZTS > CMnTS > CFTS thin films. Conventionally, illumination excites the electrons from the valence band to the conduction band and thus increases the hole concentration in the valence band, which enhances the conductivity of the film. This feature demonstrates the generation of photo current and confirms the potential use of these nanoparticles in photovoltaic applications.
Figure 4.7 (a) Schematic of the device geometry that was employed in order to study the photo response, and (b) I–V characteristics of CZTS, CFTS, CMnTS, CZTSe, and CZTSSe thin films under an AM 1.5G simulated solar illumination.

Hall Effect measurements were carried out in order to study the electrical properties of the thin films with an applied magnetic field of 0.50 T. As calculated from the Hall coefficient, all samples exhibit p-type conductivity. The resistivity, carrier concentrations, and Hall mobility of various nanoparticles are summarized in Table (4.2). The CZTSSe sample shows higher Hall mobility (13.6 cm$^2$/V–s) with a carrier concentration of $4 \times 10^{17}$ cm$^{-3}$, and lower resistivity (4 Ω-cm) when compared to all other samples, which is consistent with the higher current observed in the I–V characteristics (Figure 4.7b). The observed higher mobility of CZTSSe is due to the presence of larger grains and compact microstructure of the films, whereas CFTS and CMnTS show lower mobility. Larger grains have fewer grain boundaries, leading to lesser scattering of the charge carriers; this reduces the recombination rate of photo-generated charge carriers. The preliminary results based on optical-absorption, photo-response, and Hall measurements demonstrate that all these nanoparticles have the potential for use as an absorber layer in thin film solar cells.
Table 4.2: Electrical properties of nanoparticle films determined using the Hall measurement system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (Ω-cm)</th>
<th>Carrier concentration (cm$^3$)</th>
<th>Hall mobility (cm$^2$/V-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFTS</td>
<td>25</td>
<td>2×10$^{18}$</td>
<td>0.12</td>
</tr>
<tr>
<td>CMnTS</td>
<td>30</td>
<td>2×10$^{14}$</td>
<td>0.18</td>
</tr>
<tr>
<td>CZTS</td>
<td>15</td>
<td>1.3×10$^{16}$</td>
<td>8.5</td>
</tr>
<tr>
<td>CZTSe</td>
<td>9</td>
<td>3×10$^{17}$</td>
<td>10.2</td>
</tr>
<tr>
<td>CZTSSe</td>
<td>4</td>
<td>4×10$^{17}$</td>
<td>13.6</td>
</tr>
</tbody>
</table>

4.3.2 Device Characterization

4.3.2.1 J-V Characteristics

Figure 4.8a-c show the cross-sectional SEM images of the as-fabricated CZTS, and CZTSSe, and CZTSe solar cells. The three samples consist of well-faceted large-grain crystallites. The CZTSSe contains larger grains without any noticeable voids, whereas the CZTS sample shows small voids in the cross section of the device. The J–V characteristics of the fabricated devices are presented in Figure 4.8d and Table (4.3). The current densities of the CZTS-based solar cell exhibit a larger open circuit voltage ($V_{oc}$ of 498 mV than CZTSe-based solar cell $V_{oc}$=354 mV), which is expected because it has a higher band gap as compared to all other devices. However, due to the improved morphology and the bigger grain size, the short-circuit current, $V_{oc}$, of a CZTSe-based solar cell is found to be being significantly better when compared to the CZTS solar cell. In comparison, the CZTSSe devices show an efficiency of 7.6%, which is the highest, as expected from the Hall and photo-response measurements. It has also been observed that Se doping in CZTS enhances the electrical conductivity, mobility and solar cell power-conversion efficiency due to better grain growth and reduction of potential barriers at grain boundaries [13]. However, the device performance of the CZTSSe absorber in this study is still much lower than that which is produced by nanoparticle inks and hydrazine-based slurries [12]. We believe that increase of
the thickness of the precursor, the optimization of the annealing treatment, and the hydrazine
treatment will improve the growth of larger grains, and would ultimately lead to improved
performance of the CZTSSe-based solar cells. From Hall and photo-response measurements,
CZTSSe shows higher mobility; low resistivity leads to higher current density with a
reasonable fill factor. When compared to the rest of the devices, the CFTS devices show poor
performance due to low mobility and a higher carrier concentration, which is also confirmed
by Hall, the UV-vis absorption spectra, and photo-response measurements. Even though the
CFTS film has higher absorption, the solar cell efficiency is low because of low carrier
mobility and high carrier concentration.

Figure 4.8 SEM cross-sectional images of (a) CZTS, (b) CZTSSe, and (c) CZTSe thin-
film solar cells. The insets show digital photographs of as-fabricated CZTS and CZTSSe
solar cells, (d) Current density-voltage (J–V) characteristics of Cu$_2$MSnS$_4$/Se$_4$ (M=Zn, Mn
and Fe) nanoparticle thin-film solar cell devices that were measured under AM 1.5G-
simulated solar illumination.
Table 4.3: Quaternary chalcogenide nanoparticle based solar cell electrical performance parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>$E_g$ (eV)</th>
<th>FF (%)</th>
<th>$R_S$ ($\Omega$–cm$^2$)</th>
<th>$R_{SH}$ ($\Omega$–cm$^2$)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFTS</td>
<td>3.6</td>
<td>200</td>
<td>1.46</td>
<td>31</td>
<td>41</td>
<td>150</td>
<td>0.4±0.04</td>
</tr>
<tr>
<td>CMnTS</td>
<td>5.3</td>
<td>315</td>
<td>1.28</td>
<td>37</td>
<td>31</td>
<td>210</td>
<td>0.7±0.02</td>
</tr>
<tr>
<td>CZTS</td>
<td>15.6</td>
<td>498</td>
<td>1.51</td>
<td>56</td>
<td>8.0</td>
<td>700</td>
<td>4.5±0.12</td>
</tr>
<tr>
<td>CZTSe</td>
<td>25.1</td>
<td>354</td>
<td>1.04</td>
<td>57</td>
<td>6.0</td>
<td>420</td>
<td>5.2±0.10</td>
</tr>
<tr>
<td>CZTSSe</td>
<td>29</td>
<td>476</td>
<td>1.24</td>
<td>59</td>
<td>3.5</td>
<td>500</td>
<td>7.6±0.12</td>
</tr>
</tbody>
</table>

