Chapter - IV

PREPARATION, CHARACTERIZATION AND FABRICATION OF 
\( \text{Cu}_2\text{ZnSnS}_4 \) (CZTS) THINFILM SOLAR CELLS USING VACUUM AND NON-VACUUM TECHNIQUES

In this chapter, Copper Zinc Tin Sulphide (CZTS) thin film based solar cells prepared by vacuum thermal evaporation, chemical bath deposition (CBD), spray pyrolysis, and SILAR techniques. CZTS thin film successfully deposited on Mo coated glass substrate about the sequential vacuum thermal evaporation of ZnS, Cu, and Sn powders. In chemical methods, metal chlorides and sulphides consumed as the precursor materials. Their structural, electrical, and optical properties were studied and discussed. Prepared films have found to be polycrystalline and p-type semiconductor. CZTS thin film based solar cell having fabrication consists of some different device configurations. The photovoltaic properties of CZTS thin film solar cells were examined and their performances were tabulated.

4.1. Introduction

Development of green energy production depended on the peculiar properties of newer semiconductor materials. Thin film solar cells with various increasing efficiencies have achieved by different kinds of techniques such as physical and chemical vapour deposition methods [1]. A large part of this work has been focused on chalcopyrite and kesterite compounds. Semiconducting quaternary compound as Copper Zinc Tin Sulphide (CZTS) has shown promising applications in solar cell [2]. It is one of the most important absorber layer materials for low-cost thin film solar cells due to its semiconductor properties such as p-type conductivity [3-5], direct band gap and high absorption coefficients (>10^4 cm\(^{-1}\)), as well as the abundant and nontoxic constituent elements. CZTS gives an advantage of electronic and optical characteristics like to copper indium gallium selenide (CIGS) contributing it well
appropriated absorber layer of thin-film solar cell, yet unlike CIGS, CdTe and other thin film materials, it is combination of only non-toxic and plentiful elements [6-9]. Anxious with the availability and cost of tellurium in CdTe and indium in CIGS, as well as poisonous of cadmium have been an extensive motivator to explore considering alternative thin film solar cell absorber layers. Recent ameliorations in laboratory cells of CZTS received 12%-efficiency [10, 11].

Copper zinc tin sulfide is a I_2-II-IV-VI_4 quaternary compound found in nature. In the kesterite structure, CZTS can acquire through exchanging the trivalent In/Ga with a bivalent Zn and IV-valent Sn atoms from the chalcopyrite CIGS. The crystal energy is only 2.86 MeV/atom lesser for the kesterite than stannite proposing that both kinds can coexist; it shows from first principle calculations [12, 13]. Structural conformation obstructed by Cu-Zn cation disorder, neutron scattering and theoretical calculations predicted as the confirmation of these usual common defects [14, 15]. Almost unsystematic arrangement of Zn and Cu can direct to the dissimilarity of the structure. Since CZTS compound, the properties like diffusion length and connected carrier lifetimes are feeble (below 9 ns) [16]. In addition, its absorption coefficient and Carrier concentrations are alike to CIGS. The recombination of an E-H pair of grain boundaries and high density of active defects may be reduced to the lowest carrier lifetime. Quaternary compounds hold in possession that numerous secondary phases like CuS, SnS, ZnS, and Cu_2SnS_3. Raman scattering used to investigate these secondary phases, because peaks of Cu_2SnS_3 and ZnS overlaps with CZTS in X-ray diffraction analysis [17-19].

CZTS absorber layer has deposited by a diversity of non-vacuum and vacuum methods. The most favourable fabrication stipulations may incompatible from CIGS and they mainly reflect what has been successful with it. The manner of proceeding ways generally classified as non-vacuum deposition vs. vacuum and sulfurization/selenization vs. single step reaction techniques. Vacuum assisted ways are controlling in the now passing CIGS industry, on the contrary in the elapsed
decade, there has been growing concern and development in non-vacuum procedures having to their powerful diminish investment and pliability to coat an extensive area. A very exact challenge for CZTS and related alloy fabrication is the volatility of some elements SnS and Zn that can vanish under reaction circumstances. At temperatures higher up 500 °C CZTS will decay into binary and ternary mixtures even though, element volatility is not so much of a puzzle once CZTS formed in a vacuum. A large number of vacuum techniques, manufacturing in the success of a single-phase material has resulted with these above difficulties. To shun volatility questionable, the formation of CZTS films presently accomplished at low temperatures from some chemical methods. Oregon State University has brought out a suitable continuous flow process for mass production on an industrial scale using ethylene glycol as a solvent [20]. CZTS has non-toxic and earth abundant elements resemblance in CIGS chalcopyrite structure. Precursor materials are nearly five times inexpensive, as compared to CIGS and its availability (Cu, Sn, Zn and S) suggested that the production of sufficient energy with only 0.1% of the abundance of material resources to power the world [21]. Moreover, it has eco-friendly nature and dissimilar with CdTe. Although occasionally it mixed with selenium and the junction partner of this solar cell sometimes has CdS as the n-type layer. In this chapter describes Copper Zinc Tin Sulphide (CZTS) thin film based solar cells prepared by vacuum thermal evaporation, chemical bath deposition (CBD), spray pyrolysis, SILAR techniques and their photovoltaic performances were examined.

