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Solar cells of Cu_2ZnSnS_4 thin films prepared by chemical bath deposition method

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Solar cells based on kesterite-type Cu_2ZnSnS_4 have been successfully fabricated on ITO substrates by cost effective chemical bath deposition method. The structural properties of the material have been studied using X-ray diffraction pattern and it confirms the formation of Cu_2ZnSnS_4 with kesterite structure. The surface topography has been studied using atomic force microscope and the rms roughness of the film was found to be 3.2 nm. The chemical constituents present in the prepared films have been identified using energy dispersive X-ray analysis. The optical band gap energy of CZTS thin film was found to be 1.5 eV which is quite close to the optimum value required for solar cell application. The power conversion efficiency of fabricated Cu_2ZnSnS_4 based solar cell is 1.34%.

Keywords: Cu_2ZnSnS_4, Chemical bath deposition method, Kestrites, Solar cells, Thin films

1 Introduction

I-III-VI semiconductors have attracted much interest in recent years as their optical and electrical properties are optimum for photovoltaic and optoelectronic applications. Thin film solar cells based on CIGS heterojunction have been found to exhibit record efficiency[1] of 20.3%. However, alternative materials which are not having expensive or toxic species such as In, Ga, Te or Cd are the objective of many studies. Chalcogenide compounds with stoichiometry $Cu_2(MII)(MIV)(S, Se)_4$ (MII =Mn, Fe, Co, Ni, Zn, Cd, Hg and MIV = Si, Ge, Sn) have drawn much attention in recent past, because of abundant availability of the starting mineral phases, which are environment-friendly and non-toxic (with the exception of expensive and potentially toxic elements such as Cd, Hg and Ge) and have direct band gap, most suited for solar cell applications and other optical devices[2]. In recent years, kesterites, Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ and their alloys $Cu_2ZnSn(S,Se)_4$ (CZTSSe), are regarded as promising absorber materials for future photovoltaic systems on a terra-watt scale[3-5]. These materials have band gap energies ranging from 1.0 to 1.5 eV, which match well with the optimal spectral range of solar radiation. The high absorption coefficient of these materials[6] ($>10^4$ cm^{-1}) assures absorption of the entire incident photon flux in an absorber layer as thin as a few microns. The latest conversion efficiency[7] of 11.1% has encouraged numerous researchers to search for more feasible and low-cost production methods for large-scale employment of kesterite solar cells. CZTS has an absorption coefficient in the order of 10^4 cm^{-1} and a direct band gap of 1.5 eV and is a suitable candidate to replace CIGS as an absorber layer in thin film solar cells. The quaternary Cu_2-II-IV-VI_4 compound is considered to be a novel material for thin film solar cells (TFSC). Fischereder *et al*[8]. have used a toxic pyridine-based solution containing Cu, Zn and Sn salts along with thioacetamide as a sulphur source. However, pure Cu_2ZnSnS_4 films were formed only by annealing the precursor film above 523 K in vacuum atmosphere. The non-toxic precursor solution of Cu, Zn, Sn and thiourea (an another popular sulphur source that can readily form complexes with Cu, Zn, Sn) in methanol can easily produce kesterite type Cu_2ZnSnS_4 film.

Cu_2ZnSnS_4 thin films have been prepared by different researchers using several techniques such as spray pyrolysis technique[9], *dc* magnetron sputtering[10], sol-gel sulphurization method[11], pulsed laser deposition[12] and electron beam evaporation[13]. So far, the absorber layer of Cu_2ZnSnS_4 has been mainly deposited by thermal evaporation, sputtering or hydrazine slurry-based methods. The problem with using hydrazine as solvent is the toxic and explosive nature of hydrazine. An alternative to hydrazine based approaches is metal salt solution in organic solvents, where the salt solubility is increased and stabilized by adding amine containing complexing agent like monoethonalamine. The main drawback of the physical deposition method is that it requires vacuum chambers and large power supplies and the hydrazine based method requires specifically designed equipment for hydrazine, which is toxic and flammable. The combination of attractive optoelectronic properties and the abundance availability of constituent elements have made Cu_2ZnSnS_4 a very promising absorbing layer material for low cost thin film solar cell application. The existing preparation methods, generally, involve additional processing steps of annealing the sample at a temperature above 773 K in the presence of flowing toxic H_2S gas to obtain Cu_2ZnSnS_4. Compared to the other deposition methods, chemical bath deposition method is having advantages such as simplicity, non-hazardous, cost effective and large-scale low-cost fabrication[16]. In the present work, Cu_2ZnSnS_4 thin films have been prepared using simple chemical bath deposition method. Cu_2ZnSnS_4 thin film based solar cells have been fabricated and the cell characteristics have been studied.