4.3.2.2 Quantum Efficiency Measurements

In order to study the wavelength-dependent photo responses of the solar cells, EQE measurements are performed for all the devices (Figure 4.9a). Near the blue region (above 450 nm) of the spectrum, the EQE data shows a sudden decay in all the devices, which is due to the absorption loss of the CdS/ZnO/AZO layers [36]. From 300–350 nm, the EQE sharply increases, which is consistent with the reported literature [36]. The EQE of the CZTS solar cell shows a maximum value of 68% at 600 nm and then drops slowly from 610 nm to 745 nm. This can be ascribed to higher reflection and recombination losses due to the low carrier diffusion length of the CZTS layer [36]. In this region, when all the devices were compared, the CZTSSe device showed a stronger photo-response (≈80%). The EQE in the visible region and near the infrared region shows more potential for CZTSe and CZTSSe cells when compared to other cells. This high EQE is mainly a result of good carrier collection due to the higher carrier mobility of generated charge carriers in the absorber layer. The cut off wavelength of CZTSSe extends to near the infrared (IR) region, whereas, the CZTS solar cell showed a cut off wavelength at 900 nm. The extended cut off wavelength in CZTSSe is attributed to the lower band gap (1.24 eV) in comparison to CZTS (1.51 eV). The replacement of sulfur with selenium lowers the band gap from 1.51 eV to 1.24 eV, which increases the
current density in the CZTSSe solar cell remarkably. The CMnTS and CFTS show a weak photo response in the visible region, which could be due to poor carrier collection because of low carrier mobility. Moreover, the high series resistance ($R_S$) might be due to charge carrier recombination at the interface of Mo and the absorber layer because of voids. The low shunt resistance ($R_{SH}$) values can be attributed to the smaller grain size. Thus, further optimization in the thickness of the absorber layer and in the controlling of the grain size and the device fabrication process are essential. The band gap of Cu$_2$MSnS$_4$/Se$_4$ (M= Zn, Fe, Mn) nanoparticles is calculated from the plot of $[h\nu \times \ln(1 − EQE)]^2$ vs. $h\nu$, where $h\nu$ is the photon energy [36]. As shown in the Figure 4.9b, these determined band gap values for the Cu$_2$ZnSnS$_4$, Cu$_2$FeSnS$_4$, Cu$_2$MnSnS$_4$, Cu$_2$ZnSnSe$_4$, Cu$_2$ZnSn$(S_{0.5}Se_{0.5})_4$ are 1.53, 1.26, 1.32, 1.03, and 1.12 eV, respectively, which are in reasonable agreement with the band gap extracted from the absorption spectra measurement (Figure 4.6b).

**Figure 4.9** (a) EQE of Cu$_2$MSnS$_4$/Se$_4$ (M=Zn, Mn and Fe) nanoparticle thin-film solar cell devices that were measured under AM 1.5G-simulated solar illumination, (b) The band gap of the various quaternary chalcogenide nanoparticle absorber layers obtained from a plot of $[h\nu \times \ln(1 − EQE)]^2$ vs. $h\nu$.

### 4.4 Summary

We have synthesized Cu$_2$MSnS$_4$/Se$_4$ (M=Zn, Mn and Fe) quaternary chalcogenide nanoparticles by the thermolysis process. The nanoparticle films have high phase purity; the
absence of secondary phases is confirmed using Raman spectroscopy and XRD measurements. It has been observed that the heat treatment in the presence of an inert gas suppressed the Sn and S losses from the films. UV-vis spectroscopy data shows that the films have a high optical-absorption coefficient ($10^4 \text{ cm}^{-1}$) in the visible region, and that their optical band gap varies from 1.04 to 1.51 eV. Among all the synthesized nanoparticles, highest photo current is obtained for the CZTSSe nanoparticles. We also fabricated the solar cells with these nanoparticles and tested their device performance. The efficiency of the CZTS solar cell enhances significantly, from 4.5% to 7.6%, with selenium doping. The variation of device performance may be ascribed to the change in the micro structure and the band gap. In conclusion, the observed changes in structural, optical, and device performances due to anion/cation substitution in CZTS should be further explored for obtaining higher power-conversion efficiencies in future.

4.5 References


Chapter 5

CZTS/Silica Composites: An Efficient Light Trapping Platform

5.1 Motivation

In the progress of CZTS solar cell efficiency, the better efficiencies reported in literature are 6.8\% with thermal co-evaporation and co-sputtering [1, 2], 7.8\% with CZTS nanocrystal absorber layer [3] and 8.4\% with thermally evaporated 600 nm absorber layer [4]. The measured cell parameters corresponding to the best efficiency of 8.4\% are as follows: 19.5 mA/cm$^2$ short circuit current density ($J_{SC}$), 661 mV open circuit voltage ($V_{OC}$) with 66\% fill factor (FF). However, the maximum attainable current density $J_{max}$ was found to be 31.2 mA/cm$^2$ calculated with the assumption of 100\% absorption and collection efficiency for photon energies above the band gap. This difference between the theoretical maximum and the measured electrical current density is probably due to: a) transmittance (non-absorbance)
of near band gap wavelengths because of its lower absorption coefficient at those wavelengths and b) recombination of generated carriers due to lower minority carrier diffusion lengths (mobilities) ~ 350nm (6–30 cm²/V s) [5, 6]. The carrier diffusion length and mobility might be even worse in CZTS absorber layers prepared with CZTS nanoparticles; because of their smaller grains leads to more number of grains results in scattering of generated carriers, consequently the lower cell power conversion efficiency (PCE) than bulk CZTS solar cells. Main reason for getting less efficiency in thin film solar cells is transmission losses at near band gap region due to its lower absorption coefficient [7] and lower minority carrier diffusion lengths. According to Beer-Lamberts law \( I=I_0 e^{-\alpha t} \), these losses can be reduced by increasing a) thickness of absorber layer (t), b) absorption coefficient (\( \alpha \)) and c) locally increasing the intensity of incident radiation. But increasing the thickness results in increase in recombination of generated carriers, because of lower minority carrier diffusion lengths and \( \alpha \) cannot be increased drastically as it is material intrinsic property. The only option left is increasing the intensity of incident light locally by introducing suitable dielectric nanoparticles or plasmonic nanostructures as a scatterer. In principle, the aim is to increase the path length of the propagation within the absorber layer for absorbing more light by scattering the sunlight after it has entered from the top surface.

