Review Article

CZTS Absorber from Compound Target: Zn-Rich Target Fabrication and Deposition by Radio Frequency (RF) Sputtering Method

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Abstract

Globally, research groups are investigating CZTS thin film via various deposition methods as an absorber layer for solar cells. The challenge lies in understanding the formation of a number of secondary phases during and after the synthesis of Cu2ZnSnS4 (CZTS) and its various different structural and optical defects. The present contribution shows an in-depth review of the works carried out so far by various research groups. This review also highlights the effect of deposition parameters on the optical properties of CZTS absorber.

Keywords: Compound target, rf sputtering, Zn-rich, CZTS, Secondary phases.

INTRODUCTION

One of the most important keys to human life is energy. Mankind has been using energy in many ways to improve his living standards. The world energy consumption is increasing with growing population and industrialization. The modern world has been facing some difficulties with the traditional energy sources such as fossil fuels because of the limited resources of these sources and being non-renewable. From the environmental point of view, burning of fossil fuels causes environmental pollution. This problem with conventional fossil fuels draws the world's attention to alternative renewable energy sources like solar energy, wind energy, bio-gas, hydropower, tidal waves etc. Because of the unlimited availability and ease of use, the utilization of solar energy and wind energy are the current trend of the world in the area of renewable energy sources. Due to the geographical limitation, the wind energy has not been used extensively compared to the solar energy. The greenest and most effective way of meeting the need for electricity is the use of solar cells.

The countries that make up the United Nations signed a memorandum of understanding that if the average temperature of the earth rises by $1.6\ ^0C$ above its current level, the world is going to be in serious trouble [1]. Carbon dioxide levels have been scientifically shown to be related to increasing temperature and about 97% of climate scientists in a recent study agreed that global warming is due to human activities [2]. It is very likely that anthropogenic greenhouse gases have been responsible for most of the unequivocal warming of the Earth's average global temperature in the second half of the 20th century. Unless human habits can be changed, the world may not be useful in the way in which it is being used today for much longer [3].

Sunlight is a widely abundant, free source of energy that is always present and is not subject to the variability of the economy. If all the sunlight that hit the earth in one hour was collected at 100% efficiency, the world's supply of energy for one year would be harnessed; in 20 days, it would match the energy currently in the oil, natural gas and coal reserves [4]. About 10,000 times the amount of energy consumed each day worldwide strikes the earth from the sun in that same day $(3 \times 10^{24} J/year)$. Current estimates show that covering 0.1% of the earth's surface with solar cells having an efficiency of 10% would satisfy our present energy needs [5]. This abundance of solar energy has made it to attract much attention recently both in the political and scientific world [6]. It is noteworthy that the power generation to be met by year 2050 is 30 TW (terra watts) (1TW= 10^{12} W) [7, 8].

One of the most important components of any solar cell device is the photovoltaic (PV) absorber layer, which absorbs sunlight and transports the resulting charge carriers to electrical contacts. Band gap of the absorbing material must be small enough to allow absorption of an appreciable portion of solar spectrum and at the same time large enough to minimize the

reverse saturation current density. Direct band gap semiconductors (1.2 to 1.7 eV) with high absorption coefficient are preferred for the purpose. Currently, the most commonly used solar cell absorber is approximately 100 micro meters thick made from multi-crystalline silicon (Si) due to its high efficiency (>20%), low cost (<0.5 $/W), and good reliability (<25 years). In addition to efficiency, cost and reliability, an ideal PV absorber technology should also have low capital expenditures (to rapidly finance and build a large number of new solar cell fabrication plants) and be composed of chemical elements that are environmentally friendly, abundant in the Earth's crust, and not concentrated in one geographical region of the planet.

Recently, the semiconductor Copper-Zinc-Tin-Sulfide or Cu_2ZnSnS_4 (CZTS) has attracted attention as a promising material for use as absorber material in solar cells [9, 10]. It has a high theoretical efficiency (based on bandgap) and can be used as a thin film to limit material usage. It is formed entirely from earth abundant, inexpensive, non-toxic elements [11]. Since its introduction in 1997 as a thin film in photovoltaic device with an efficiency of merely 0.66%, CZTS has quickly made significant advances in its efficiency.

Copper-Zinc-Tin-Sulfide (CZTS) is derived from the CIGS structure by the isoelectronic substitution of two Indium (or Ga, respectively) atoms by one Zn and one Sn atom. As a consequence, CZTS has some similar properties as CIGS. It is referred to as kesterite (space group I4) and can be derived from the sphalerite structure by duplicating the unit cell. The kesterite mineral structure is the most stable phase of CZTS. Lattice constants for CZTS are a = 0.54 nm and c = 1.09 nm; from this one can calculate with the atomic masses of Cu, Zn, Sn and S the density of CZTS, which is ≈4.6g/cm³. The doping of this material occurs by internal defects. Cu-atoms sitting on the places of Zn atoms (Cu on Zn antisite) causes p-conductivity. That means that one would not necessarily aim for stoichiometric CZTS. Small deviations from stoichiometry may also lead to the formation of secondary phases.

CZTS is a p-type non-toxic semiconductor [12]. As a photovoltaic device, it has a theoretical efficiency limit of 32.2 to 32.4%[10, 12-15]. Thus, it is a very viable material for the future of the industry. It has a band gap of between 1.0-1.7 eV, and it has a large absorption coefficient of ~10^4 to 10^6 cm⁻¹ [11, 16-18].

Rapid progress in the development of kesterite CZTS-based materials has advanced its conversion efficiency from 6.8 to more than 12.7 % [19]. Thus a very thin layer of film (0.45 to 2μm) can absorb over 90% of the photons over the spectrum with photon energy higher than the band gap [20, 21].

In this work, recent developments of CZTS absorber are reviewed. Firstly, we introduce the deposition methods, substrates and the most common absorber materials. Secondly, material availability, fabrication of a CZTS compound target and the effect of deposition parameters on the CZTS absorber are also discussed.

CZTS Thin Film Deposition Methods

Generally, any thin film deposition follows the sequential steps: a source material is converted into the vapor form (atomic/molecular/ionic species) from the condensed phase (solid or liquid), which is transported to the substrate and then allowed to condense on the substrate surface to form the solid film. Depending on how the atoms/molecules/ions/clusters of species are created for the condensation process, the deposition techniques are broadly classified into two categories, viz. Physical methods and Chemical methods.

Electrochemical Deposition Method

This is a process that uses electrical current to reduce cations of a desired material from a solution and coat that material as a thin film onto a conductive substrate surface. Electro deposition is also the process of coating a thin layer of one metal on top of different metal to modify its surface properties. It is done to achieve the desired electrical and corrosion resistance, reduce wear and friction, improve heat tolerance and for decoration. This deposition method is anticipated to have the advantages of being low cost, environmentally friendly (does not use toxic chemicals for most applications) and capable of producing large-area films. In addition, the electrolytic bath can be reused for a long period of time and recycled. Therefore, electro deposition is a prospective technique toward industrial level. For the CZTS thin film, electrodeposition for copper, zinc, and tin is a room temperature process, which does not require excessive amounts of energy. This method differs from vacuum technology which requires considerable energy in order to create the vacuum condition.

Electrodeposition of precursor layers were performed galvanostically in a conventional electrochemical cell assembly at room temperature by [13]. The group reported that Mo foil substrate 200 μm thick with exposed area 1×1 cm² was used as a working electrode, while Titanium mesh was used as a counter inert electrode. The electrolyte for the electrodeposition of Cu-Sn contains 0.026 M Copper-sulfate ($CuSO_4 \cdot 5H_2O$) 0.15 M Tin-sulfate ($SnSO_4$), 2 M Methane sulfonic acid ($CH_3 SO_3H$), 0.01 M Hydroquinone ($C_6H_4(OH)_2$) whereas Zn was electrodeposited from commercial electrolyte bath. pH of the Cu-Sn electrolyte and Zn electrolyte were 1.1 and 5.5, respectively. The desired thickness of the film was 500 nm (±20 nm). On the other hand, 200 nm Zn layer was deposited on Cu-Sn layer using current density 2 mA/cm² with 6 minutes deposition time.