4.2. Preparation of Cu$_2$ZnSnS$_4$ (CZTS) thin films

4.2.1. Vacuum Evaporation

The CZTS thin films were prepared using a vacuum coating unit (High Vacuum Company, Bangalore) Model 12A4D. The vacuum deposition of CZTS thin films done by sequential thermal evaporation of their precursors at a background pressure around 1×10^{-6} mbar; we fabricated CZTS thin films on Mo coated ITO glass substrates by vapour-phase sulfurization of thermally evaporated precursors. This
process consisted of two stages with the sequential evaporation of precursors followed by the vapour-phase sulfurization. We formed the stacked precursors on the substrates by depositing ZnS, Cu and Sn layers with thermal evaporation orderly [22]. The little amount (~ 0.001g) of materials was placed in molybdenum boat with different compositional ratios of the Cu : ZnS : Sn layers of 2:1:1, 2:1.5:1 and 2:2:1. The boat was heated indirectly by passing current through the electrodes. The substrates were cleaned with chromic acid, ultrasonic cleaner, soapy water, distilled water and then with acetone. The source-substrate distance was maintained at 10 cm. Rotary drive was used to obtain the uniform coating. After reaching high vacuum (1×10⁻⁶ mbar) in the vacuum chamber, slowly current was applied to the electrodes to heat the substance. A source shutter was used to stop the deposition of the film on the substrate. When all the parameters (vacuum, the rate of evaporation, substrate temperature, etc.) were optimized, then source shutter was removed and deposition of the film starts on the substrate. The rate of evaporation was maintained at ~1.4 Å/Sec. All the films were prepared at room temperature. The rate of evaporation and thickness of the as-deposited films were measured using the quartz crystal monitor (“High Vacuum Company” Digital thickness monitor Model-DTM 101) fixed to the unit. The thickness of all the films was measured to be 0.9 μm to 1.7 μm. Moreover, the thicknesses of the three layers are an according to the ratio of the constituents. Using a cracker source to sulfurized the deposited films in an annealing furnace in the atmosphere of N₂ +H₂S (5%) at temperature of 550 °C for 2 hours [23]. After sulfurization process, the CZTS thin films were subjected to fabricate solar cells and to examine their characterizations.

4.2.2. Chemical bath deposition (CBD)

The solution based deposition of CZTS thin films done by CBD technique. The bath solution consists of required amount of copper chloride (2M), Zinc chloride (1.2M), tin chloride (1M) and thiourea (8M) were added in a mixture of solvent consisting ethanol/water (3:7). Clear yellow solution was formed after being stirred at
room temperature for ten minutes. The substrate dipped in the solution for 24 hours. A thin coating with white Coloration appeared on the substrate. The coated substrate removed at the end of the deposition, washed in deionized water, dried in air at 110 °C temperature [24]. Finally, the annealing temperature was elevated to 500 °C and then sulfurization of deposited films in an annealing furnace in the atmosphere of N₂ + H₂S (5%) at temperature of 550 °C for 2 hours. The samples were annealed in the pressure-controllable furnace with N₂ + H₂S (5 wt %) gas ambient - sulfurization – to supply additional sulfur into CZTS film. After pumping down to 1.0 × 10⁻² torr and fluent the Ar gas to remove the initial oxygen, a mixture gas of N₂ + H₂S (5 wt %) was introduced into the furnace once the temperature reached to 550 °C. Annealing time and ramping rate were 1 hour and 5 °C/min, respectively [25]. The prepared polycrystalline CZTS thin films examined to analyze morphological, optical, electrical, and photovoltaic characterizations. Using weighing method the thickness of the deposited films was measured to be 1 μm to 1.3 μm.

4.2.3. Spray pyrolysis deposition (SPD)

Thin films of CZTS obtained using the spray pyrolysis deposition (SPD) technique from an aqueous solution. Copper chloride, Zinc acetate, tin chloride, and thiourea (CH₄N₂S) used as Copper, Zinc, Tin, and Sulfur precursors. Solutions with different molar ratio were prepared at 0.01 M: 0.005 M: 0.005 M: 0.04 M using deionized water. Using a hot plate, the substrate heated to the deposition temperature. The deposition parameters such as the spraying distance 20 cm from the nozzle to the substrate and the carrier gas pressure were set at previously optimized values [26]. Thus, the spraying distance was 20 cm and kept constant for all depositions. The temperature, the number of spray sequences and the Cu: Zn: Sn: S ratios investigated in this study. The prepared samples were annealed in the pressure-controllable furnace with N₂ + H₂S (5 wt %) gas ambient sulfurization to supply additional sulfur into CZTS film. After pumping down to 1 × 10⁻² torr and fluent the Ar gas to remove the initial oxygen, a mixture gas of N₂ + H₂S (5 wt %) was introduced into the
furnace once the temperature reached to 550 °C. Annealing time and the ramping rate was 1 hour and 5°C/min, respectively. The thickness of all the films was measured to be 1 μm to 1.3 μm.

4.2.4. Successive ionic layer adsorption and reactive (SILAR) deposition

CZTS thin films deposited using 0.1M CuCl₂, 0.05M ZnSO₄, and 0.05M SnCl₂ for cationic solutions and anionic solution was freshly prepared thioacetamide (C₂H₅S) for this deposition process. The CZTS thin film formation depends on the adsorption, reaction, and rinsing times were detailed in the literature [27]. One SILAR cycle contained four steps: (a) the substrate immersed into the first reaction containing the aqueous cation precursor, (b) rinsed with water, (c) immersed into the anion solution, and (d) rinsed with water. The experiment carried out in 30, 60, 90 and 120 SILAR cycles, so that the obtained thickness of these films varied in the range from 1 μm to 1.5 μm. The substrates were first cleaned using distilled water and dried in air and the deposited films were subjected to morphological, optical, electrical and photovoltaic characterizations.