Recently, researchers started exploring different techniques for light trapping and have received a lot of attention in silicon based solar cells [8-10]. Embedding nanoparticles in the active layer and surface texture leads to higher absorption of light [8-10]. Especially, metal nanoparticles have been embedded in the absorber layer of solar cell to enhance the optical absorption due to localized surface plasmon resonance (LSPR) [11]. However, the metal nanoparticles themselves absorb the light, losses some portion of incident light and also acts as a recombination centers for generated carriers [12]. To overcome these issues, researchers from the University of Utah proposed a novel idea of scattering of light by embedding silica nanoparticles in the silicon solar cell absorber layer [9]. In crystalline silicon (c-Si) solar cells, Nagel et al. have predicted 23% absorption enhancement with 200nm SiO₂ particles in 1\( \mu \)m thick c-Si [9] and about 15% efficiency enhancement has been predicted through coupled optical and electrical calculations for this system [10]. Incorporating silica nanoparticles has more advantages over metal nanoparticles (LSPR); as silica nanoparticles
are lossless in the visible region (because silica imaginary part of refractive index is zero), allows light directly to couple into the solar cell and silica surface has low dangling bonds with extremely low surface recombination velocities [12]. In motivation of above, we embedded the silica nanoparticles into the CZTS active layer; studied the effect of its position in the absorber layer on optical absorption and cell performance parameters theoretically and experimentally as well.

5.2 Experimental Section

5.2.1 Preparation of Cu$_2$ZnSnS$_4$ and Silica Nanoparticles

In a typical synthesis of 8 nm-sized Cu$_2$ZnSnS$_4$ nanoparticles, 50 mM of CuCl$_2$, 25 mM ZnCl$_2$, and 25 mM SnCl$_2$ were added to 400 mM of oleylamine (amine-to-precursor molar ratio of 1:4) in a three-necked round-bottom flask. The reaction mixture was heated at 120 °C for 15 min. to form the metal-amine complex under nitrogen atmosphere. At this point, 100 mM of sulfur was added into the mixture, resulting in an immediate color change of the reaction mixture to light brown. Later, the temperature was raised to 220 °C at a rate of 5 °C/min with a further heating for 2 h. The obtained nanoparticles were collected from the growth solution by precipitation with acetone, followed by centrifugation and hence re-dispersion in hexane. After several hexane/isopropanol extractions, the final product was dried under vacuum.

To synthesis silica nanoparticles (diameter = 150 nm), we employed a modified Stober synthesis process [13]. Solution (soln.1) containing 9.5 ml ammonia (30%) in 50 ml ethanol (99%) is taken. Another solution (soln. 2) is prepared by mixing 5 ml of TEOS in 30 ml ethanol. Now, soln. 2 is added drop wise (0.5 ml/minute) to soln. 1 under stirring conditions and an argon blanket. The reaction mixture is kept on stirring for 12 hours. Thereafter, the silica particles are centrifuged out and cleaned via repeated centrifugation and re-dispersion process. The so obtained silica nanoparticles are then dried and used further.
5.2.2 Ink Formulation and Thin Film Deposition

As-prepared nanoparticles were first dispersed in toluene (150 mg/mL) to make the nanoparticle ink. Next, we took 15 mg of silica NPs and added them to CZTS nanoparticles ink followed by a 24 hour ball-milling process so as to obtain a uniformly textured ink. We have prepared CZTS nanoparticles ink with and without silica nanoparticles. To make a multi-layered CZTS thin film, first we used knife coating process to obtain a CZTS thin layer (10 microls of CZTS ink, layer 1) over Mo substrate. To get a second layer (layer 2) embedded with silica NPs we coated (via knife coating procedure only) CZTS+silica ink (10 microls) over layer 1. Thereafter, we again knife coated a third coat of CZTS ink (10 microls) over layer 2. The overall procedure thus resulted in formation of a CZTS thin film which is embedded with 150 nm silica particles in middle of the active layer and the same procedure followed for particles placed atop and bottom of absorber layer.

5.2.3 Surfactant Removal and Sulfurization

After each coating, the thin films were annealed at 400 ºC for 30 min with a continuous flow of argon gas in a tubular furnace to remove the capping agent (amine in our case) and to improve the conductivity. After the annealing, the films were sulfurized using sulfur powder heated at 550 ºC for 30 minutes with a continuous flow of argon in a tubular furnace. The residual sulfur was removed by dipping the film in isopropyl alcohol for 2 min.

5.2.4 Solar Cell Assembly and Processing

Fabricated CZTS solar cells device stack consist of glass/ Mo/ CZTS: SiO₂ NPs (900 nm)/ CdS (50 nm)/ ZnO (100 nm)/ Al: ZnO (300 nm)/Al (contact). A 50 nm thick CdS film was deposited by chemical bath deposition [14]. Further intrinsic ZnO was deposited on CdS by dielectric sputtering and Al doped ZnO was deposited on intrinsic ZnO by metal sputtering. On top, Al contacts were deposited through thermal evaporation system. Finally,
the total area (1.44 cm$^2$) of all the devices was defined by mechanical scribing of the samples. The schematic of the device structure is shown in Figure 5.1.

Figure 5.1 Schematic diagram of CZTS thin-film solar cell with embedded silica nanoparticles.

5.2.5 Characterization Techniques

The as-prepared nanoparticles were characterized using XpertPANAlytic X-ray diffractometer with Cu Kα radiation (λ= 1.54 Å), Raman scattering (Lab RAM HR 800 Micro laser Raman system in back scattering geometry using the 514.5 nm line of Ar$^+$-laser as an excitation source). Transmission electron microscopy (TEM) images were obtained with JEOL JEM 2100F, field emission gun transmission electron microscope (FEGTEM) at an accelerating voltage of 200kV. The optical properties of quaternary chalcogenide nanoparticles were measured by UV-visible absorption and transmittance spectroscopy (Lambda 950-Perkin Elmer). The photo voltaic (PV) characteristics of the fabricated devices were measured using a Keithley 2400 source meter and a Newport solar simulator (model number 91160) with AM 1.5 G illumination.
5.2.6 Simulation Methodologies

To explore the enhancement in optical absorption and cell performance parameters with embedded silica NPs into CZTS absorber layer, we performed optical absorption and Mie scattering calculations with Lumerical’s FDTD multi coefficient model (MCM) [15], which essentially solves the Maxwell equations using Finite Difference Time Domain (FDTD) technique. Sampled data for optical constants of CZTS absorber material were taken from reference [16] and for other materials silica (SiO$_2$), cadmium sulfide (CdS), zinc oxide (ZnO) is taken from reference [17].

5.3 Results and Discussion

5.3.1 Structural Investigation

Figure 5.2 (a) XRD spectrum of CZTS nanoparticles. The XRD peaks have been indexed to tetragonal CZTS (ICDD No: 00-026-0575), (b) Raman spectra of CZTS nanoparticles.