In [22], anhydrous chloride salts, with purities higher than 98%, of $CuCl_2$, $Sn\ Cl_2$ and $Zn\ Cl_2$ were dissolved in an IL prepared by mixing choline chloride ($C_5H_{14}ONCl$) and ethylene glycol ($C_2H_6O_2$) at a molar ratio of 1:2. Copper zinc tin films (type A) were co-deposited at constant potential mode on a copper-coated glass substrate. A thin copper layer of thickness 100 nm was e-beam deposited on a piece of soda lime glass to form the copper/glass substrate which acts as the working electrode during electrodeposition. The copper/glass substrates were ultrasonically cleaned in acetone and rinsed thoroughly with propanol followed by deionized water. Cyclic voltammetry was conducted to determine the reduction potentials of the metal salts. A three-electrode system was used with a silver/silver chloride (Ag/AgCl) as the reference electrode and a platinum (Pt) foil as a counter electrode.

Electron beam deposition method

E-Beam evaporation is one of the physical vapor deposition (PVD) techniques whereby an intense, electron beam is generated from a filament and steered via electric and magnetic fields to strike source material and vaporize it within a vacuum environment. At some point as the source material is heated via this energy transfer its surface atoms will have sufficient energy to leave the surface. At this point they will traverse the vacuum chamber, at thermal energy (less than 1 eV), and can be used to coat a substrate positioned above the evaporating material. Electron beam guns can be classified into thermionic and plasma electron categories respectively.

Araki, H *et al.*, [23] Studied preparation of Cu_2ZnSnS_4 thin films by sulfurization of stacked metallic layers. The precursor films having composition ratios of Cu/(Zn+Sn) <1, Zn/Sn>1, were approximately 0.4 to 0.6 μm thick. After deposition, the samples were sulfurized in an atmosphere of N_2 + sulfur vapor from which the thickness increased from 1.0 to 1.4 μm. The composition ratios were Cu poor for Zn+Sn (Cu/(Zn+Sn) <1), Zn rich for Sn (Zn/Sn >1) and S poor (S/Metal <1).

In [24], the 0.7-μm-thick Mo electrode layers were formed on alkali-glass substrates by sputter deposition. A two-layer structure was adopted for the CZTS absorber layers with a total thickness of ~1200 nm. To fabricate the first CZTS layers [t = 400 nm], precursors were deposited by electron-beam and RF magnetron sputtering deposition using Cu, Sn, and ZnS targets to form a Cu/Sn/ZnS/Mo/alkali-glass structure, which was then sulfurized at 853 K for 20 minutes in 20 volume [%] H_2S and 80 volume [%] N_2 at atmospheric pressure. The heating and cooling rates were 5 and 10K/min, respectively. The second CZTS layers [t = 800 nm] was similarly fabricated by depositing second set of precursors to form ZnS/Sn/Cu/CZTS

(1)/Mo/alkali-glass and sulfurizing them in H_2S-N_2 gas at 773 K for 60 min.

Spray Pyrolysis Deposition Method

The thermal spray process of thin film fabrication refers to a range of deposition conditions wherein a stream of molten particles impinges onto a growth surface. In this process, thermal plasma or a combustion flame is used to melt and accelerate particles of metals, ceramics, polymers or their composites to high velocities in a directed stream towards the substrate. The thermal spray chamber has three parts namely the vacuum chamber, the substrate holder and the vacuum system. The sudden acceleration of a particle upon impact at the growth surface lead to lateral spreading and rapid solidification of the particle forming a "Splat" in a very short time. The characteristics of this splat are determined by size, chemistry, velocity, degree of melting and angle of impact of the impinging droplets, and by the temperature, composition and roughness of the substrate surface. Spray pyrolysis is a versatile and low-cost technique, which is extensively used to deposit selenide, sulphide and oxide semi- conductor films.

Studied the Preparation and characterization of spray-deposited Cu_2ZnSnS_4 thin films [25]. The Cu_2ZnSnS_4 thin films were deposited by spray pyrolysis technique starting with an aqueous solution containing cupric chloride (0.01 M), zinc acetate (0.005 M), stannic chloride (0.005M) and thiourea (0.04M). Excess thiourea was taken to compensate the loss of sulphur during pyrolysis. The solution was sprayed, using a pneumatically controlled air-atomizing spray nozzle onto heated glass substrates held at various substrate temperatures in the range 563–723K. The substrate temperature was maintained to an accuracy of 75 K using a digital temperature controller.

Deposited CZTS thin films by home-built chemical spray pyrolysis unit onto soda lime glass (SLG) and fluorine doped tin oxide (FTO) substrates [26]. In the deposition, copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), tin chloride ($Sn\ Cl_4$) and thiourea [$(NH_2)_2CS$] were used as precursor. The molar concentration of $CuCl_2.2H_2O$, $ZnCl_2.2H_2O$ and $SnCl_2.5H_2O$ were kept constant at 0.04 M, 0.02 M and 0.02 M respectively whereas the concentration of $(NH_2)_2CS$ was varied from 0.12 M to 0.18 M. The substrate temperature was kept constant at 325^0C.

Pulsed Laser Deposition (PLD) Method

This is a physical vapor deposition technique where a high-power pulsed laser beam is focused to strike a target of desired composition. Material is then vaporized and deposited as a thin film on a substrate facing the target. This process can occur in ultra-high vacuum or in the presence of a background gas, such as oxygen when depositing films of oxides. PLD has advantages of high deposition rate, low substrate

temperature and high-quality films, thus widely used in thin film preparation. This technology is simple to operate, and can easily control the laser repetition rate, incident power energy and other experimental conditions [27].

In [28], the samples were prepared by the standard PLD method. A KrF excimer laser (wavelength: 248 nm, pulse width: 10 ns, repetition rate: 30 Hz) was used in this experiment. The PLD chamber was evacuated with a diffusion pump into 2×10^{-2} Pa, then laser pulses were focused onto a sintered CZTS target pellet with an energy density of $0.7 - 1.5$ J/cm^2, and the ablated fragments were deposited to a fused soda lime glass (SLG) substrate and a Mo-coated SLG substrate at room temperature. The substrate–target distance was 35 mm. The substrate was cleaned by ultrasonic cleaning using organic solvents and UV cleaning for 10 s. The CZTS pellets used as a target were synthesized by the solid-state reaction of Cu_2S, ZnS, and SnS_2 powders mixed in a 1: 1: 1mol ratio.

Surgina, G. D *et al*., [29] Studied the Effect of Annealing on Structural and Optical Properties of Cu_2ZnSnS_4 Thin Films Grown by Pulsed Laser Deposition, the deposition of CZTS thin films was performed at room temperature by the reactive PLD in H_2S flow in a dedicated home-made setup with the base pressure $P \approx 10^{-4}$ Pa. The laser energy density chosen was $E \approx 7.5$ J/cm^2 with the repetition rate $\nu = 20$ Hz. An alternate ablation with the number of laser pulses of pre-calibrated sub-monolayer portions from the metallic Cu and alloyed $Zn_{0.9}$-$Sn_{1.1}$ targets (prepared by arc melting) was used to deposit CZTS thin films at room temperature. The reactive H_2S gas pressure during depositions was P = 5 Pa, while the target/substrate distance was 3 cm. The fused quartz plates ($14 \times 7 \times 1$ mm^3) transparent in the wide optical region were used as substrates and were cleaned in an ultrasonic bath using ethanol and acetone prior to the deposition.

Spin-Coating Deposition Method
Spin coating is a procedure used to deposit uniform thin films to flat substrates. Usually a small amount of coating material is applied on the center of the substrate, which is either spinning at low speed or not spinning at all. The substrate is then rotated at high speed in order to spread the coating material by centrifugal force. A machine used for spin coating is called a spin coater, or simply spinner. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent isusually volatile, and simultaneously evaporates. So, the higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the viscosity and concentration of the solution and the solvent. A widely studied phenomenon in spin-coating is the coffee ring effect. Spin coating is widely used in microfabrication of functional oxide layers on glass or single crystal substrates using sol-gel precursors, where it can be used to create uniform thin films with nanoscale thicknesses.