4.2.5. Characterization

The structure of the prepared films was studied by X-ray diffraction studies using a Rigaku X-ray diffractometer (XRD) using Cu Kα (1.54 Å) irradiation. The surface morphology of the films was studied using scanning electron microscopy (SEM;VEGA 3 TE SCAN). Element analysis of the product was measured by energy dispersive spectrometer (EDS) equipped with the above SEM. Raman and Photoluminescence spectrums were recorded by He - Ne laser (633 nm, 18 mW) and a triple monochromator (Renishaw Invia Raman Microscope). The photocurrent-voltage (J-V) characteristics of the devices were measured using white light from a xenon lamp (max.150 W) using a sun 2000 solar simulator (Sponsor: MHRD-NEW DELHI & NCPRE - IIT-BOMBAY). Light intensity adjusted using a Si solar cell to AM-1.5. Incident light intensity and active cell area were 100 mWcm⁻² (one sun illumination) and 0.4 cm² (0.5 × 0.8 cm) respectively.
4.3. Results and discussion

4.3.1. X-ray diffraction Analysis

Single-phase Cu₂ZnSnS₄ (CZTS) thin films were prepared in this work using vacuum and solution based deposition methods. The CZTS films are then obtained by the sulfurization of the precursor in a quartz glass tube furnace in an atmosphere of N₂ +H₂S containing sulphur vapour. The stability region of CZTS is not large and small blunders in the stoichiometry can cause the precipitation of sham phases with mischievous effects on the photovoltaic cell characteristics. In addition to the investigation of the formation of spurious stages, XRD can be used to give information about film stress, imperfection and domain size. XRD measurements are performed to investigate the crystal structure of the film, as the effect of annealing temperature and the composition of the growth material ratio is varied. The micro structural parameters, such as grain size, internal stress, and micro strain, dislocation density were calculated from the XRD data using the following relations. The grain size was calculated using Scherrer’s equation [28],

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(4.1)

Where, \( D \) is the grain size, \( \lambda \) is the wavelength of CuKα radiation, \( \theta \) is the diffraction angle and \( \beta \) is the full-width at half-maximum. The lattice strain (\( \varepsilon \)) is calculated using the relation [29],

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

(4.2)

The value of dislocation density was calculated using the relation [30],

\[ \delta = \frac{1}{D^2} \]  

(4.3)

Fig. 4.1 shows the XRD pattern of Cu₂ZnSnS₄ (CZTS) thin films with different compositional ratios of Cu: ZnS: Sn layers of 2:1:1, 2:1.5:1 and 2:2:1 prepared by thermal evaporation on molybdenum substrate. The samples were of
good crystalline nature and diffraction peaks of Cu₂ZnSnS₄ thin films can be conclusively indexed as a tetragonal phase with the lattice constants of a=5.426 Å and c=10.835 Å, which are in good agreement with the reported values and in the standard card (JCPDS - 26-0575). As shown in Fig.4.2, sulfurization of the deposited thin films possesses a polycrystalline structure of peaks attributed to (002), (110), (112), (200), (211), (105), (312), (314) and (332) of Cu₂ZnSnS₄ (CZTS) appeared, which can be confirmed by the powder diffraction File (JCPDS - 26-0575). Moreover, the intensity of the (002) and (112) is the strongest, indicating that the thin films correspond to the kesterite structure, which belongs to the tetragonal system. The XRD patterns of thin film samples indicated that not only the highly oriented and it has polycrystalline nature. The diffraction peaks of (002) and (101), indicate the presence of CopperZincTinSulfide [31]. It is evident that the grain size increases with increasing concentrations of Zinc (Zn) in the elemental composition.

In addition, there are too disunited peaks from CuS (JCPDS- no. 075-2233) and SnS (JCPDS no. 073-1859). When the sulfurization time, gradually increases from 10 min, 20 min, 30 min and 40 minutes at 550 ºC, the phases of CuS and SnS vanish, but there are some X-ray diffraction peaks from SnS₂ (JCPDS no. 022-0951) except those from Cu₂ZnSnS₄ (CZTS). When the sulfurization time is about 30 and 40 minutes, the peaks from binary phases become invisible, and there are only the peaks of Cu₂ZnSnS₄ (CZTS). The result indicates that the annealed thin films show a mixture of Cu₂ZnSnS₄ (CZTS) polycrystalline phase with SnS, CuS, and SnS₂ as intermediates, and there is only the CZTS phase with the sulfurization temperature at 550 ºC. The films have the preferred (002) orientation, and the intensity of the peak (002) is increased with the increase of the sulfurization time.