For analyzing the crystal phase of the as prepared nanoparticles, X-ray diffraction (XRD) and Raman analysis were carried out. Figure 5.2a shows the XRD pattern of the CZTS nanoparticles prepared at large scale. The observed peaks are matches well with the kesterite structure of CZTS (ICDD No: 00-026-0575). Crystallite size estimated from FWHM of the
(112) peak using Scherrer formula is 8 nm [18], which is in agreement with the TEM data. However, ternary and quaternary nanoparticles XRD results cannot confirm their crystal structure due to the same peak positions of two phases (kesterite and stannite) and also for some of the secondary phases such as ZnS and Cu$_2$SnS$_3$ [19]. Therefore, we employed the Raman spectroscopy measurements for the phase analysis of CZTS nanoparticles. Figure 5.2b shows the Raman spectroscopy data for CZTS nanoparticles. Raman data shows the broad peak at 338 cm$^{-1}$ corresponds to the CZTS kesterite phase (Figure 5.2b) [19]. The Raman peak observed at 338 cm$^{-1}$ which corresponds to the A$_1$ phonon mode of kesterite structure is in good agreement with the literature [19, 20]. The FWHM of Raman peak is larger than those observed in bulk CZTS. The broadening in Raman spectrum is attributed to the phonon confinement in the nanoparticles [21]. Thus, the XRD and Raman results confirm that our nanoparticles are in kesterite phase of CZTS and other secondary phases are absent.

5.3.2 Morphological Analysis

![TEM images](image)

**Figure 5.3** TEM images of (a) CZTS nanoparticles, (b) SiO$_2$ nanoparticles.

To reveal the CZTS and silica nanoparticles morphology, nanoparticles were dispersed in hexane (CZTS), ethanol (silica) and characterized by transmission electron microscope. Figure 5.3 shows the transmission electron microscope images of CZTS nanoparticles. The
CZTS and silica nanoparticles are close to mono disperse and spherical in shape. The average particle size of CZTS is 8±2 nm and silica is 150 nm.

5.3.3 Effect of Silica Particles Depth in the Absorber Layer

5.3.3.1 Optical Properties

Dispersive nature of optical constants was fitted with Lumerical’s FDTD multi coefficient model (MCM) [22]. Experimental sampled data and FDTD data fit are shown in Figure 5.4a for comparison. Accuracy of FDTD fit reflects the accurate results from optical simulations. Figure 5.4b shows that, near band gap wavelengths > 700 nm wavelengths require active layer thickness more than 1 μm for complete absorption. But, thickness more than diffusion length of minority carriers leads to recombination of carriers, consequently reduction in short circuit current density and efficiency. Hence using larger thickness of active layer won’t be useful any more, but if we are able to capture within the thickness of diffusion lengths of minority carriers, with some trapping mechanism it will be of great use to enhance the efficiency of the cell.

**Figure 5.4** (a) Optical constants (n, k) of CZTS used in optical calculation in comparison with FDTD fit, (b) Absorption co-efficient and absorption depth in CZTS as function of wavelength.
Angular distribution of scattered radiation (Mie scattering phase diagram) was calculated for 150 nm sized silica nanoparticle embedded in CZTS absorber layer are plotted in Figure 5.5a. From the Mie scattering phase diagram (Figure 5.5a.) implies that scattering from nanoparticle favors the forward direction (Light is incident along the Y axis); which is the nature of Mie scattering from larger particles at longer wavelengths. Here, we observe that lower wavelengths are scattered more in backward direction, while higher wavelengths in forward direction. Near-field intensity $|E|^2$ distribution around the silica NP at maximum scattering cross section wavelength (760 nm) from Mie scattering calculations are shown in Figure 5.5b, 5.5c and 5.5d.

![Figure 5.5](image)

**Figure 5.5** (a) Mie scattering phase diagram to show angular distribution of scattered radiation. Electric field intensity ($|E|^2$) distribution around the silica NP in (b) XY, (c) YZ, and (d) XZ planes from Mie scattering calculations.

Absorption ($Q_{abs}$) and scattering ($Q_{scat}$) cross sections are calculated for 150 nm sized silica nanoparticle embedded in CZTS absorber layer are plotted in Figure 5.6a. Scattering cross section ($Q_{scat}$) is maximum at about 760 nm with FWHM of 285nm (540-825 nm) shown in Figure 5.6a. These wide-range large $Q_{scat}$ values near the band gap of absorber layer
results in enhanced optical path length of scattered light consequently increase in optical absorption (charge carrier generation rate) and the same will reflects especially on short circuit current density. Maximum absorption cross section ($Q_{abs}$) at lower wavelength region might be due to absorption of optical near-field by CZTS layer and small peak at 760 nm is because of absorption of scattered radiation. We studied experimentally the influence of the embedded silica nanoparticles on optical absorption by varying particle positions (depth) in the active layer. UV-visible absorption spectroscopy was carried out from 300-950 nm. Figure 5.6b shows the absorption spectra of CZTS samples with silica nanoparticles at different depths in the active layer and it is the best for the sample with particles at its middle, then for particles atop and minimum for particles at the bottom (still it is more than the reference i.e. without nanoparticles). This is because, sample with particles at its middle captures both forward (lower wavelengths) and backward (higher wavelengths) scattered light effectively as active layer is on either side of the NPs. But, when NPs at the top only forward (lower wavelengths) scattered light will be absorbed efficiently as active layer is beneath the particle and for NPs at the bottom only backward (lower wavelengths) scattered light will be captured as absorber material is present above the NPs. Hence, the best optical absorption enhancement with NPs is achieved by placing at middle, then for particles atop and finally lower absorption for particles at bottom, electrically this sequence may not be true.

**Figure 5.6** (a) Absorption ($Q_{abs}$) and scattering ($Q_{scat}$) cross section for 150 nm silica nanoparticles embedded in CZTS absorber layer, (b) Optical absorption spectra of CZTS nanoparticles with embedded silica nanoparticles at different depths.
5.3.3.2 Electrical Properties

Figure 5.7a shows the calculated carrier generation rate in the XY-plane about 10 nm above for 150 nm particles embedded in the CZTS absorber layer. The enhanced carrier generation rate is clearly scene in vicinity of particle due to near field enhanced absorption effect. Electrical performance parameters measured for different particle configurations (Figure 5.7b) and are tabulated in Table 5.1. The best performance parameters are observed for NPs at the middle as expected from optical absorption measurements with efficiency (η=5.3%). But, the cell with NPs at the bottom is electrically better than the NPs atop i.e. electrically these two cases are altered from measured optical absorption. This altered electrical efficiency from optical absorption for particles atop might be because of (a) silica (highly resistive) NPs are closer to CZTS/CdS interface results in increase in series resistance (Rs), observed experimentally, (b) recombination of generated carriers at CZTS/SiO$_2$ interface in depletion region leads to reduced J$_{SC}$. These two effects in combination leads to lower power conversion efficiency for particles placed atop. But, for particles at the bottom of cell are closer to CZTS/Mo interface leads to improvement only in Rs and minimal affect on J$_{SC}$.