Aaron, D *et al*., [30], spin coated five successive layers of CZTSSe onto Mo-coated soda lime glass slides using precursor slurries that were heat treated in a sulfur-rich atmosphere using a hot plate temperature setting of as high as 540^0C, the films generated were of final thickness of ~2.5 mm and a S/(S + Se) ratio of 0.4 ± 0.1.

Sol-Gel Deposition Method
Sol–gel process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides, especially the oxides of silicon and titanium. The process involves conversion of monomers into a colloidal solution (*sol*) that acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides.

Sun, Y. M *et al*., [31] Stated that the starting materials in the preparation of the CZTS thin film are Copper chloride (1.9 M), zinc chloride (1.15 M), tin chloride (1 M), and thiourea (8 M), respectively, which were dissolved in deionized water, ethanol, and polyethylene- glycol as precursor solution. The clear yellow solution was formed when stirred at 45^0C for 40 min. The sol solution was spin coated on soda lime glass substrates at 2500 rpm for 40 seconds to form a film and then the film was annealed at 110^0C for 10 minutes for drying. The coating and drying processes were repeated 3 times. One part of the as-coated films were annealed for 1 hour under Ar ambient at 120, 160, 240, and 310^0C, respectively, and the others were annealed for 1 h under sulphur (S) atmosphere at 360, 400, 440, and 480^0C, respectively in a tubular furnace with two zones, where one zone was for laying the as-coated thin film, and the other was for laying S source.

Ruan, C *et al*., [32] reported Electrical properties of $Cu_XZn_YSnS_4$ films with different Cu/Zn ratios, in the CZTS films were prepared in a nitrogen-filled glove box by the sol–gel method using copper acetate [Cu(CH3COO)$_2$·H$_2$O], zinc acetate [Zn(CH3COO)$_2$ ·2 H$_2$O], stannous chloride (SnCl$_2$·2 H$_2$O) and thiourea [SC(NH$_2$)$_2$] as starting precursors and 2-methoxyethanol and monoethanolamine (MEA) as a solvent and stabilizer. The molar ratio of Cu/Sn was 2 in the mixture solution and the molar ratio of S/Sn ([S/Sn]) was 4.4 in the mixture solution. However, the molar ratio of Cu/Zn ([Cu/Zn]) was 2.8, 2.3, 2.0 or 1.8 in the mixture solution. The reaction solution contained in a beaker was kept inside a heating oven at 450 °C for 1 h. The solution was dropped onto the glass surface, which was rotated at 2000 rpm for 20 seconds. After deposition by spin-coating, the films were dried at 150 °C for 10 min on a hotplate in a nitrogen-filled

glove box. The procedures from coating to drying were repeated ten times.

Successive Ionic Layer Adsorption and Reaction (SILAR) Deposition Method

Preparation of thin films using SILAR method have several attractive features: the low deposition temperature avoids high temperature effects such as inter-diffusion, contamination and dopant redistribution. Apart from the obvious advantages in terms of energy saving foremost advantage is growth rate of film is easily controlled by varying adsorption and reaction time. In this first step of SILAR process, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: first, the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations. In last step of a SILAR cycle, the excess and unreacted species Ap, X, Y, and the reaction byproduct from the diffusion layer are removed.

Deposited thin films of Cu_2ZnSnS_4 by a simple wet chemistry method known as SILAR [33]. The standard recipe was: 0.02 M $CuSO_4$, 0.01 M Zn SO_4, 0.02 M Sn SO_4 solutions were dissolved in H_2O to give Cu^{2+}, Zn^{2+}, Sn^{2+} anions, while 0.16 M Na_2S was dissolved in H_2O to give (S^{2-}) cations. For photo electrochemical (PEC) measurements, CZTS thin films were deposited on fluorine doped tin oxide (FTO) coated glass substrates. The active area of the films deposited onto the FTO and substrate was $2cm^2$. The uniform and well adherent CZTS thin films were obtained on glass and FTO substrates using SILAR method by repeating a sequential immersion of substrates in the solutions of cationic (Cu^{2+}, Zn^{2+}, Sn^{2+}) and anionic (S^{2-}) precursors followed by rinsing in deionized water after every immersion. An immersion time of 30 seconds was kept constant for each precursor. In initial process step, the substrate was immersed in cations (Cu^{2+}, Zn^{2+}, Sn^{2+}) solution for 30 seconds, which will have adsorbed (Cu^{2+}, Zn^{2+}, Sn^{2+}) ions on the substrate. After immersion of this substrate in sulfur (S^{2-}) anions, for 30 seconds, the reaction occurred at the substrate surface to form CZTS, consists one cycle. The rinsing and adsorption time were varied in such a manner that CZTS films get deposited onto the substrates. A thin layer of CZTS film resulted after immersing the substrate sequentially in respective precursors for 10 cycles.

In 2013 [34] also reported Aqueous chemical growth of Cu_2ZnSnS_4 (CZTS) thin films: Air annealing and photo electrochemical properties. In order to obtain CZTS films, this group reported that the well cleaned glass and stainless steel (SS) substrates were dipped first in a beaker containing cationic precursor solutions of 0.1 M CuCl, 0.05 M $ZnCl_2$ and 0.05 M $SnCl_4$ in 1:1:1 ratio, where Cu^{1+}, Zn^{2+} and Sn^{4+} ions get adsorbed

onto substrate surface. After immersion of the substrate into cationic precursor, substrates were rinsed with double distilled water placed in 2nd beaker to remove loosely bounded cations. Then the substrates were immersed in 3rd beaker containing anionic precursor of 0.2 M C_2H_5NS solution, where S^{2-} ions react with pre-adsorbed Cu^{1+}, Zn^{2+} and Sn^{4+} cations to form CZTS layer on the substrate. This completed one cycle for the deposition of CZTS film. By repeating such cycles, the CZTS film thickness was increased to the desired thickness.

Thermal Evaporation Method

One of the common methods of Physical Vapor Deposition (PVD) is thermal evaporation. This is a form of thin film deposition, which is a vacuum technology for applying coatings of pure materials to the surface of various objects. The coatings, also called films, are usually in the thickness range of angstroms to microns and can be a single material or can be multiple materials in a layered structure. The materials to be applied with Thermal Evaporation techniques can be pure atomic elements including both metals and non-metals or can be molecules such as oxides and nitrides. Thermal Evaporation involves heating a solid material inside a high vacuum chamber, taking it to a temperature which produces some vapor pressure. Inside the vacuum, even a relatively low vapor pressure is sufficient to raise a vapor cloud inside the chamber. This evaporated material now constitutes a vapor stream, which traverses the chamber and hits the substrate, sticking to it as a coating or film.

Deposited Cu_2ZnSn $(Se_xS_{1-x})_4$ by thermal evaporation technique on glass substrate at substrate temperature of 413K and film thickness of 750 nm [35]. In this investigation, appropriate atomic weights of Cu, Zn, Sn and Se with high purity 99.999% for $Cu_2ZnSn(Se)_4$ alloy, and appropriate atomic percentages of high purity Cu, Zn, Sn and S were used to prepare the $Cu_2ZnSn(S)_4$ alloys. The constituent was mixed together and put it into a quartz tube and then sealed under vacuum of 10^{-4} Torr. The sealed ampoules were placed in a programmable furnace. The elements were reacted first at certain temperature and time. The temperature was increased slowly to assure a congruent melt. Next, the material was slowly cooled down to room temperature to form a CZTS (Se) ingot. The last step was to ground the alloys into a fine powder to use for evaporation. The glass substrate was maintained at 413 K during the deposition. The deposition was performed after a system base pressure of ($8x10^{-5}$ Torr) was reached in the vacuum chamber. The deposition of the Cu_2ZnSn $(Se_xS_{1-x})_4$ material was done by passing high current, through the resistance heating source when it is loaded with CZT (S, Se).