Fig. 4.3 shows the XRD pattern of CZTS thin films prepared by chemical bath deposition method. The XRD analysis shows that the thin films are kesterite phase CZTS with lattice parameters a = 5.409 Å and c = 10.642 Å that is almost in good agreement with the standard data from JCPDS card no. 26-0575. The planes are
oriented in the direction (002), (110), (112), (200), (211), (105), (312), (314), and (332). The films exhibit tetragonal crystal structure with the highest intensity peak corresponds to (112) and (200) preferred orientation. The (112) peak is stronger than other peaks. In general, the preferential orientation of the films is along the (112) direction. Although, as annotated previously the presence of binary phases is forever anticipated in the CZTS is quaternary thin films. Certain extent of weak peaks was perceived, with a line width suitable with that of the kesterite reflection. The peak at low angle is consistent with a 2ax2ayx kesterite super cell, yet this wonderful upright is a coincidence. Here, as seen from Fig. 4.3, the peaks at 15° and 26.4° point out the diffraction from (001) plane of SnS₂ [32] and (120) plane of SnS [33], distinctly divulging the presence of these secondary phases in the as deposited films. For annealed and sulfurized samples shows the diffraction patterns also peaks at 44.927°, which corresponds to (105) plane of CZTS [34]. The peak from (120) plane of SnS intensifies in both samples. Howbeit, the peaks from CZTS are conspicuous in both of these samples. This indicates that in both annealed and sulfurized samples, the SnS phase was found with the majestic CZTS phase. It is evident from the grain size increases with increasing thickness.

Fig. 4.4 shows XRD pattern of CZTS thin films prepared by spray pyrolysis on molybdenum substrate. The substrate temperatures at Tₘ=100° C and 150°C exhibits the phase appears not textured and preferred orientation, if present is weak. Extra small invisible peaks are observed due to lattice mismatching between substrate and absorber layer. This is a probable sign of the intrinsic nature of stacking faults in the structure. The substrate temperatures at Tₘ=200 ⁰C, Tₘ=250 ⁰C and Tₘ=300 ⁰C shows the thin films are kesterite phase CZTS with lattice parameters a = 5.3928 Å and c = 10.746 Å which is almost in agreement with the standard data from JCPDS card No 26-0575. The XRD patterns of the Tₘ=200 ⁰C and Tₘ=250 ⁰C sample exhibits there is no major difference observed between the peak levels. Although, the variation of peak intensity in (110) plane was only observed. Substrate
temperatures at $T_s=300\,^0\text{C}$ the planes are oriented in the direction $(110), (112), (200), (211), (105), \text{and} (312)$. The films exhibit tetragonal crystal structure. The highest intensity peak corresponds to $(112)$ preferred orientation. The $(112)$ peak is stronger than other peaks. In general, the preferential orientation of the films is along the $(112)$ direction. The samples seem only made of kesterite phase. Two additional small peaks are present near the $(112)$ most intense peak. This is a possible indication of the presence of detrimental faults in the structure.

The X-ray diffraction patterns of the CZTS thin films, grown at different SILAR cycles on molybdenum substrate are shown in Figure 4.5. The XRD analysis shows that the thin films are kesterite phase CZTS with lattice parameters $a = 4.8928\,\text{Å}$ and $c = 10.536\,\text{Å}$ which is almost in agreement with the standard data from JCPDS card No 26-0575. The XRD patterns of the 30 and 60 SILAR cycles exhibits there is no major difference observed between the peak levels. Although, the variation of peak intensity in $(314)$ and $(008)$ planes was only observed. SILAR cycles at 90 and 120 exhibits the planes are oriented in the direction $(110), (112), (200), (211), (105), (312), (314), \text{and} (008)$. The planes are highly oriented in the direction of $(110)$ and $(112)$. The films exhibit tetragonal crystal structure. The highest intensity peak corresponds to $(112)$ preferred orientation is stronger than other peaks. The major unusual peaks are present in the diffraction pattern of kesterite. The broadening is larger so we can assume that those peaks belong to a secondary phase. The presence of multiple orders of the same diffraction signal, just two reflections witnesses a reasonable firm texture of these binary and spurious phases.

Quaternary compounds hold in possession numerous secondary phases and like those, that executions of CZTS solar cell can affect by their presence. Secondary phases can supply shunting current footpaths by means of the solar cell and feign as recombination centres, both dishonouring solar cell performance. All secondary phases own a mischief effect on CZTS performance and it appears from the literature
large of them are both difficult to expose and generally present. Usual phases comprise CuS, SnS, ZnS, and Cu$_2$SnS$_3$. Employing, in this technique the binary compounds like ZnS, Cu$_2$SnS$_3$ superimposes with CZTS. Because of this signification, the acknowledgment of these compounds is very complex by hereditable techniques [35]. Additional method as if Raman scattering investigated to assist characterize CZTS structure.

### 4.3.2. Raman Analysis

Raman spectroscopy is one of the greatest potential instruments for deciding the crystalline structure and quality of thin films, in the existing of absorber defects strongly influenced to change their shape and position of Raman peaks, another in the form of structural non-uniformities or secondary compounds [36]. For the purpose of accomplish improve device execution in PV cells supported on CZTS thin film layers and to make better the usage of Raman tool as a dominate technique for valuation for the purpose of crystalline quality and identification of binary phases in these potential emerging material semiconductors, it is needful to acquire outstrip information of their vibrational properties.