2 Experimental Details

The Cu_2ZnSnS_4 thin films have been deposited using chemical bath deposition method. Analytical reagent grade (AR) chemicals $Cu(NO_3)_2$, $Zn(NO_3)_2$, $SnCl_4$, and thiourea (0.20 M, 0.10 M, 0.15 M and 0.40 M) were dissolved in methanol. Monoethanolamine (MEA) was used as a stabilizer to prevent formation of precipitates[17]. The solution was stirred for 1 h at room temperature to yield a clear and transparent solution using magnetic stirrer.

The possible reaction mechanism for the formation of CZTS film is as follows:

$$Cu(NO_3)_2 \rightarrow Cu^{2+} + 2NO_3^- \quad \ldots(1)$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad \ldots(2)$$

$$SnCl_2 \rightarrow Sn^{2+} + 2Cl^- \quad \ldots(3)$$

$$NH_2\text{-}\overset{\overset{S}{\|}}{C}\text{-}NH_2 \longrightarrow NH_2\text{—}\overset{+}{C}\text{=}NH + H^+ + S^{2-} \quad \ldots(4)$$

The over all ionic reaction is:

$$2Cu^{2+} + Zn^{2+} + Sn^{2+} + 4S^{2-} \rightarrow Cu_2ZnSnS_4 \quad \ldots(5)$$

The precursor solution consists of metal ions and thiourea complex and thiourea interacts with metal ion via sulphur atom.

Hence, the Cu_2ZnSnS_4 formation is according to the equation:

$$2Cu\,(NO_3)_2 + Zn\,(NO_3)_2 + SnCl_2 + 4\,NH_2\text{-}\overset{\overset{S}{\|}}{C}\text{-}NH_2 + 8H_2O \;\big\downarrow\; Cu_2\,Zn\,Sn\,S_4 + 6\,NH_4NO_3 + 2NH_4Cl + 4CO_2 \quad \ldots(6)$$

CZTS thin films were deposited on ITO substrates by simple chemical bath deposition method without sulphurization. The prepared Cu_2ZnSnS_4 thin films were annealed in air at 623 K for 1 h. Figure 1 shows the structure of the fabricated CZTS based solar cell (ITO/CZTS/CdS/Al) which has been fabricated. The CdS nano particles have been deposited onto Cu_2ZnSnS_4 films by successive ionic layer adsorption and reaction (SILAR) method. The substrate with Cu_2ZnSnS_4 films were immersed in the cationic precursor solution cadmium nitrate ($Cd\,(NO_3)_2.4H_2O$) for 20 s for the adsorption of cadmium ions on to the Cu_2ZnSnS_4 surface and then rinsed in deionized water to remove the loosely bound species of Cd^{2+} ions. Then, it was dipped in the anionic precursor solution sodium sulphide (Na_2S) for 20 s. Sulphide ions reacted with the adsorbed cadmium ions forming CdS. Now the ITO glass substrate with Cu_2ZnSnS_4