Figure 5.7 (a) Generation rate (XY-plane) about 10 nm above for 150 nm particles embedded in CZTS absorber layer, (b) JV characteristics of CZTS thin film solar cells with embedded silica nanoparticles at different depths.
Table 5.1: Solar cell electrical performance parameters for silica nanoparticles placed at various positions in CZTS absorber layer.

<table>
<thead>
<tr>
<th>Particle position</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V$ (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>$R_S$ (Ω·cm$^2$)</th>
<th>$R_{SH}$ (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>15.6</td>
<td>500</td>
<td>58</td>
<td>4.5±0.1</td>
<td>8</td>
<td>420</td>
</tr>
<tr>
<td>Top</td>
<td>14.6</td>
<td>477</td>
<td>56</td>
<td>3.9±0.1</td>
<td>12</td>
<td>392</td>
</tr>
<tr>
<td>Middle</td>
<td>18.2</td>
<td>503</td>
<td>58</td>
<td>5.3±0.1</td>
<td>4</td>
<td>500</td>
</tr>
<tr>
<td>Bottom</td>
<td>16.4</td>
<td>499</td>
<td>60</td>
<td>5.0±0.2</td>
<td>5</td>
<td>397</td>
</tr>
</tbody>
</table>

5.4 Summary

In conclusion, we have fabricated the CZTS solar cells with 150 nm sized silica nanoparticles at the top, middle and bottom of the absorber layer for light-trapping. The best optical absorption and electrical efficiency (η=5.3%) is observed for particles placed at the middle of the absorber layer; this is 18% more than that of the reference cell (η=4.5%). Particles placed on the top lead to higher optical absorption but lower conversion efficiency compared to particles at the bottom. This is possibly due to a combination of increased series resistance as they are adjacent to CZTS/CdS interface plus (CZTS/SiO$_2$) interface recombination in the device depletion region when the nanoparticles are situated there.

5.5 References


Chapter 6

Summary and Future Scope

The aim of this thesis is to fabricate high-quality quaternary chalcogenide thin films, to analyze the properties of thin-film materials, and to evaluate the performance of the thin films in solar cells. This chapter summarizes the results from the study.

We developed a fast and consistent process for the fabrication of high-quality CZTS thin films using a single-step electrodeposition process from an aqueous solution, which resulted in kesterite phase absorber layers that can be used in solar cell devices. We have demonstrated an experimental methodology to control the defects and the structural and optical properties of the CZTS film. The role of the deposition potential in the compositional, structural, and optical properties of CZTS films has been highlighted. This work demonstrates the optimization of single-bath deposition for CZTS films in a reproducible manner. We found that good quality films were obtained at a potential of -1.4 V versus Ag/AgCl. XRD
and Raman spectra revealed the kesterite crystal structure of the fabricated CZTS samples. UV-vis spectroscopy data showed that the films have a high optical absorption coefficient ($10^4 \text{ cm}^{-1}$) in the visible region; its optical band gap ranged from 1.1 to 1.8 eV, depending upon the type of deposition potential. XPS and EDX data also revealed that the film that was deposited at -1.4 V versus Ag/AgCl demonstrated an appropriate stoichiometry of the chemical composition as well as the valance states of the constituent elements, when compared to all other deposition potentials. An analysis of the nucleation and growth mechanism identified a diffusion-controlled instantaneous nucleation process. We fabricated the solar cells with the optimized deposition potential (-1.4 V vs. Ag/AgCl) and achieved a power-conversion efficiency of 5.0%. The external quantum efficiency (EQE) curve indicated that the CZTS absorber layer had an optical band gap of 1.5 eV, with a device EQE value of more than 60%. The extracted carrier life time (5.2 ns) from the TRPL data clearly demonstrated the reasonable electronic properties of the CZTS thin film.

The second part of this work reported the development of a simple and robust solution-based synthesis method for the fabrication of efficient CZTS thin-film solar cells. This solution-based approach provided better control over the stoichiometry and the particle sizes that ranged from 2.5 to 8 nm, by controlling the amine-to-precursor molar ratio. We demonstrate the synthesis of as much as 20 g of quaternary chalcogenide nanoparticles powder in a single reaction, without a size-sorting process. XRD and Raman data have confirmed the kesterite phase of the CZTS nanoparticles. The XPS data has further confirmed the presence of four constituent elements that have appropriate valence states. A low-cost, binder-free single solvent (toluene) was used to formulate the nanoparticle ink; the films were deposited by the doctor blade method. We have performed multiple heat treatments to remove surfactants and to improve the conductivity of the films. The UV-vis spectroscopy data showed that the films have a high optical absorption coefficient ($10^4 \text{ cm}^{-1}$) in the visible region; its optical band gap was estimated to be 1.51 eV. The fabricated devices exhibit efficiencies ranging from 3.6% to 4.5% depending on the CZTS particles average diameter. Comparison of EQE data suggests that our current is mainly restricted by collection losses.
The third part of this work reported the fabrication of CZTS-based solar cells that had high efficiencies, and were prepared by cation/anion substitution in the CZTS thin films. The substitution of Zn with Fe and Mn showed phase transformation from kesterite to stannite. The absorption characteristics showed that the earth-abundant compound Cu$_2$MSnS$_4$/Se$_4$ (M=Zn, Mn and Fe) had band gaps in the range of 1.0 to 1.5 eV, with high optical absorption coefficients (~$10^4$ cm$^{-1}$) in the visible region. The efficiency of CZTS solar cell is enhanced significantly from 4.5% to 7.6% with selenium doping. It has been proposed that the variation of device parameters with anion/cation substitution may be attributed to the change in the electronic structure of bulk CZTS thin films; this change affects the performance of the device in turn. The further improvement in the power-conversion efficiency was achieved by embedding silica nanoparticles (150 nm) into the CZTS active layer. The effect of the depth of the silica particles on the optical absorption and cell performance in the CZTS absorber layer were studied theoretically and experimentally. We fabricated the CZTS solar cells with silica nanoparticles of 150 nm at the top, middle, and bottom of the absorber layer, for light-trapping. The best optical absorption and electrical efficiency ($\eta=5.3\%$) was observed for particles that were placed at the middle of the absorber layer, which was 18% more than that of the reference cell ($\eta=4.5\%$). The particles that were placed at the top led to higher optical absorption, but lower conversion efficiency when compared to the particles at the bottom. This is possibly due to a combination of an increased series resistance due to their being adjacent to the CZTS/CdS interface and the CZTS/SiO$_2$ interface recombination in the device-depletion region when the nanoparticles are present there.