In [36], the starting materials are Cu, Zn, Sn and S with a nominal purity of at least 99.999% mixed together to prepare Cu_2ZnSnS_4 crystal. The mixture was

introduced in an evacuated and sealed quartz tube under a vacuum of 10^6 Torr. The tube was inserted into the furnace where the temperature was raised to 1000°C and maintained at this temperature for 48 hours. After homogenization of the melts, the tube was cooled. The obtained crystal was black color with length of 20mm. Crushed powder of this ingot was used as raw material for the thermal evaporation to obtain Cu_2ZnSnS_4 thin films. The Cu_2ZnSnS_4 thin films were prepared by co evaporation of the CZTS powder in a high vacuum system with a base pressure of 10^6 Torr. An open ceramic crucible was used. Thermal evaporation sources were used which can be controlled either by the crucible temperature or by the source powder. The glass substrates were heated at 150°C. Typical as deposited films thicknesses were 500nm.

Dip-coating deposition method

In this process, thermal energy is supplied to a source from which atoms are evaporated for deposition onto a substrate. The vapour source configuration is intended to concentrate heat near the source material and to avoid heating the surroundings. Heating of the source material can be accomplished by any of several methods. The simplest is resistance heating of a wire or stripe of refractory metal to which the material to be evaporated is attached. Larger volumes of source material can be heated in crucibles of refractory metals, oxides or carbon by resistance heating, high frequency induction heating, or electron beam evaporation. The evaporated atoms travel through reduced background pressure in the evaporation chamber and condense on the growth surface.

Reported the Influence of pH on structural, optical and electrical properties of solution processed Cu_2ZnSnS_4 thin film absorbers [37]. Copper (III) nitrate hemipentahydrate ($Cu(NO_3)_2$ $2.5H_2O$), Zinc acetate dihydrate ($Zn(CH_3COO)_2$ $2H_2O$), Tin (II) ethylhexanoate (($CH_3(CH_2)_3CH(C_2H_5)CO_2)_2Sn$), and thiourea ($CH_4N_2S$) were separately dissolved in a mixture of ethanol and glacial acetic acid. These prepared solutions were mixed at room temperature. To regulate pH values, it was adjusted by adding a few drops of triethanolamine to the final solutions. The molar ratios of the Cu:Zn:Sn:S elements in the solutions were 2:1:1:4. Three different solutions with the pH values of 4.0, 4.5, and 5.0 were obtained in that way.

In the Synthesis of Cu_2ZnSnS_4 thin film absorbers by sulfurizing dip-coated precursors [38], reported that the precursors were annealed in an inert atmosphere (Ar) at 400 and 500°C respectively. Copper (II) acetate monohydrate, zinc (II) acetate dihydrate, tin (II) chloride dihydrate, and thiourea were used for the preparation of solutions. The metal ion ratio of the base solution was Cu- poor and Zn-rich. The solution of 0.667 M metal ions and 1.333 M thiourea was prepared by dissolving the metal salt and thiourea in a mixed solution of water and ethanol (30%), then stirring for 3

h at 45°C. The ethanol acts as a dispersion agent. Soda lime glass substrates were cut to a size of 15 × 25 mm and cleaned in an ultrasonic water bath followed by ultra-sonication in acetone, ethanol, de- ionized water and acetone, each for 20 minutes. The substrates were dipped into the solution and for removing the solvents, the precursors were flattened by using a N_2 gas-jet. Then, they were dried at 200°C for 15 minutes in air using a hot plate. The dipping and air- jet processes were repeated 10 times to obtain the desired thickness.

Facile synthesis of Cu_2ZnSnS_4 absorber layer for thin film solar cells using a highly stable precursor solution was reported by [39]. The CZTS precursor solution was prepared by dissolving 1.6M Copper chloride, 1M Zinc acetate dihydrate, 0.8M Tin chloride dihydrate and 6.4M Thioacetamide in 10 ml of 2-methoxyethanol under stirring for 10 minutes to get yellow color transparent solution. Molybdenum coated soda lime glass was used as the substrate to prepare the CZTS films. The Molybdenum coated soda lime glass slides were washed with ethanol and then sonicated using isopropyl alcohol for 10 min, followed by the nitrogen purge using a nitrogen gun. CZTS film was prepared using the precursor solution and then dried at 130°C followed by annealing at 500°C for 30 min in the presence of argon gas.

Sputtering Method

Discovered by Groove in 1852, sputtering process is one of the advantageous and viable techniques for the growth of magnetic, semiconducting thin films, which provides uniform growth and composition in the layers; in addition, less material loss occurs. The deposition of high melting point materials is difficult to grow by vacuum evaporation. Therefore, sputtering is inevitable and alternative technique, which is known for several years to grow heat resistance, corrosion resistance, low friction, decorative coatings etc., for optical and electrical applications. Compared with conventional vacuum deposition, sputter coating has many merits, such as precisely controlling the stoichiometry of elements, obtaining the film with high density, full use of raw materials, freely choosing the deposition site, reducing the contamination for vacuum chamber, the higher uniformity degree of the film, and suitability for the preparation of larger scale CZTS thin film solar cells [40].

Direct current magnetron sputtered Cu_2ZnSnS_4 thin films using a ceramic quaternary target was reported by [41]. The group stated that the CZTS thin films were fabricated on soda-lime glass substrates using a direct current (DC) magnetron sputtering method. A quaternary stoichiometric Cu_2ZnSnS_4 ceramic target with 99.99% purity and 50.8 mm diameter was used for the sputtering. The target was a pressed plate formed at 500°C and 30 MPa from mixture of fine-grained Cu_2S, ZnS and SnS_2 at the ratio of 1:1:1. Prior to deposition, the soda-lime glass

substrates (with a size of 17 mm x 17 mm) were ultrasonically cleaned in sequence in acetone, ethanol and ultra-pure water, blow-dried by N_2 jet, and then mounted in a sputtering system. The base pressure for sputtering deposition was 5×10 Pa. Ar gas flow rate was 30 sccm and working pressure was maintained at 0.5 Pa. The distance between target and substrate was fixed at 70 mm. Fifteen minutes pre-sputtering was carried out to remove any undesirable contaminants from the quaternary target prior to the actual sputtering process.

In a paper, titled Fabrication and characterization of Cu_2ZnSnS_4 thin films by sputtering a single target at different temperature [17], reported that a series of precursors for CZTS films were deposited on Mo-coated soda-lime glass (SLG) by co-sputtering of ZnS, SnS, and Cu in a sputtering chamber. The Cu was deposited by a DC source, SnS and ZnS were deposited by RF source. Before deposition, the sputtering chamber was evacuated to the pressure below 5×10^{-4} Pa. Ar was used as working gas and the pressure was maintained at 0.5 Pa during the deposition that lasted 20 minutes for all the targets. During the deposition, the sputtering powers for ZnS, SnS, and Cu were 150 W, 65 W, and 15 W, respectively.

Jheng *et al.,* [42] reported Effects of substrate temperature on the Cu_2ZnSnS_4 films deposited by radio-frequency sputtering with single target. The CZTS films were grown at 500^0C on Mo-coated SLG substrates with the area of 5×5 cm^2 by using RF magnetron sputtering in pure Ar gas atmosphere. Radio Frequency power of 80 W was applied to the quaternary CZTS alloy target, while 15 W, 25 W, and 35 W RF power was used for the binary ZnS alloy target. Substrate temperature was maintained at 500^0C during the sputtering process. An additional etching step was performed in a KCN-containing aqueous solution (10% KCN) to remove segregated $Cu_{2-x}S$ on the surface. The 60-nm-thick CdS layer was grown by chemical bath deposition (CBD). The bath was maintained at 70^0 C and contained deionized H_2O, NH_4OH (31.25mL, 0.015M $CdSO_4$ solution and 1.5 M thiourea in deionized water. A 50-nm thick intrinsic-ZnO and a 250-nm thick conductive-ZnO: Al (Al_2O_3 2 wt. %) film was deposited in sequence by using RF magnetron sputtering at room temperature as window layers.