In addition to X-ray analysis, Raman measurements used to analyze on of CZTS thin films prepared by the CBD and thermal evaporation methods. In Fig. 4.6 and 4.7 shows, two major peaks are perceived nearly 287 cm$^{-1}$ and 337 cm$^{-1}$ assigned due to the A1 symmetry of Kesterite phase [20]. The A1 modes are pure anion modes that correspond to the vibration of sulphur atoms surrounded by motionless adjoining atoms. A support peak of the main point at 348 cm$^{-1}$ and a coarse peak at about 365 cm$^{-1}$ were also perceived, which is in agreement with the reported results are attributed to the transverse (TO) and longitudinal Optical (LO) modes of Kesterite CZTS phase respectively [37]. Lack of peak at 277 cm$^{-1}$, which is a peculiarity peak of Stannite phase the thin films implies that the CZTS formed in the annealed and sulfurized samples exhibit dominant Kesterite phase [38], which is
favourable because of its suitability thus an absorber in the solar PV. Thus, the presence of these four peaks such as 287 cm\(^{-1}\), 337 cm\(^{-1}\), 348 cm\(^{-1}\), and 365 cm\(^{-1}\) in the Raman spectra verifies the reformation of Kesterite phase in the compound. Strong and acuminate major peak point outs that the well crystalline quality of the compound. The \(I_4\) group space symmetry shifts to a disordered kesterite type \(I_{42m}\) symmetry, which is the same for stannite [39]. It has also reported that the peak at 331 cm\(^{-1}\) related to the reality of local structural irregularities within the disorganized cation sub lattice [40].

In Fig. 4.8 and 4.9 shows, Raman spectroscopy measurements studied on thin films of CZTS prepared by spray pyrolysis deposition and SILAR methods. In both spectra the dominant peak is located at 334 cm\(^{-1}\), indicating that CZTS with the kesterite/stannite structure is the most influential phase exist in the samples. In both spectra indicating that, CZTS of kesterite and stannite structure with the impressive peaks are situated at 330–332 cm\(^{-1}\). The Raman scattering peak at 287 cm\(^{-1}\) can be attributed to either the A mode of KS at 284.30 cm\(^{-1}\) or the A1 mode of ST at 277.12 cm\(^{-1}\). The peak at 346 cm\(^{-1}\) can be attributed to either the E (TO) mode of KS at 351.55 cm\(^{-1}\) or the E (TO) mode of ST at 346.01 cm\(^{-1}\). The peak at 364 cm\(^{-1}\) can be attributed to either the E (LO) mode of KS at 366.35 cm\(^{-1}\) or the E (LO) mode of ST at 364.87 cm\(^{-1}\); and the peak at 373 cm\(^{-1}\) can be attributed to either the B (LO) mode of KS at 374.05 cm\(^{-1}\) or the B2 (LO) mode of ST at 370.63 cm\(^{-1}\) respectively. This predominant peak suits to A1 vibration mode, where exclusively S-anions are implicated. The space symmetry changes from kesterite group \(I_4\) to a confused kesterite phase \(I_{42m}\) symmetry, which is the identical for stannite phase. It has also reported that the peak at 331 cm\(^{-1}\) colligated to the entity of structural irregularities within the disordered cation sub lattice.

As shown in Fig. 4.6 - 4.9, the Raman spectrum of CZTS thin films prepared by above vacuum and non-vacuum methods also describes the presence of other
binary phases such as SnS and SnS$_2$, which are in well agrees with the results of XRD [41]. More importantly, the failure of strong peaks at 352 cm$^{-1}$ and 271 cm$^{-1}$ rejects the existence of $\beta$-ZnS phase [42, 43]. The Raman spectra results are in appropriate congeniality with the XRD discoveries. However, there was no peak detected in the Raman spectrum similar to SnS phase. Either this might be due to the very little inhomogeneity in the compound or small amount of SnS phase in the sample. Overall, the Raman spectrum separates the presence of $\beta$-ZnS phase and confirms the formation of dominant CZTS phase in the samples.

4.3.3. Surface Morphological Analysis

SEM images, of vacuum thermal evaporated p-type CZTS thin film of thicknesses ranging from 0.9 $\mu$m to 1.7 $\mu$m shown in Fig 4.10 (a-d). The films are fully covered, homogeneous, well adherent, and free from crystal defects such as pinhole and cracks. The result shows that the film consists of compact structure grains with sub-micron size and low roughness, which is suitable for the absorber of thin film solar cells. As chemical bath deposition, Fig.4.11 (a-d) shows the SEM image of chemical bath deposited and annealed CZTS film. Annealed CZTS film composed of particles having size ranging from 50 to 300 nm. Particle size and crystallite size are different. Crystallite size is always smaller than particle size because a particle constitutes many crystallites. Moreover, the efficiency of thin film solar cell (TFSC) increases with the increasing crystal size of the absorber layers.

SEM images, of spray pyrolysis and SILAR deposited p-type CZTS thin film shows in Fig.4.12 and 4.13. In Fig.4.12 (a-e), it can be seen that a large amount of micro grains exists on the glass. After the annealing, although the surface morphology is still coarse, large agglomeration of grains and few voids in the film observed, which is beneficial in photovoltaic application. In addition, we also see that the grains covered with cluster. Due to volume contraction arising from the evaporation of volatile products, cracks exist in the film. Organic binders in the CZTS precursor sol-gel could prevent the formation of cracks. High temperature
annealing could improve the crystalline nature and increase the grain size of thin films. In Fig. 4.13 (a-d) shows, the SEM micrograph of SILAR deposited CZTS thin film. The formation of sub-micrometer crystallites distributed more or less uniformly over the surface is evident from the figure. Some holes indicating porosity and agglomeration of small crystallites also seem to be present in a certain regions on the film surface. The sizes of crystallites are from 75 nm to 84 nm.