Based on these results from this study, some recommendations for future CZTS research are:

- In the present study, we have achieved an efficiency of 5.0% with single step electrodeposition process. Further studies can be focused on the improvement of CZTS grain size and film roughness, which are some of the existing challenges and needs to be addressed for an efficient solar cell design.

- The experimentally observed structural and band gap variations are interesting in case of impurities incorporation in CZTS, and should be further explored in perspective of material and device performance.
The doping properties of CZTS thin films should be better understood for the optimization of defects and optoelectronic properties. The obtained low fill factor and shunt resistance are necessary to investigate for further improvement. Need to investigate the effect of embedded silica particles size on optical absorption and solar cell performance parameters.

**Table 6.1:** Summary of all the solar cell electrical performance parameters fabricated by different methods.

<table>
<thead>
<tr>
<th>Electrodeposition Approach</th>
<th>Sample</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (mV)</th>
<th>FF (%)</th>
<th>R&lt;sub&gt;S&lt;/sub&gt; (Ω·cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>R&lt;sub&gt;SH&lt;/sub&gt; (Ω·cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTS</td>
<td>17.8</td>
<td>485</td>
<td>57.5</td>
<td>5</td>
<td>510</td>
<td>5.0 ± 0.10</td>
<td></td>
</tr>
<tr>
<td>Chemical Synthesis Approach</td>
<td>8 nm</td>
<td>15.6</td>
<td>500</td>
<td>58</td>
<td>8</td>
<td>420</td>
<td>4.5 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>6 nm</td>
<td>14.5</td>
<td>494</td>
<td>58</td>
<td>9</td>
<td>418</td>
<td>4.3 ± 0.11</td>
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<tr>
<td></td>
<td>5 nm</td>
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<td>493</td>
<td>57</td>
<td>9</td>
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<tr>
<td></td>
<td>3.5 nm</td>
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<td>491</td>
<td>58</td>
<td>10</td>
<td>390</td>
<td>3.8 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>2.5 nm</td>
<td>13.2</td>
<td>490</td>
<td>56</td>
<td>10</td>
<td>300</td>
<td>3.6 ± 0.12</td>
</tr>
<tr>
<td>Anion/Cation Substitution in CZTS</td>
<td>CFTS</td>
<td>3.6</td>
<td>200</td>
<td>31</td>
<td>41</td>
<td>150</td>
<td>0.4 ± 0.04</td>
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<tr>
<td></td>
<td>CMnTS</td>
<td>5.3</td>
<td>315</td>
<td>37</td>
<td>31</td>
<td>210</td>
<td>0.7 ± 0.02</td>
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<tr>
<td></td>
<td>CZTS</td>
<td>15.6</td>
<td>498</td>
<td>56</td>
<td>8.0</td>
<td>700</td>
<td>4.5 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>CZTSe</td>
<td>25.1</td>
<td>354</td>
<td>57</td>
<td>6.0</td>
<td>420</td>
<td>5.2 ± 0.10</td>
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<tr>
<td></td>
<td>CZTSSe</td>
<td>29</td>
<td>476</td>
<td>59</td>
<td>3.5</td>
<td>500</td>
<td>7.6 ± 0.12</td>
</tr>
<tr>
<td>Silica Nanoparticles placed at Different Depths</td>
<td>Reference</td>
<td>15.6</td>
<td>500</td>
<td>58</td>
<td>8</td>
<td>420</td>
<td>4.5 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>Top</td>
<td>14.6</td>
<td>477</td>
<td>56</td>
<td>12</td>
<td>392</td>
<td>3.9 ± 0.10</td>
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<tr>
<td></td>
<td>Middle</td>
<td>18.2</td>
<td>503</td>
<td>58</td>
<td>4</td>
<td>500</td>
<td>5.3 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>16.4</td>
<td>494</td>
<td>60</td>
<td>5</td>
<td>397</td>
<td>5.0 ± 0.20</td>
</tr>
</tbody>
</table>
Appendix I

Cu$_2$ZnSnS$_4$ Thin Film Solar Cell with Graphene Window Layer

AI.1 Motivation

Cu$_2$ZnSnS$_4$ (CZTS) solar cells with highest power conversion efficiency of 8.6% have been reported by IBM research group recently [1]. In this solar cell, aluminium doped zinc oxide (AZO) films have been used as transparent conducting window layer. However, AZO has strong absorption in the IR region of the spectrum which limits the photo generated current [2, 3]. Moreover, the thickness of the transparent conducting window layer plays an important role in trade-off between transparency and conductivity. For films with greater thickness, conductivity is more while transmittance suffers [4, 5]. To overcome these issues for growing demand in optoelectronic applications, there is a need to develop alternative high quality, low cost transparent electrodes. Graphene has the potential to replace the AZO due to
its high transparency, good electrical conductivity and absence of the thickness dependent interference effect [4-6]. In this chapter, we have demonstrated the graphene as a transparent conducting window layer in CZTS based solar cell to replace Al:ZnO (AZO).

AI.2 Experimental Section

AI.2.1 Cu$_2$ZnSnS$_4$ Electrodeposition

CZTS thin films were deposited on Mo coated glass by single bath electro deposition method followed by sulfurization. The aqueous electrolyte bath contains 0.02mol/L CuSO$_4$, 0.01mol/L ZnSO$_4$, 0.02mol/L SnCl$_2$ with 0.2 mol/L tri-sodium citrate, 0.01mol/L tartaric acid and 0.01mol/L Na$_2$SO$_4$ in deionised water. Three electrode-electrochemical cell was used for deposition. The cell contains Ag/AgCl as a reference, platinum wire as counter and Mo coated glass substrate as a working electrode. The tri-sodium citrate was used as a complexing agent for the precursors. The pH of electrolyte solution was maintained to 4.0-5.0. The Mo coated glass (2×2 cm$^2$) was cleaned ultrasonically with soap solution, acetone, isopropyl alcohol (IPA) and deionized water (DI) water and finally dried by flowing nitrogen. All electrochemical experiments were performed using Autolab PGSTAT multichannel potentiostat. The CZTS thin films were deposited at fixed potential of -1.4 V versus Ag/AgCl by amperometry technique. The deposition was carried out at room temperature. After deposition the films were cleaned with DI water and dried at room temperature. Further the film underwent for sulfurization using sulfur powder heating at 550 °C for 30 minutes with continuous argon flow in tubular furnace. The residual sulfur was removed by dipping the film in isopropyl alcohol for 2 min.