Xie *et al.,* [43] reported the Fabrication of Cu_2ZnSnS_4 thin films using a ceramic quaternary target. The ceramic quaternary target was made from finely mixed Cu_2S, ZnS and SnS_2 powders with a mole ratio of Cu_2S: ZnS: SnS_2 = 0.9: 1.1: 0.9. The size of the target was 360 mm$\times$80 mm $\times$5 mm and the purity is higher than 99.99%. The sputtering was carried out at room temperature using Ar as the working gas with a pressure of 0.7 Pa. The base pressure of the sputtering chamber is 3.0 10^3 Pa and the substrate to target distance is 50 mm. Both glass and Mo coated glass were utilized as the substrate. The sputtering power for

the quaternary target is 250 W and the sputtering time is 2 h. After sputtering, the samples were then sent to a quartz tube for sulfurization. The tube was evacuated to a base pressure of 2.0×10^3 Pa and then mixed N_2 (60%, volume concentration) + H_2S (40%, volume concentration) gas was filled into the tube until the pressure reached 0.05 MPa. Samples in the tube were heated to the setting sulfurizing temperature at a heating rate of 20 C/min and kept at the temperature for 10 min. Finally, the samples were cooled down to room temperature naturally. Sulfurizing temperatures were kept at 460^0C, 490^0C, 520^0C, 550^0C and 580^0C respectively.

Jo *et al.,* [44] reported Single elementary target-sputtered Cu_2ZnSnS_4 thin film solar cells. The results showed that with the exception of the 2Cu 1Zn target, all values of the optical band gap obtained were close to 1.0, with a noticeable decrease in Eg with increasing Cu content. The higher value of ~1.15 eV for 2Cu 1Zn may be due to the contribution of the $SnSe_2$ phase, which has a higher Eg of ~1.62 eV.

Reported optimization of post-deposition annealing in Cu_2ZnSnS_4 thin film solar cells and its impact on device performance [45]. The method employed for the growth of the Cu_2ZnSnS_4 thin films is RF-magnetron sputtered pre-cursors deposited on Mo coated SLG. Two types of precursors were prepared with the following structures: (ZnS/SnS2/Cu) and (ZnS/SnS2/ Cu). For each type, two sets of absorbers were prepared, one with excess Zn and another with the ideal composition. For both types of precursors, the maximum temperature and the dwelling time at maximum temperature for the post-deposition annealing were varied from 200 to 400°C and from 15 to 20 minutes, respectively. The application of the post-deposition annealing to the full cells based on the first type of precursors (ZnS/SnS2/Cu) has shown that annealing at 200°C leads to an improvement of the solar cell efficiency by a factor of 2 while a post-deposition annealing at 300°C leads to an efficiency improvement by a factor of 11.

Substrates

In chalcogenide technologies, the nature of the substrate, and the composition and processing of buffers and contacts have a significant effect on the final device performance and its stability. Substrate serves as a mechanical support for the film and in electronic applications it usually serves also as an insulator. The need for long-term stability in thin film substrates makes it imperative that no chemical reactions occur which could change the properties of the film. The substrate must therefore fulfill certain requirements as to mechanical strength and there must be adequate adhesion of the film to the substrate, not only at normal temperature but also during relatively large temperature changes. These changes may arise during the preparatory stage of operation (degassing at high

temperature), during the deposition of the film (onto heated or cooled substrate) and sometimes during the operation of the thin film system. A high dielectric strength is also required. To ensure constant temperature of the surface and sufficient heat removal during the operation of electronic elements, an appropriate heat conductivity is necessary. Further, to form the films with defined and reproducible electrical and other parameters, the surface of the substrate should be flat and smooth. These characteristics should be accompanied by a number of practical requirements, such as the possibility of vacuum processing and the availability and price of the material. In some applications, even its weight may be an important factor. Absence of contamination is, however, necessary in all cases. It is, in general, possible to say that there is no material that would satisfy all these requirements. The most widely used substrates for polycrystalline films are glass, fused silica and ceramics (mostly based upon Al_2O_3). Organic materials that have also been tested (e.g. Mylar or Teflon), have the advantage of low specific weight, but they cannot endure a high temperature and are used therefore only in special cases. For a single-crystal epitaxial growth the most frequently used materials are the single crystals of alkali halides, silicon, germanium, sapphire and mica. The alkali content of different glasses is very important, especially that of sodium. Often used is Pyrex (composition: 80.5% SiO_2, 12.9% B_2O_3, 3.8% Na_2O, 2.2% Al_2O_3, and 0.4% K_2O) or fused silica, which besides its chemical inactivity is temperature-resistant to a considerable degree. The substrates with higher alkali content are often the cause of instability in the electrical and other properties of thin films. For example, Na_2O is practically immobile up to 4% concentration; at higher concentrations, however, and especially at elevated temperature and intensity of electric field, it can travel rather easily in the glass. Together with moisture, it forms a layer of high conductivity on the surface and causes electrolytic corrosion of the film especially in the neighborhood of negative contacts. From this point of view, a glazed ceramic is a better material even when the alkali content of the glazing is about the same. The reason lies in the better heat conductivity of the material, which means a lower operating temperature of the surface with the same electric current. The surface of glass can be made relatively flat and smooth.

Soda Lime Glass Substrate

Glass is the most common substrate material used by manufacturers of CZTS/CIGS modules. It is available in large quantities at low cost. However, the choice of a given glass is of prime importance for the final device quality. As an example, Sodium (Na) often present in common glass, diffuses through the Mo film into the growing absorber, and plays a crucial role in the device performance as it diffuses to the grain boundaries, catalyzes oxygenation and passivation of Se vacancies favors the formation of $MoSe_2$ (or MoS_2) [46,

47] and plays a role in the growth of Cu(In, Ga)Se$_2$. Soda-lime glass (SLG) contains 73% silica, 14% Na_2O, 9% CaO (by mass) as well as other elements in smaller quantities (<1%). It has a coefficient of thermal expansion of about $9 \times 10^{-6} K^{-1}$, a thickness range of 2000 to 5000μm and a density of 2.4 to 2.5 kg/m^3. Soda-lime glass (SLG) can withstand a temperature of up to 600^0C. These elements provide sources of alkali impurities such as Na, which diffuse into the Mo and CIGS films during processing. Sodium plays an important role in the growth and final properties of CIGS solar cells. Moreover, soda lime glass has a thermal expansion coefficient of 9×10^{-6}/K [48], which provides a good match to the CIGS and Mo films.

Most Common Absorber Layer Materials

The absorber layer is the region where light is absorbed, and the photocurrent is initiated. The band gap of the absorber should thus be suitable for the absorption of photons. The absorber is usually 100 times thicker than the window layer, and preparedly of p-type conductivity.

Cadmium Telluride (CdTe)

CdTe is an excellent absorber with large absorption coefficient ($>10^4$ cm^{-1}) [49]. It has a near-optimum direct bandgap of 1.45 eV at room temperature [50] which is suitable for efficient photo conversion. Therefore, an absorber layer of only a few micrometers thick is sufficient to absorb a maximum fraction of the AM1-AM1.5 solar spectrum [51]. A film layer can absorb 99% of incident radiation in the visible range). CdTe can be grown to be n-type or p-type without extrinsic doping, simply by changing the composition and also it can be doped to be n- or p-type. Hence, it can form a mono-junction [49]. In addition, CdTe suffers from very high surface recombination velocities and this makes the surface recombination loss unacceptably high which means that it is suitable only for use in a heterojunction solar cell. CdTe has a record efficiency of 20.4% [52].

Copper–indium–gallium–Diselenide (CIGS)

This material is known as a promising option in photovoltaic technology due to its high performance, low cost and stability [53, 54]. The efficiency of CIGS solar cell is already reached above 20% for laboratory scale samples. The efficiency of 20.3% and 20.4% was obtained from the CIGS solar cells on the glass and flexible polymer substrate respectively [55]. Although the CIGS thin film solar cell has reached to maturity level that can go easily for mass production, but there are still some optimizations that needs to be done for further increase in efficiency and reduce cost.