Fig. 4.14 (a-d) shows the atomic force microscope (AFM) surface topography of as-deposited and sulfurized samples prepared by vacuum thermal evaporation, chemical bath deposition (CBD), spray pyrolysis, and SILAR techniques. In Fig. 4.14 (a,b)exhibits AFM images of vacuum thermal evaporated and chemical bath deposited CZTS thin film shows, there is no considerable morphological change with stoichiometry variations and except for the sulfurized samples. When the sulfurization time is about 40 minutes, rearranging of the small grains and increases their size considerably. AFM images, of spray pyrolysis and SILAR deposited p-type CZTS thin film shows surface roughness of CZTS layers with different substrate temperature and SILAR cycles has been shown in Fig. 4.14 (c-d). Surface roughness increases after sulfurization, whereas roughness decreases slightly for non-sulfurized samples like SILAR deposited films. The roughness decrease for the as-deposited samples with increase in film thickness, while for the sulfurized samples roughness increases with increase in sulfurization time from 10 - 40 mins.

Elemental profiles determined from the EDX scan are shown in Fig. 4.15 (a-d), which demonstrates the presence of a Sn-rich grain near the junction layer. According to EDX analysis, shows that the sizeable textured grains are CZTS and the pettier grains near the interface between CZTS and the rear contact metal layer are CuS, which is phase-separated out of the initial Sn-rich columnar small hard particles. As far as shunning phase separation is involved, apart from the deposited CZTS close to its stoichiometry in the range of Cu/Sn = 1.7 – 1.8 and Zn/Sn = 1.2 – 1.3. This implies that the most favourable stoichiometry for high efficient PV
cells. The energy dispersive spectrum (EDS) shows that the relative elemental ratios for Cu:Zn:Sn:S were consistent with the 2:1:1:4 stoichiometry. The spectrum divulges that the film is Cu poor and Zn rich, Cu/(Zn + Sn) = 0.79 and Zn/Sn = 1.3, which makes better the photo conversion efficiency [44].

4.3.4. Optical properties of the CZTS thin films

4.3.4.1. UV –VIS spectral analysis of the CZTS thin films

The optical properties of the films deposited on Mo coated glass substrates were determined from the absorption measurements in the range 300–1100 nm. Fig. 4.16 - 4.23 shows the absorption spectra of CZTS films formed by sequential vacuum evaporation and chemical deposition methods like CBD, SPD, and SILAR. The optical absorption is more than 75% in the visible range for the polycrystalline film deposited from different molar ratios. It decreases lightly when the film is formed by changing their composition ratios (A = 70%). However, in the case of the CZTS thin films prepared from the above methods, transmission of much lesser value is observed in the visible range as compared to absorption spectra in the case of the monolayer film and of large absorption coefficient(>10^5 cm^{-1}) for the CZTS film. Based on the obtained both optical measurements, the square of absorption coefficient (αhv) \(^2\) are plotted as a function of light energy (hv). A steep optical absorption feature obtained, indicating that good homogeneity in the shape and size of the grains as well as low defect density obtained at near the band edge. As can be seen, (αhv) \(^2\) vary almost linearly with hv above the band gap energy (E_g). E_g was attained from UV-VIS analysis based on the following equation [45],

\[
αhv = k (hv - E_g)^m
\]  

(4.4)

Where, α is the light absorption coefficient, h is the Planck constant and ν is the frequency of the incident light, k is the force constant and m is the direct or indirect band transition. In Fig. (4.17, 4.19, 4.21 and 4.23) shows that an extrapolation method in conjunction with the above equation produces E_g; the band gap is
estimated to be 1.48, 1.51, 1.50, and 1.53 eV by extrapolating the straight-line part of the \((\alpha h\nu)^2\) versus \(h\nu\) curve to the intercept of the horizontal axis. These values are quite close to the theoretical optimal value of a single-junction solar cell. It shows that the preparation conditions do not affect the optical absorption of the film, however the optical band gap value slightly increases (1.53 eV). The absorbance and optical band gap of the films prepared in the present study agrees well with the values observed for CZTS films grown by vacuum thermal evaporation, chemical bath deposition (CBD), spray pyrolysis, and SILAR techniques.

4.3.4.2. Photoluminescence analysis of the CZTS thin films

Figure 4.24 represents room temperature photoluminescence (PL) spectrum of CZTS films prepared by vacuum thermal evaporation, chemical bath deposition (CBD), spray pyrolysis, and SILAR techniques at an emission wavelength of 960 nm, which is the peak position on a broad PL spectrum collected as a function of wavelength at room temperature. The PL measurements are to create carriers by optical excitation with photon energy above the band gap of the films (1.48, 1.51, 1.50, and 1.53 eV). The peak positions corresponds to 1.36, 1.39, 1.41 and 1.43 eV, which is smaller than the estimated band gaps of 1.48, 1.51, 1.50 and 1.53 eV from the optical measurement. However, Figure 4.25 exhibits time resolved PL spectrum observed near 860 nm (~1.34 - 1.47 eV) is almost recognizable to the PL at 960 nm unless for a maximum amount of disorder (noise) due to the disabled luminescence signal produced at 860 nm. Since the nature of pulsed excitation source (15 kHz), generates approximately 5000 times excess of carriers as large as steady-state concentration during continuous illumination at the same power density. For the determination of a carrier lifetime, of a few nanoseconds extracted from fitted by a single exponent. With this value of the lifetime and with a conservative assumption of electron mobility \((\mu_n)\) of \(5\text{cm}^2/\text{Vs}\), we estimate the lower bound of the diffusion length \((L_n)\) and the depletion width \(W_D\) of electrons in CZTS [46],

\[
L_n \sim (D_n \tau)^{1/2} = [\mu_n (kT/q) \tau]^{1/2}
\]  