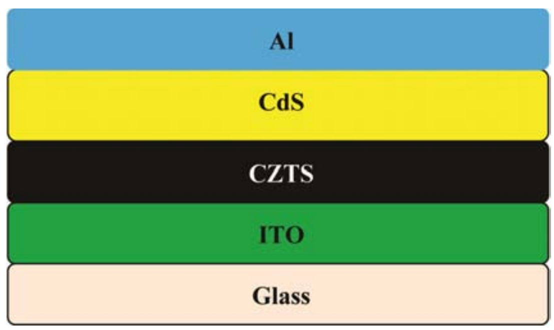

Fig. 1 — Schematic diagram of CZTS thin film based solar cell

and CdS was dipped in deionized water. After that the CZTS/CdS layer was slowly dried in vacuum, a layer of Al was thermally evaporated on top of the CdS through a shadow mask under a pressure of ~10^{-6} Torr. The Al layer acts as a electrode for making external electrical connection. This resulted in the formation of solar cell with structure ITO/CZTS/CdS/Al.

Structural properties of Cu_2ZnSnS_4 thin films were studied using X-ray diffractometer SHIMADZU (Model 6000) with CuK_α radiation (k_α=1.54056A˚). Surface morphology and compositional study of the thin films were carried out using scanning electron microscopy, (Raith) attached with an energy dispersive X-ray analysis (EDAX) analyzer and the optical properties were studied using the absorbance spectra recorded using UV-Vis-NIR spectrophotometer (Jasco V-570). The J-V characteristics of the cell were recorded using a Keithley 4200-SCS meter. A xenon lamp source (oriel, USA) with an irradiance of 50 mW/cm^2 was used to illuminate the solar cell (equivalent to AM 1.5 irradiation).

3 Results and Discussion

Figure 2 shows the X-ray diffraction pattern of the Cu_2ZnSnS_4 thin film. Diffractogram of the film shows broad peaks obtained at the 2θ positions 28.26° and 47.28°, which are identified to be the reflections from (112) and (220) planes of tetragonal type kesterite structure of Cu_2ZnSnS_4 (JCPDS, card no.26-0575). The diffraction peaks from (112) and (220) planes of Cu_2ZnSnS_4 coincide with the peaks from (110) and (220) planes which correspond to the ZnS. Being quaternary compound, Cu_2ZnSnS_4 often contains other binary and ternary phase and it is difficult to control the stoichiometry. Thus, it requires good control over synthesis parameters to obtain the desired phase of the material. The grain size of the Cu_2ZnSnS_4 thin film was calculated using Scherer's equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad \ldots(7)$$

where λ is the wavelength of X-ray radiation, β the FWHM and θ is the Bragg angle. The average grain size was found to be 28 nm. The obtained lattice constants were a =5.432 Å and c = 10.852 Å. These values are found to be in good agreement with reported lattice parameters a=5.427 Å and c = 10.848 Å (JCPDS, card no.26-0575).

Figure 3 shows the atomic force microscope (AFM) image of Cu_2ZnSnS_4 film. The root mean square (rms) roughness was found to be 3.2 nm and the image also indicates the formation of smooth and compact film. The SEM image of CZTS thin film is shown in Fig. 4. The image shows the smooth and homogeneous nature of the film without the presence of any cracks or voids. The elemental composition of Cu_2ZnSnS_4 thin film was determined by energy dispersive X-ray analysis and the spectra is shown in Fig. 5. The elemental composition of the film is Cu-18.15 at%, Zn-17.54 at%, Sn-16.03 at%, S-48.28 at%, and the ratios, Cu/(Zn + Sn) is 0.54, Zn/Sn is 1.09 and S/[Cu] +[Zn]+[Sn] is 0.93. Tanaka *et al*[11]. have reported that higher efficiencies can be obtained