Material Availability

Although Thin Film Solar Cell (TFSC) technology is currently very encouraging, there is a growing demand for alternative materials to the well-established CdTe, CIGS and Si-variants. The abundance

of indium and tellurium in the Earth's crust is estimated to be 0.05 ppm and 0.001 ppm, respectively. This is significantly lower when compared to copper, zinc and tin with respective values estimated to be 25, 71 and 5.5 ppm. Furthermore, due to toxicity issues the heavy metal cadmium has experienced legislative action in some countries causing industries to restrict or completely refrain from its use. Thus, there is a need to search for and identify new thin film material compounds and structures, which utilize more sustainable and non-toxic elements in conjunction to excellent device performance. It is important to realize that the latter reason is significant in reinforcing the development and commercial viability of these new technologies.

Fabrication of the Compound Target

Pressing and sintering are the most common mechanisms used to form solid parts from powders. Pressing occurs first, then sintering. In addition to the powder constituents, binders, deflocculates, lubricants may also be present in the mixture. Powder pressing, and hence powder forming in general, is best suited to flat parts with 2-dimensional geometry and little thickness. To begin the manufacturing process, a known amount of powder is filled into a die. Rate of die filling is based largely on the flowability of the powder. Powders that flow readily can be poured at higher rates. Pouring can also be an automated process. Once the die is filled, a punch moves vertically towards the powder and applies pressure to the powder, compacting it to the correct geometry. The amount of force necessary for a pressing operation is to a large degree based on the material. For example, pressing aluminum powder generally requires lower force, while pressing iron powder requires relatively higher force. Pressing force also depends upon powder characteristics, additives and desired density of the green compact. The preparation of the CZTS single target starts with the mixing of CuS, ZnS and SnS_2 powders at a desired weight ratio of Cu: Zn: Sn: S. The powders can be mixed by using a ball milling method at the rotating speed of up to 300 rpm for at least 3 hours in stainless steel mold. The mix is then pressed into a pellet form at a pressure of say $1.38 \times 10^5 Pa$, and then transferred to a vacuum furnace for hot sintering treatment. The pellet is then sintered at a temperature range of 400^0C to 600^0C for at least 8 hours after which it is taken for microstructure and phase characterizations in order to identify the sintering conditions that may yield the single-phase CZTS structure. Afterward, CZTS target is prepared in accord with the optimum sintering conditions.

Formation and annealing of CZTS absorber layer

Parthibaraj, V *et al*., [56] achieved a CZTS absorber layer deposited on glass substrate by RF magnetron sputtering using commercially available sputtering target which is composed of finely mixed Cu_2S, ZnS and SnS_2 with ratio 2:1.5:0.5. The growth parameters such as sputtering power, working pressure, target and substrate distance and sputtering time were fixed at 75Watt, 10^{-5} mTorr, 3 cm and 30 minutes, respectively. The film was grown in argon ambient with partial pressure of 10^{-3} mTorr.

Wang, D *et al.*, [27], deposited about 1μm thick Mo layer on soda-lime glass slides by DC magnetron sputtering. Cu_2ZnSnS_4 films were deposited on Mo/SLG substrates by RF magnetron sputtering using a home-made Cu_2S-ZnS-SnS_2-S mixed powder target. Prior to film deposition, the sputter vacuum chamber was evacuated to less than 5×10^{-5} Pa. Firstly, CZTS films was deposited on Mo/SLG substrates at 150°C, using high purity Ar as working gas with a flow rate of 30 sccm. The sputtering pressure was maintained at 0.6 Pa. Secondly, the glass/Mo/CZTS samples were placed in a quartz tube resistance furnace sulfurization system under high purity argon atmosphere. The sample was annealed at 550^0C for 1 hour.

Zhao, Q *et al*., [17], reported that CZTS thin films were deposited on Mo-coated soda-lime glass substrates by RF magnetron sputtering with a CZTS single compound target (3-inch diameter and 4 mm thick) at different temperatures. The non-stoichiometric CZTS pellet was synthesized by the solid-state reaction of Cu_2S, ZnS, SnS_2 and S powders mixed at 2:1.8:1:1.2 mol ratio. The substrates were placed on a rotating heater plate and the distance between target and substrate was fixed as 8 cm. The deposition chamber was evacuated to a background pressure of 5.0×10^{-4} Pa by using a turbo molecular pump (TMP). The substrates were heated up by rotating heater plate to different temperatures (ranging from 400°C to 550°C) with a heating rate of 35°C/min. Before as-deposited process, pre-sputtering process was done for 5 minutes. The Argon working pressure of 0.5 Pa was used and RF power for the CZTS compound target was 70W. The thin films were deposited for 130 minutes at temperatures 400°C, 450°C, 500°C and 550°C, respectively. Finally, the samples were cooled down to room temperature naturally.

In Direct current magnetron sputtered Cu_2ZnSnS_4 thin films using a ceramic quaternary target by [41], the CZTS thin films were fabricated on soda-lime glass substrates using a direct current (DC) magnetron sputtering method. A quaternary stoichiometric Cu_2ZnSnS_4 ceramic target with 99.99% purity and 50.8 mm diameter was used for the sputtering. Prior to deposition, the soda-lime glass substrates (with a size of 17mm x 17mm) were ultrasonically cleaned. The base pressure for sputtering deposition was 5×10^{-4} Pa. Ar gas flow rate was 30 sccm and working pressure was maintained at 0.5 Pa. The distance between target and substrate was fixed at 70 mm. A fifteen-minute pre-sputtering was carried out to remove any undesirable contaminants from the quaternary target prior to the actual sputtering process. Films with a thickness of about 500 nm were obtained.

In addition, the films deposited at the DC power of 50 W and substrate temperature of 120 °C were sealed in a quartz crucible with high purity S powder and sulfurized in a furnace at 450-700 °C for 30 minutes.

Feng, J *et al.*, [57] reported that the CZTS thin-film absorber layer was prepared using a two- step process. At the first step, a Denton radio frequency (RF) magnetron sputtering system was used to prepare the as-deposited CZTS thin films. A near stoichiometric ratio of Cu_2ZnSnS_4 sputtering target (2 inch in diameter and 0.25 inch in thickness) was formed by hot pressing. Clean soda lime glass (SLG) ($25 \times 50 \times 1$ mm^3) was used as a substrate. Before SLG was put into the vacuum chamber, SLG was ultrasonically cleaned in the deionized water, acetone, ethanol, and subsequently dried in a nitrogen gas stream. After the deposition chamber was evacuated to a background pressure of 6×10^{-6} Torr, CZTS thin films were deposited in an Ar atmosphere with an RF power of 75 W and a pressure of 6 mTorr. The deposition time was adjusted in order to obtain films with a thickness of about 1000nm. At the second step, the as-deposited CZTS thin films were sulfurized in a horizontal tube furnace. The CZTS samples were positioned in the mid-plane of the chamber and a quartz container with sulfur powder was located at approximately 3 cm ahead of samples in the direction of Ar gas flow. The as- deposited samples were sulfurized in Ar atmosphere (the flow rate was set at 35 sccm) with heating temperatures of 400, 450, 500 and 550^0 C, respectively, for 30 minutes (the heating rate was set at 10^0C/min). After the sulfurization process completed, these samples were cooled to room temperature naturally.