(4.5)
\[ W_D = \left( \frac{2\varepsilon_0 \varepsilon_s V_{bi} / qN_A}{\varepsilon_0} \right)^{1/2} \quad (4.6) \]

Where, \( D_n \) is the diffusivity of electrons in CZTS. The \( V_{bi} \) is the band bending of CZTS at the CdS/CZTS interface, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon_s \) are the dielectric constant of CZTS, and \( N_A \) is the p-type carrier density of CZTS [47]. The sum of the estimated depletion width and the minority carrier diffusion length is close to the CZTS absorber thickness (~1µm), suggesting a good collection of carriers across the entire absorber thickness. Electrons and holes relax to their respective ground states in the conduction and valence band. They can then recombine radiatively as most free carrier or excitations. The PL spectra are CZTS thin films showed not only the well-known defect band, but also the evidence for bound excitation recombination. These results show a good polycrystalline quality of CZTS films. The absence of band-to-band transitions in PL spectra confirms the defect type recombination is the dominant recombination channel in this material due to the large number of possible intrinsic defects [48]. The peak positions suffer red shift as Cu/ (Zn+Sn) ratio of the CZTS thin films increased, which shows the same variation trend with the optical band gaps determined by transmission and reflection measurements. The correlation between PL and absorbance results may ascribe to the presence of the same defect, which has a state with an energy separation from one of the band edges, which is only weakly composition dependent. The failure of the yellow emission (YE) band confirms the improvement of crystalline quality, decreasing the density of native defects in the lattice and on increasing the grain size and hence diminishing the total grain boundary surface [49]. The presence of blue shift of the PL band peak confirms the donor-acceptor recombination process [50].

4.4. Electrical properties of the CZTS thin films

Four probe and Hall measurements indicate that CZTS thin film exhibits p-type conductivity to resistivity from 1.5 to 2.96 Ω-cm, the carrier concentration increased from 9.1×10^{16} to 2.09 x 10^{18} N (cm^{-3}) which depends on the increase in
elemental content in the precursor, preparation methods and parameters. The measured resistance decreased from $3.25 \times 10^3$ to $7.31 \times 10^2$ $\Omega/$sq. With increasing Cu: Zn: Sn composition in the precursor, indicating that main Cu-rich and Zn-rich powders have the smallest grain resistance [51].

The electrical properties of the films attributed to the enhanced grain size. The large grains in the material reduced the grain boundaries, thus effectively reducing the recombination of the charge carriers. The crystallite size increased with the increase in Cu/Zn concentrations [52] similar to that in previous reports [53, 54].

4.5. Device Fabrication and J-V characterization of the CZTS /CdS Solar Cell

In general, CZTS solar cells are composed of the front contact (i-ZnO), the window layer (n-CdS) and p- CZTS layer that is absorber made on top of Mo back contact. In this solar cell device, CdS layer is called window layer or buffer layer. Since direct contact of i-ZnO with CZTS forms bad contact for solar cell [55], CdS buffer layer is necessary to prepare high efficiency CZTS solar cell. CdS thin films have a good optical transmittance and wide band gap of 2.43 eV. Normally CdS films may deposit by a variety of techniques. CBD have proved simple and inexpensive technique to deposit good quality CdS layers. Highest efficiency of CZTS solar cells was achieved using CdS layer prepared by CBD [56, 57]. In this study, alternatively efficient CZTS solar cells also prepared by thermally evaporated CdS thin film. CdS layer deposition details given in next chapter 5. In CZTS solar cell device, light absorption in CdS layer does not contribute to photocurrent, therefore the reduction of CdS film thickness is necessary to avoid quantum efficiency and short-circuit current losses [54]. However, reducing the film thickness increases the possibility of local shunting or excessive forward current. Mo was used as a back contact material is a metal on the bottom of the absorber whose role is to collect the carriers from the absorber and deliver them to the external load.
To form a p-n junction with the n-type CdS thin film deposited on the p-type CZTS absorber layer with desired thickness by vacuum evaporation/CBD methods. The surface of CZTS thin film is too rough towards entirely covers by CdS thin film, leading to a shortage between front contact and back contact. To prevent leakage intrinsic ZnO (i-ZnO) thin film coated on CdS before 500~1000 nm transparent conducting oxide (TCO) thin film deposited as the front contact layer of the cell [58].

J–V characteristics of finished solar cells under 1-sun illumination showed in Figure 4.26 – 4.29. Despite a very thin absorber thickness (1 µm), short-circuit current (J_{sc}) is reasonably good. The maximum J_{sc} attainable from thermal evaporation method with a 1000 nm-thick absorber, band gap energy (E_g) of which is 1.48 eV, is 17.3 mA/cm^2. If we take into account of the anticipated losses in J_{sc} from transparent conducting oxide (i-ZnO) and CdS, as estimated by the measured quantum efficiency for wavelengths <520 nm (E_g of CdS), the maximum J_{sc} reduces to 23.4mA/cm^2. Our CZTS solar cells of i-ZnO/CdS/ 1µm CZTS, suggesting reasonably good collection of the photo-generated carriers. Figure 4.26 shows the photocurrent density-voltage (J-V) characteristics of CZTS heterojunction solar cells. The conversion efficiency (\eta) of the thermal evaporated CZTS solar cell is 5.6 % with short circuit current density 17.3 mA/cm^2, open circuit voltage 0.549 V and fill factor 59 %. As compared to the conversion efficiency (\eta) of chemical bath deposited CZTS solar cell is 2.63 % with short circuit current density 12.59 mA/cm^2, open circuit voltage 0.58 V and fill factor 36 % (Fig.4.27). The details showed in tables 4.2 and 4.3.