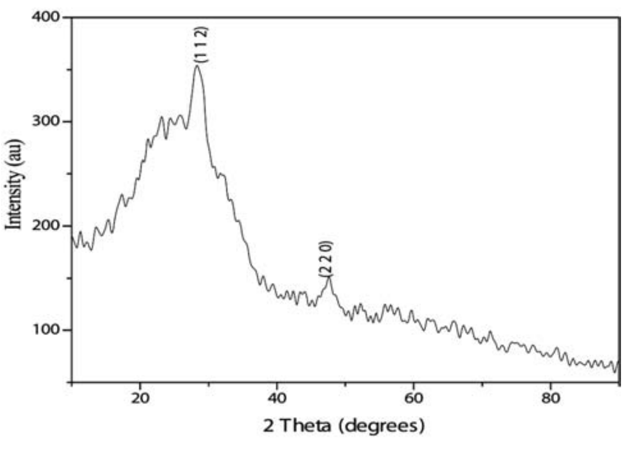

Fig. 2 — X-ray diffraction pattern of CZTS thin film

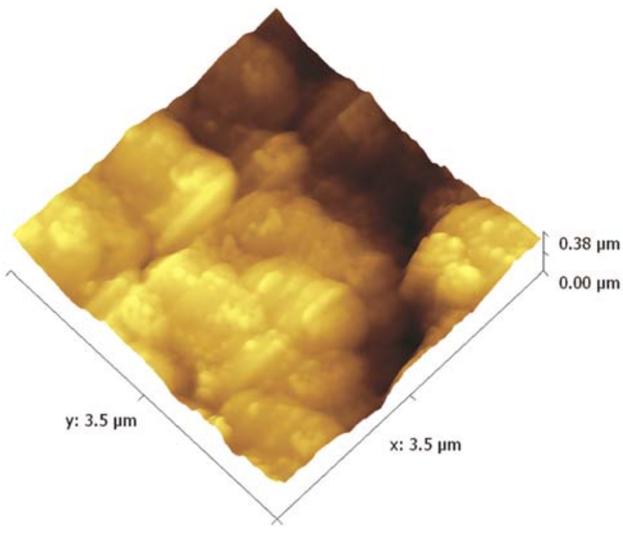

Fig. 3 — Atomic force micrograph of CZTS thin film

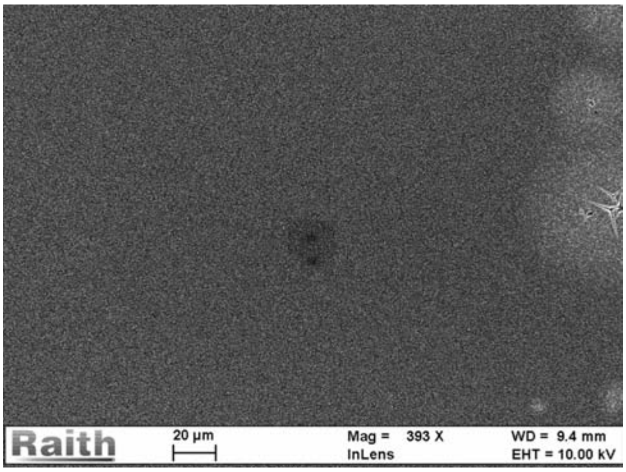

Fig. 4 — SEM image of CZTS thin film

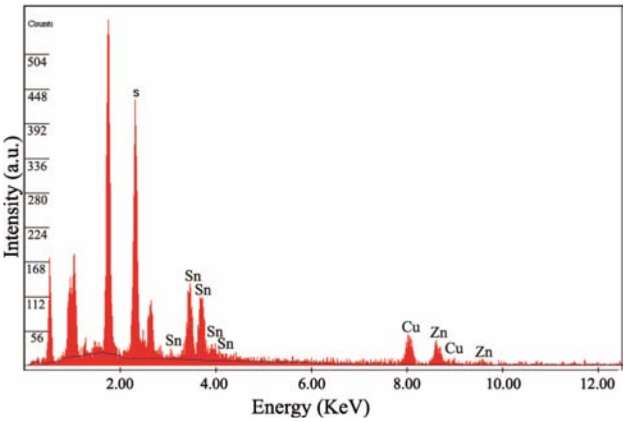

Fig. 5 — EDAX spectrum of CZTS thin film

using Cu poor, Zn rich absorber layer in solar cells[11]. Cu poor surface is required for optimizing the electronic level alignment and minimizing interface recombination, tuning of stoichiometry can be considered as a pathway to high efficiency.