AI.2.2 Graphene Synthesis Process

Graphene films were grown on Cu foils (Sigma Aldrich 25 µm thick, 99.98% pure) at 1000 °C in an electric tube furnace under ambient pressure. Before growth, copper foils (2×2 cm$^2$) were cleaned with acetone, iso propyl alcohol (IPA) and DI water to remove the organic impurities on the Cu foil. After cleaning with DI water the foils were dipped in diluted hydro fluoric acid to remove the native oxide of copper. Finally, foils were dried with N$_2$ and
pressed between two cleaned quartz glass slides to keep it as straight as possible. A typical growth procedure is: (1) load a piece of the Cu foil into the quartz tube, and then heat the tube to 1000 °C with the protection of N₂/H₂ flow; (2) initiated the reaction by introducing the CH₄ at 1000 °C, and maintain the reaction for 30 min; (3) cool down the furnace to room temperature purging with N₂/H₂ gas.

**AI.2.3 Graphene Transfer Process**

Transfer of large area single layer graphene onto target substrates is a critical step in the use of CVD grown graphene for practical applications. Poly-(methyl Methacrylate) (PMMA) has been used as a carrier material for transferring graphene. The PMMA solution was spin coated on graphene/copper foils at 4500 rpm for 30 s and dried in air. Diluted FeCl₃ and HCl were used to etch the copper, and the PMMA/graphene film was floated on the surface of the etchant solution. The graphene layer grown on back side of the Cu substrate removed prior with mechanical scrubbing. The PMMA/graphene film was moved to DI water several times to rinse the etchant residue. After rinsing, the PMMA/graphene film was directly transferred onto target substrate. The PMMA was consequently dissolved in chloroform for 15 minutes. Figure AI.1 shows the transfer process of graphene grown on Cu foil onto a target substrate.

**Figure AI.1** Schematic diagram of graphene layer transfer process.
### AI.2.4 Fabrication of the Cu$_2$ZnSnS$_4$ Reference Solar Cell

The device stack consist of glass/ Mo/ Absorber (700 nm)/ CdS (60 nm)/ i-ZnO (100 nm)/ Al: ZnO (300 nm)/Al (contact) (Figure AI.2). A 60 nm thick CdS film was deposited by chemical bath deposition [7]. Further intrinsic ZnO was deposited on CdS by dielectric sputtering and Al doped ZnO was deposited on intrinsic ZnO by metal sputtering. On top, Al contacts were deposited through thermal evaporation system. Finally, the total area (1.44 cm$^2$) of all the devices was defined by mechanical scribing of the samples.

### AI.2.5 Fabrication of the Graphene-based Cu$_2$ZnSnS$_4$ Solar Cell

The AZO electrode was exchanged by graphene and rest of the layers remained the same as the CZTS reference cell. After transferring the graphene layer, the solar cell was annealed at 150 °C for 15 min to enable the flattening of the graphene film and enhance the adhesion between graphene and i-ZnO. Subsequently the PMMA layer was dissolved in chloroform for 15 min. Finally, the Al contact was deposited on top of the graphene. The active area of the solar cells in all the schemes were maintained constant (1.44 cm$^2$) by mechanical scribing.

![Figure AI.2 Schematics of the CZTS solar cell structure.](image-url)
AI.2.6 Characterization Techniques

Electrodeposition experiments were performed using a potentiostat/galvanostat (Metrohm Instruments-302 N) at room temperature. A conventional three-electrode cell configuration was employed; it included a Mo coated glass that had an area of $3 \times 3 \text{ cm}^2$ as a working electrode, a platinum wire as the counter, and Ag/AgCl as the reference electrode. The transferred graphene films were characterized using Raman scattering (Lab RAM HR 800 Micro laser Raman system in back scattering geometry using the 514.5 nm line of Ar$^+$ laser as an excitation source), field emission gun scanning electron microscope (FEGSEM) (JEOL JSM-7600F FEG-Scanning Electron Microscope operated at 15 kV. AFM measurements were carried out using a Digital Instrument's Veeco-Nanoscope IV Multimode scanning probe microscope in tapping mode. The chemical composition were analyzed by X-ray photoelectron spectroscopy (Thermo VG Scientific MultiLab, ESCA Probe using Al $K\alpha$ ($h\nu = 1486.6 \text{ eV}$) that was used as the exciting source. The optical properties of graphene films were measured by UV-visible transmittance spectroscopy (Lambda 950-Perkin Elmer). The photovoltaic (PV) characteristics of the fabricated devices were measured using a Keithley 2400 source meter and a Newport solar simulator (model number 91160) with an illumination of AM 1.5 G. External quantum efficiency (EQE) measurements were performed by a double source illumination system (Xenon lamp, QTH lamp) combined with a monochromator. All measurements were performed at room temperature.

AI.3 Results and Discussion

AI.3.1 Graphene: Structural, Optical, Electrical, and Morphological studies

Raman spectroscopy is the important and non destructive tool for the structural analysis of graphitic materials, and has also become a powerful tool for explaining electrons and phonon behavior of graphene. Figure AI.3a represents the Raman spectrum of the single layer graphene exhibiting D, G, 2D peaks. The D peak (1350 cm$^{-1}$) intensity is very less compared to G (1582 cm$^{-1}$) and 2D peak (2700 cm$^{-1}$). The FWHM of 2D peak is 30.5 cm$^{-1}$ and the 2D peak intensity high compared to D and G peaks [8]. These results are suggesting the single layer graphene with very less defects. High transparency and conductivity is
required for the use of graphene as a substitute for transparent conducting window layer in solar cells.

![Raman spectra and UV-Visible transmittance spectra of graphene.](image)

**Figure AI.3** (a) Raman spectra of graphene layer transferred onto silicon substrate, (b) UV-Visible transmittance spectra of graphene.

The UV-visible transmittance spectra have been measured for the transferred graphene layer in the wavelength range of 300-1200 nm (Figure AI.3b). Light transmission in graphene is determined from absorption, due to its π-conjugated system [6]. As a result of this, high transparency is expected in thinner films of graphene. In principle, the sheet resistance of the graphene layers should decrease with increasing number of layers. Therefore, it is expected that the thicker the film, the larger the number of layers, the smaller sheet resistance but simultaneously transparency decreases. In order to tune the transparency and sheet resistance, we have varied the synthesis conditions. The transmittance spectrum of graphene is quite flat from 600 to 1200 nm. The optical transmittance of the graphene is inversely proportional to the number of layers. The transmittance of single layer graphene is about 90% (%T) is measured at 600 nm wavelength and is quite flat.