In Control of composition and properties by the use of reflector wall in RF sputter deposition of Cu_2ZnSnS_4 thin films by [58], the sputtering apparatus used was a batch-type ultra- high vacuum sputtering system equipped with a reflector wall. The magnetron cathode (76.2 mm dia.) was mounted on the bottom plate of the chamber. The distance between the target and the substrate was 55 mm. A sintered quaternary CZTS plate with a composition of Cu: 24.7, Zn: 14.9, Sn: 11.4 and S: 49.0 in atomic % was used as the target. The discharge gas was Ar (99.9995% in purity), of which the flow rate was controlled by using a mass flow controller. The chamber was evacuated to below 7.0×10^{-4} Pa prior to deposition by using an oil diffusion pump. Dis- charge pressure was set at 3.0 Pa for an Ar flow rate of 5 sccm by adjusting the pumping speed. The cathode discharge was generated by applying a 13.56 MHz RF-power of 50 W to the electrode. The temperature of the reflector wall was the room temperature and 400°C. Substrates used were borosilicate glass plates ($50 \times 50 \times 0.9$ mm^3). Substrate temperature was changed from room temperature to 400°C. The thickness of deposited thin films was adjusted to about 500 nm by changing deposition time.

Surgina, G. D *et al.*, [29] reported that the deposition of CZTS thin films was performed at room temperature by the reactive PLD in H_2S flow in a dedicated home-made setup with the base pressure $P \approx 10^{-4}$ Pa. The first series of as-deposited CZTS films was annealed in vacuum ($< 10^{-5}$ Pa) in the temperature range $T_{ann}=$ 300 to 500°C for 3 min (SVA). The second series of CZTS films was subjected to LAN (in pure N_2 atmosphere at $P \approx 10^5$ Pa; base pressure in annealing chamber $P \approx 10^{-4}$ Pa) in the range $T_{ann} =$ 200 to 400°C for 3 hrs.

heng, B. T *et al.*, [42] Reported that the Cu_2ZnSnS_4 thin films were deposited on bare soda-lime glass (SLG) substrates by a one-step radio frequency magnetron sputtering process. Glass substrates were ultrasonically cleaned with the sequence of ace- tone, alcohol and de-ionized water. Sputtering process was carried out in Ar atmosphere with working pressure of 0.5 Pa and Ar flow rate of 30 sccm. The distance between target and substrate was 6 cm while RF sputtering power was maintained at 100W. Substrate temperature was also maintained at 50 °C, 100 °C, 150 °C and 200 °C. The total deposition time of the CZTS films is 60 min.

In Cu_2ZnSnS_4 thin film deposited by sputtering with Cu_2ZnSnS_4 compound target by [59], the precursor of the CZTS thin films was deposited by RF magnetron single sputtering with a CZTS compound target at room temperature. The precursor was annealed in a H_2S (5%) and N_2 atmosphere. Soda Lime Glass (SLG) and Mo-coated SLG substrates were used for the fabrication of the precursor. The CZTS compound target was adjusted to the composition of the Cu- poor and Zn-rich compound target, which is important for achieving a high conversion efficiency. The pressure of the Ar sputtering gas was 0.5 Pa. The RF powers were 100W. The sputtering time was adjusted to obtain a film thickness of about 0.6 μm. The annealing temperature was increased from room temperature to the target temperature at 5 °C/min. The target temperature was maintained for 2h. Then, the temperature was decreased to 100°C at 5°C/min followed by natural cooling. The annealing temperature ranges from 200 to 500°C respectively.

Song, X *et al.*, [40] Reported that the CZTS thin films were grown on $1cm \times 1cm \times 1mm$ single crystal double-side polished ZnS (100) wafers by RF magnetron sputtering from a single 4″ CZTS target. Prior to film deposition the sputter chamber was evacuated to 4×10^{-4} Pa while the working pressure was controlled at 2.7 Pa with feeding Ar gas at a flow rate of 60 sccm into the reaction chamber. The sputtering processes were carried out with an RF power of 50 Watt. Substrate temperature was varied at 400 °C, 450 °C, 470 °C and 500 °C, respectively. Before each deposition, the target was pre-sputtered for around 15 minutes to remove any contamination. The thickness of

each CZTS layer was approximately 300 nm with a growth rate of approximately 5 nm/min.

Nakamura, R *et al.*, [60] reported that the CZTS thin films were deposited on glass substrates by RF magnetron sputtering process from a sintered pellet target (2 inch and 4 mm thick). The non-stoichiometric CZTS pellet was synthesized by the solid-state reaction of Cu_2S, ZnS, SnS_2 and S powders mixed at 2:1.5:1:1 mol ratio. The glass substrates (25mm × 25mm) were ultrasonically cleaned in acetone, distilled water, and ethanol, and dried in a nitrogen gas stream before being put into the vacuum chamber. The deposition chamber was evacuated to a background pressure of $3.0×10^{-4}$ Pa, using a turbo molecular pump (TMP). First, the as-deposited thin films were deposited on glass from a quaternary CZTS target, using high-purity argon (20 sccm) discharged with an RF power of 80 W. The working pressure during the deposition was at 1.6 Pa. Before as-deposited process, the pre-sputter process has been done. The pre-sputter pressure was at 1.6Pa, using high-purity argon (20sccm) discharged with an RF power of 40 W. The pre-sputtering time is 2 min. The substrates were placed on a rotating heater and the distance between target and substrate was fixed as 6.5 cm. The substrate temperature varied from 350 to 500^0C in the increment of 50^0C. All of the thin films were deposited for 1 h. After the deposition, all CZTS thin films were annealed in a furnace in the atmosphere of Ar +H_2 S (5%) at a temperature of 520^0C.

He, J *et al.*, [61], reported that the CZTS absorber layers were fabricated using a radio frequency (rf) magnetron sputtering method on soda lime glass substrates. A quaternary compound target with 2-inch in diameter, 4 mm thickness and 99.99% purity attached to a Cu plate was used for sputtering. Prior to deposition, soda-lime glass substrates were cleaned in acetone, methanol, ethanol and deionized water. The chamber pressure before deposition and during the deposition was maintained at $3.2 × 10^{-6}$ Torr and 10 m Torr, respectively. During the growth of the CZTS layer, the Ar gas flow rate and rf power were maintained at 30 SCCM and 90 W respectively. The sputtering time was adjusted to obtain 1200nm thick CZTS films.

Inamdar, A. I *et al.*, [62] Reported that cleaned soda lime glasses (SLG) were used throughout the experiment. On top of SLG, Mo was deposited using sputtering technique for 104 minutes at room temperature. The chamber operating pressure was maintained at $3.7 × 10^{-2}$ Torr. During the growth of the Mo layer, the RF power and Ar gas flow were maintained at 125 Watt and 9 sccm. The same parameters were used for Mo sputtered films all through the experiment. On top of Mo coated SLG, CZTS were sputtered. The sputter vacuum chamber was exiled to less than $3.5 × 10^{-5}$ Torr. Ar gas was acquaint with a flow rate of 10 sccm as working gas. The operating pressure during CZTS sputtering was maintained at 4.2

$× 10^{-2}$ Torr. Only substrate temperatures were changed on this work. Rest of the parameters remained unchanged throughout the experiment. 300^0C, 350^0C, 370^0C, 400^0C and 450^0C temperatures were used. The as-grown thin film was then thermally annealed in an N_2 atmosphere at different temperatures ranging between 350 and 550 °C for 20 minutes with a time to reach those temperatures of 20 minutes.

In [63], the sputtering of the absorber was carried out at room temperature using argon gas as the working gas at a pressure of 0.7 Pa. The base pressure of the sputtering chamber is $3.0 × 10^{-3}$ Pa and the substrate to target distance is 50 mm. Both glass and Mo-coated glass were utilized as the substrate. The sputtering power for the quaternary target is 250 W. Samples in the tube were heated to the setting sulfurizing temperature at a heating rate of $20^0C/min$ and kept at the temperature for 10 min. Finally, the samples were cooled down to room temperature naturally.

Effect of deposition parameters on the optical properties of CZTS absorber
Again, [17] obtained the band gap (Eg) of the four CZTS films at growth temperatures of 400°C, 450°C, 500°C, and 550°C as 1.59 eV, 1.56 eV, 1.52 eV and 1.47eV respectively. It has been observed that with increase in the growth temperatures, the band gap values shift to lower energies. The band gap energy of the CZTS thin film is dependent on the composition. Therefore, when the temperature is at 500°C, the CZTS thin film not only has good crystal quality and large grain size, but also the proper band gap energy (i.e. 1.52eV) that is very close to the optimum band gap energy of semiconductor used for photovoltaic device.