Figure 4.28 shows the photocurrent density-voltage (J-V) characteristics of spray and SILAR deposited CZTS heterojunction solar cells. The conversion efficiency (\eta) of the spray deposited CZTS solar cell is 1.98 % with short circuit current density 21 mA/cm^2, open circuit voltage 0.26 V and fill factor 36.2 %. As compared to the conversion efficiency (\eta) of SILAR deposited CZTS solar cell is
1.22 % with short circuit current density 9.28 mA/cm\(^2\), open circuit voltage 0.32 V and fill factor 41 % (Fig.4.29). The details had shown in tables 4.4 and 4.5.

Figure 4.30 shows the external quantum efficiency (EQE) measured at zero bias as well as at a reverse bias. Improved EQEs observe at longer wavelengths at the reverse bias, which indicates some difficulty in collecting photo carriers created deep in the absorber [59]. The application of a reverse bias extends the depletion layer into the absorber layer so that larger fractions of the minority photo-carriers are swept by the field, with a resultant increase in photocurrent [60]. The external quantum efficiency (EQE) of the deposited CZTS thin films using above-mentioned methods are shown in Figure.

4.6. Summary

Eco-friendly p-CZTS/n-CdS thin film solar cells successfully fabricated by sequential vacuum evaporation and chemical deposition methods like CBD, SPD, and SILAR. The Corresponding values of photocurrent characteristics of the optimized cell efficiencies of 5.6%, 2.63%, 1.98%, and 1.22% were achieved respectively. Quaternary compounds hold in possession that numerous secondary phases like CuS, SnS, ZnS, and Cu\(_2\)SnS\(_3\). Raman scattering used to investigate these secondary phases, because peaks of Cu\(_2\)SnS\(_3\) and ZnS overlaps with CZTS in X-ray diffraction analysis. The deposited films were good crystalline nature and diffraction peaks of Cu\(_2\)ZnSnS\(_4\) thin films can be conclusively indexed as a tetragonal phase with the lattice constants of a=5.426 Å and c=10.835 Å, which are in good agreement with the reported values and in the standard card. The deposited thin films possesses a polycrystalline structure of peaks attributed to (002), (110), (112), (200), (211), (105), (312), (314) and (332) of Cu\(_2\)ZnSnS\(_4\) (CZTS) appeared, which can be confirmed by the powder diffraction File (JCPDS - 26-0575). Moreover, the intensity of the (002) and (112) is the strongest, indicating that the thin films correspond to the kesterite structure, which belongs to the tetragonal system. The sulfurization process
that helps to increase high crystalline phase of the deposited films. The deposited CZTS films were annealed at 500°C, to avoid forming binary compounds.

CZTS thin films prepared by spray pyrolysis at T_s=100°C and 150°C exhibits the phase appears not textured and preferred orientation, if present is weak. Extra small invisible peaks are observed due to lattice mismatching between substrate and absorber layer. This is a probable sign of the intrinsic nature of stacking faults in the structure. In the Raman spectra presence of peaks at 287 cm⁻¹, 337 cm⁻¹, 348 cm⁻¹, and 365 cm⁻¹ verifies the reformation of Kesterite phase in the compound. Strong and acuminate major peak point outs that the well crystalline quality of the compound. The I4 group space symmetry shifts to a disordered kesterite type I42m symmetry. The SEM images show that the surface of the films is fully covered, homogeneous, well adherent, and free from crystal defects such as pinhole and cracks. The result shows that the film consists of compact structure grains with sub-micron size and low roughness, which is suitable for the absorber of thin film solar cells. The PL measurements are to create carriers by optical excitation with photon energy above the band gap of the films (1.48, 1.51, 1.50, and 1.53 eV). The peak positions corresponds to 1.36, 1.39, 1.41 and 1.43 eV, which is smaller than the estimated band gaps from the optical measurement.

Absorption is more than 75% in the visible range for the polycrystalline film deposited from different molar ratios. It decreases lightly when the film is formed by changing their composition ratios (A = 70%). A high absorption coefficient as above 10⁴ cm⁻¹ and an optical band-gap energy of the CZTS samples about 1.48 to 1.53 eV achieved were in these experiments, which is very close to the optimum value for a solar-cell absorber. Electrical measurements indicate that CZTS thin film exhibits p-type conductivity to resistivity from 1.5 to 2.96 Ω-cm, the carrier concentration increased from 9.1×10¹⁶ to 2.09 x 10¹⁸ N (cm⁻³) with increasing Cu: Zn: Sn composition in the precursor, indicating that main Cu-rich and Zn-rich powders have the smallest grain resistance. The electrical properties of the films were attributed to
the enhanced grain size. The large grains in the material reduced the grain boundaries, thus effectively reducing the recombination of the charge carriers.

In conclusion, CZTS films can be prepared using the ratio 2:1:1 for Cu: Sn: ZnS elements as a precursor with better optical, structural and electrical properties of vacuum thermal evaporation technique. As compared to other non-vacuum methods, it has showed that the highest current-voltage (I-V) characteristic properties of the cell have a strong dependence on the photovoltaic parameters of the thin films. The conversion efficiency (η) of the thermal evaporated CZTS solar cell is 5.6 % with short circuit current density 17.3 mA/cm², open circuit voltage 0.549 V and fill factor 59 %.
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