The band gap of the Cu_2ZnSnS_4 film has been determined using the relation:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^{1/2} \qquad \ldots(8)$$

where α is the absorption coefficient, A is the constant, E_g is the energy gap and $h\upsilon$ is the incident photon energy. The optical band gap is deduced by extrapolating the straight line portion of the $(\alpha h\upsilon)^2$ versus ($h\upsilon$) plot to meet the $h\upsilon$ axis shown in Fig. 6. The band gap energy was found to be 1.5 eV, which is in good agreement with previously reported value[11]. This band gap value is quite close to the optimum band gap required for a solar cell absorber layer.

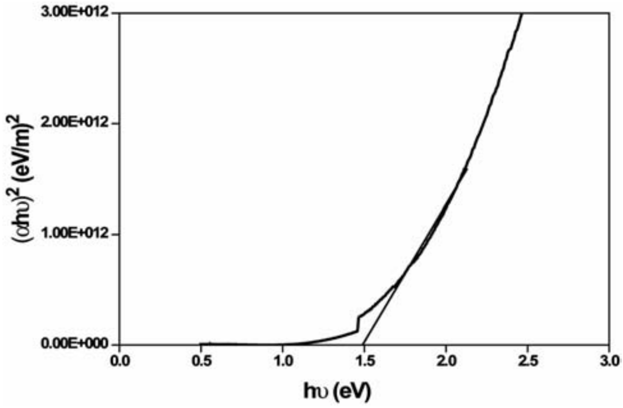

Fig. 6 — Band gap of CZTS thin film

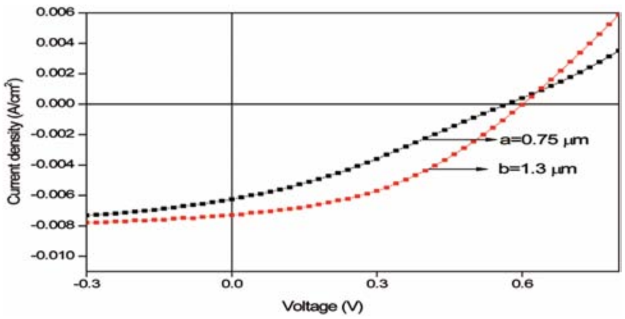

Fig. 7 — J –V characteristics of CZTS thin film solar cells

The J-V characteristics of CZTS/CdS solar cells fabricated using different CZTS absorber layer thicknesses have with CdS as a buffer layer, are shown in Fig. 7. The Cu_2ZnSnS_4 thin films with thickness of 0.75 µm exhibit a power conversion efficiency (η) of 1.08% with short circuit density (J_{sc}) of 6.25 mA/cm^2, open circuit voltage (V_{oc}) of 0.56 V and fill factor (FF) of 30.37%. On increasing the CZTS film thickness from 0.75 to 1.3 µm, the power conversion efficiency (η) increased from 1.08% to 1.34 % and (J_{sc}) increased from 6.25 to 7.06 mA/cm^2, fill factor(FF) increased from 30.37% to 33.37% and the open circuit voltage (V_{oc}) nearly same. The small grain size may be the reason for the low efficiency. The obtained power conversion efficiency of 1.34% is considerably better than the reported values of Bent *et al*[14]. and Patil *et al*[15].

4 Conclusions

In conclusion, Cu_2ZnSnS_4 thin film based solar cells have been fabricated using chemical bath deposition method. The X-ray-diffraction pattern revealed the formation of kesterite structure Cu_2ZnSnS_4 films. The surface morphology is observed to be smooth and homogeneous in nature. The optical band gap has been found to be 1.5 eV. Cu_2ZnSnS_4 based solar cell has been fabricated and a power conversion efficiency of 1.34% has been achieved.

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