Zhu, Y *et al.*, [41], showed that the. The optical absorption coefficients of the CZTS films prepared at 35 and 50 W are higher than that of the amorphous films prepared at 20 and 65 W, but yet lower than the reported 10^4 cm^{-1} for CZTS films deposited with RF sputtering and annealed at elevated temperature in Ar-S (g) ambient. The lower absorption coefficients of prepared CZTS films could be attributed to the deviation of Cu and Sn stoichiometry and the lack of sulfurization process. Relatively high absorption was observed at long wavelength regime, which may suggest the presence of some compounds other than CZTS in the film. The band gaps of the amorphous thin films prepared at rf powers of 20 and 65 are 1.96 eV and 1.88 eV, respectively. CZTS crystals begin to form in the films at DC powers of 35 and 50 W, causing a decrease in band gap. The lowest value of 1.65 eV was obtained at 50 W.

Feng, J *et al.*, [57], reported that all the sulfurized CZTS thin films show a high optical absorption co- efficient larger than 10^4 cm^{-1} when the incident photon energy ranges from 1.2 to 3 eV. The

optical band gaps are determined to be 1.37, 1.45, 1.53 and 1.61 eV for the CZTS films sulfurized at 400, 450, 500 and 550 ^{0}C, respectively. This research group concluded that the optical band gap increases with the increase of the sulfurization temperature.

Parthibaraj, V *et al.*, [56] Showed that the optical transmittance spectrum of CZTS thin film deposited at substrate temperature 573 K was recorded in the wavelength range 400-2500 nm. The transmittance spectrum suggests that the maximum transparency is around 40%. At a longer wavelength range, the spectrum consists of interference pattern. It reveals that the film has good average absorbance. The absorption coefficient on the other hand is found to be larger than 10^{-4} cm^{-1} in the visible region. This type of film can absorb the photon energy consisting of the visible and infrared regions and therefore, can be considered as an excellent absorber material for thin film solar cells. The estimated direct optical band gap of the CZTS films is about 1.51 eV.

Kusano, E *et al.*, [58] Obtained band gaps of 1.82, 1.74, and 1.68 eV respectively for the samples. Thin films deposited by using the heated reflector wall yield narrower band gaps than those deposited without using the reflector wall or by using the unheated reflector wall. In addition, the band gap decreases gradually with increasing substrate temperature. However, it is shown that the use of the heated reflector wall decreases the band gap, resulting in the improvement of optical absorption properties of thin films.

In [59], the transmittance analysis results of CZTSe thin films showed that all the thin films have good optical performance. The transmittance of the thin films could be almost 0% in the visible region (from 380 nm to 780 nm) and more than 50% in the wavelength ranged from 1200 nm to 2000 nm. Among them, the CZTSe thin films annealed at 400°C showed very high transmittance in near infrared region, while the thin film without annealing treatment got the lowest transmittance. The average transmittance in near infrared region increased as annealing temperature increasing ranged from 300°C to 400°C and decreased as annealing temperature increased from 400°C to 550°C. With the increase of annealing temperature, the average transmittance of the thin films decreased, the transmission ability became weak. It might be affected in the process of thin film recrystallized at the high temperature environment, and this led to the transmission rate's reduction. These results were related to the surface morphology of the thin film caused by deposition mechanism and annealing treatment. The band gaps obtained for the thin films annealed at different temperature revealed that a relative-optimum band gap of 1.48 eV for all the thin films was obtained with the annealing temperature of 400°C. While the other samples clearly showed that the partially

disordered Kesterite structure has a band gap between 1.00 eV and 1.20 eV. After annealing treatments, the band gaps had significantly improved.

Nakamura, R *et al.*, [60] reported that the band gap energies of the samples deposited by both processes are determined to be 1.4–1.5 eV, except for the sample annealed at 200°C and the precursor deposited by the co-sputtering process because of their different sulfur contents.

In the work of [40], transmittance (T) and reflectance (R) of the obtained CZTS film were measured at room temperature. The absorption coefficient (α) was larger than 10^4 cm^{-1}. The band gap is estimated to be 1.51 eV, which is quite close to the optimum band gap for a solar cell.

Xie, M *et al*., [43], indicated that the transmittance increases as the wavelength increased to nearly 800 nm and the reflectance is around 15% in the tested wavelength range. A number of waves appear in the reflectance spectra which may be from the coherence of the light wave since the tested CZTS film is 2 microns thick, which is obviously bigger than the wavelength of the incident light. Yet, a shake appears in the spectra at a wavelength of around 900 nm which may be attributed to the use of two different lamps at wavelength range of lower than 900 nm and above 900 nm. Accordingly, the band gap of the obtained CZTS films is determined to be 1.55 eV which is very close to the band gap reported in the literature and the optimal band gap for single junction solar cells.

He, J *et al*., [61] showed that the determined band gap (E_g) of the four as-deposited CZTS films are 1.60, 1.65, 1.77, and 1.86 eV, respectively. Band gap of as-deposited thin films grown at different substrate temperature are larger than that of other experimental and theoretical values reported by other researchers and the E_g increases gradually with the decrease in substrate temperature. This is possibly due to the fact that secondary phase such as ZnS (E_g = 3.2 eV) easily occurs under the lower growth temperature. Therefore, the presence of ZnS in as-deposited CZTS thin films is possibly responsible for the larger E_g. Compared with the as-deposited thin films, E_g values of four post-annealed CZTS films are 1.57, 1.64, 1.71, and 1.78eV, respectively. Obviously, the optical band gaps of post-annealed thin films are smaller than those of as-deposited thin films. It is probably due to the combined effect of internal compressive stress and the various chemical compositions. On the one hand, internal compressive stress releases in post-annealed CZTS thin films. The relaxations of internal compressive stress make crystal lattice expand and thus the expansion of lattice will diminish the band gaps of CZTS films. On the other hand, after post-annealed process, the chemical composition of thin films has changed.

Inamdar, A. I *et al*., [62], the band gap energies at the zero absorption coefficients are found to be 1.65, 1.51, 1.45, and 1.4 eV for the four samples respectively. These band gap energy values are consistent with reported values.

Xie, M *et al*., [63], reported that to evaluate the optical band gap of the sulfurized films, the refection and transmittance spectra of the films were recorded by a UV-VIS-NIR spectrometer. The band gap of the obtained CZTS films in this paper is estimated to be 1.57 eV.

Abdullahi, M *et al*., [64] reported that the sample of 450 nm thickness is having an average transmittance of 0.0092%. This is a clear indication that the sample is almost opaque. This indicates that these films grow with a high density of native defects (vacancies, interstitial and antisite). The average transmittance of the samples annealed at 523, 623 and 723K is 4%, 8% and 16% respectively. As the annealing temperature increases, the transmittance increases. Low transmittance values in thin films indicates high absorption. The direct optical band gaps of the samples are found to be 1.80, 1.52 and 2.30 eV, respectively. From this, the band gap energy (E_g) of the film deposited at 523K is quite close to the optimum value for CZTS. It has been observed that the as-deposited and the films deposited at 623K and 723K exhibited much higher band gap than the film annealed at 523K. The presence of ZnS phase causes the enlargement of the optical band gap since this phase has a large band gap of 3.5eV. It has been noted that the value of the band gap for the annealed samples though influenced by secondary phases increases with increase in the annealing temperature. All the samples showed absorption coefficient greater than 10^4 cm^{-1} and fundamental absorption edges with complex structures.

CONCLUSION

This article has focused on the recent developments in deposition of CZTS thin films from compound target by rf sputtering technique. Here, a brief overview of the rf sputtering, substrates and the optical properties of the films has been given. Although significant progress in the performance of CZTS absorber has been achieved in recent years, substantial further improvements are necessary to overcome the negative effects of secondary phases of this material. Some research areas are identified to accelerate this process. A low temperature post-annealing treatment is observed to reduce the concentration of Cu_{Zn} and Zn_{Cu} defects and consequently increase the effective Eg.

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