AFM was carried out on transferred graphene films for confirming the thickness as well as to understand the topography of the graphene layers. Figure AI.4a shows the AFM image of the single layer graphene after transferring onto a silicon substrate. The thickness of the graphene layer was measured at an edge from AFM height analysis and found to be 1.21 nm, which are well matches with the reported literature [9]. Figure AI.4b shows the scanning electron microscope (SEM) image of graphene grown on a silicon substrate. The graphene...
surface shows the micron sized wrinkles due to the different thermal expansion coefficients of the graphene and copper [10].

![Figure AI.4](image)

**Figure AI.4** (a) AFM image of single layer graphene on Si. The inset shows the height profile of graphene monolayer, (b) FESEM image of graphene on copper foil grown at ambient pressure.

The X-ray photoemission spectroscopy (XPS) data (Figure AI.5a) show the C 1s peak, where the main peak at 284.4 eV indicates that most of the atoms are in the sp² state of carbon [11]. Figure AI.5b shows the I-V characteristics of graphene film transferred onto Si/SiO2 substrate. Two silver metal contacts were deposited to measure the electrical conductivity of the films. The current voltage (I-V) plot shows linear behavior which confirms the ohmic nature of the contacts. The sheet resistance of the film was found to be 6 kΩ/sq.

![Figure AI.5](image)

**Figure AI.5** (a) XPS spectrum of the C 1s core level state of CVD grown graphene, (b) I-V characteristic of graphene film.
AI.3.2 Device Characterizations

AI.3.2.1 J-V Measurements

Figure AI.6 shows the J-V characteristics of the reference CZTS thin-film solar cell fabricated with the standard AZO and graphene based window layer measured under AM 1.5 G illuminations. Table (1) shows the summary of the solar cells electrical parameters that are derived from the J-V data. From J-V characteristics, we observe that device with graphene window layer showed an efficiency of 4.3% with a $V_{oc}$ of 480 mV, a $J_{SC}$ of 15.5 mA/cm$^2$, and a FF of 54%, very close to that of the AZO window layer reference cell (5.0%). The active area of the device is 1.44 cm$^2$. All the electrical parameters of the devices are similar, a significant variation in the $R_S$ from 5-100 $\Omega$-cm$^2$. By comparing the solar cell performance of the graphene-based CZTS solar cell and the standard CZTS solar cell, these two reasons might be responsible for the poor performance of the graphene based solar cell: (1) the sheet resistance of the graphene is higher compared to AZO, (2) poor interfacial contact between graphene and i-ZnO (this may be due to the high roughness of CZTS). It is expected that the device performance will be enhanced by improving the sheet resistance of the graphene layer and the contact between graphene and i-ZnO surface can be improved.

![Figure AI.6](image)

Figure AI.6 The J–V curves of AZO and graphene based CZTS solar cells.
Table AI.1: Electrical performance parameters of the reference and graphene-based CZTS solar cells.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF (%)</th>
<th>$R_S$ (Ω-cm$^2$)</th>
<th>$R_{SH}$ (Ω-cm$^2$)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO</td>
<td>17.8</td>
<td>485</td>
<td>57.5</td>
<td>5</td>
<td>510</td>
<td>5.0±0.1</td>
</tr>
<tr>
<td>Graphene</td>
<td>15.5</td>
<td>480</td>
<td>54</td>
<td>120</td>
<td>465</td>
<td>4.3±0.1</td>
</tr>
</tbody>
</table>

AI.3.2.2 Quantum Efficiency Measurements

Figure AI.7 shows the wavelength-dependent external quantum efficiency (EQE) curve for the CZTS solar cells fabricated with the standard AZO and graphene based window layer. In both cases, the EQE sharply increases from 360 nm and then drops rapidly at 400 nm due to the absorption of the ZnO and AZO layers; it reaches a maximum value of 65% at 540 nm, and then drops slowly at about 800 nm due to the lower absorption coefficient of CZTS at near-band gap wavelengths. The EQE results demonstrate the potential of utilizing the graphene as a window layer to replace AZO in the CZTS solar cells. Graphene based device shows the higher quantum efficiency in the visible and NIR region. The improved quantum efficiency in NIR region caused the high transmittance in the NIR due to the low free carrier absorption loss [12].

![Figure AI.7](image)

Figure AI.7 External quantum efficiencies of AZO and graphene based CZTS solar cells.
AI.4 Summary

In summary, we have demonstrated that the CVD grown graphene can efficiently serve as the window layer for CZTS solar cells to replace AZO. A power conversion efficiency of 4.3% has been achieved, which is significant for a large active area up to 1.44 cm$^2$. Moreover, the graphene-based CZTS solar cell exhibits excellent optical and electrical properties such as enhanced quantum efficiency in the NIR compared with the standard AZO-based CZTS solar cell. With more effort in reducing the sheet resistance of graphene, higher power conversion efficiency of the graphene-based CZTS solar cell is achievable.

AI.5 References


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List of Publications


2. Balakrishna Ananthoju, Sundara Murthy Mopurisetty, Himanshu Tyagi, D. Bahadur, N.V. Medhekar, Swaroop Ganguly, M. Aslam, Efficiency enhancement in Cu$_2$ZnSnS$_4$ solar cells with silica nanoparticles embedded in absorber layer, Accepted in *IEEE Photovoltaics*.


7. S. Mopurisetty, Balakrishna Ananthoju, Mohit Bajaj, M. Aslam, Swaroop Ganguly, Broad-band absorption enhancement in lower absorption coefficient region in CZTS solar cells with embedded Aluminum nanoparticles into absorber layer, Accepted in *IEEE Photovoltaics*.


10. Chandan Das, Balakrishna Ananthoju, M. Aslam, Balasubramaniam Kavaipatti Electron-selective $\alpha$-TiO$_2$/graphene as photo-corrosion inhibition layers for Cu$_2$O photocathodes. (Submitted to *ACS Applied Materials and Interfaces*)


**Conference Proceedings**


**National and International Conferences**


2. **Balakrishna Ananthoju**, Farjana J Sonia, M Aslam, Electrochemical deposition and characterization of high quality Cu$_2$ZnSnS$_4$ thin films for solar cell applications, 1st
International Conference on Chemical, Nano and Sustainable Engineering, Kuala Lumpur, Malaysia.


5. **Balakrishna Ananthoju**, Sundara Murthy Mopurisetty, Himanshu Tyagi, D. Bahadur, N.V. Medhekar, Swaroop Ganguly, M. Aslam, Efficiency enhancement in \( \text{Cu}_2\text{ZnSnS}_4 \) solar cells with silica nanoparticles embedded in absorber layer, 42nd IEEE PVSC, USA.


**Papers to be Communicated**


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