Cu₂ZnSnS₄ Thin-Films Grown by Dip-Coating: Effects of Annealing

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ABSTRACT

Recently Cu₂ZnSnS₄, i.e. Copper Zinc Tin Sulphide (CZTS), has emerged as a potential candidate for low-cost solar photovoltaics (PV) material because of it is relatively non-toxic and ingredient elements are earth abundant. However, achieving phase controlled, stoichiometric film of CZTS using low-cost technique is the key issue in development of CZTS based solar cell. Here, we report a study on structural and optical properties of CZTS films grown by dip-coating in view of its application as an absorber in thin film solar cells. The films were deposited by dipping glass substrates into the solution prepared by dissolving cation metal salts and thiourea in methanol. It is followed by drying the films in air at fixed temperature. The dip coated films were then annealed at 623 K, 723 K and 823 K. The influence of annealing on various structural and optical properties of the films were investigated by means of X-ray diffraction (XRD), Raman scattering spectroscopy, Scanning electron microscopy (SEM) and Diffused reflection spectroscopy. It was observed that the film annealed at 823 K shows good quality Kesterite structure of CZTS with preferred orientation of (112), (220) and (312) planes as revealed by the XRD pattern. The diffuse reflection spectra confirm the direct band-gap of 1.42 eV, which is very close to the optimum value for the semiconductor material as an absorber in solar-cells. Raman scattering with two different excitation wavelengths showed that other binary phases including the parasitic phases such as ZnS were not present. It also confirmed the characteristics signature of dominant CZTS phase in the film.

Keywords—Cu₂ZnSnS₄, Thin films, Chemical Synthesis, X-Ray Diffraction, Raman Scattering spectroscopy

INTRODUCTION

Despite remarkable advancements of chalcogenide material-systems, especially $\text{CuInGa}(\text{S},\text{Se})_2$ (CIGS) and CdTe , in development of efficient photovoltaic (PV) modules, the scarcity of resources of Indium (In) and Tellurium (Te) in the earth-crust [1] as well as environmental concerns related to cadmium in CdTe have forced researchers to pursue new earth-abundant and non-toxic absorber materials for the development of sustainable thin-film solar PV. One of the most promising candidates in this quest is $\text{Cu}_2\text{ZnSnS}_4$, i.e. Copper Zinc Tin Sulfide (CZTS), as all its ingredient elements have abundant resources in the nature [2]. Moreover, high absorption coefficient and direct band-gap make it apt for low cost thin-film PV technology. These factors together led to a quick development in the CZTS based thin film PV research in last few years, which is evident from the rise of record power conversion efficiency to 12.6 % [3] in a very short span. Although, this is quite impressive, the value is still far below the Shockley-Queisser limit for a single junction cell based on CZTS (~30%) [4]. The major challenge in the fabrication of CZTS based solar cell is the deposition of defects-free, stoichiometric CZTS film without allowing other parasitic secondary phases to form. Further, it is equally important to achieve such a film using the deposition process, which is cost-effective and commercially scalable for sustainable thin film PV technology. The solution based chemical synthesis is a potential thin-film deposition technique that meets these criteria. Interestingly CZTS is one of the rare materials for which the record efficiency is achieved using a chemical deposition [3]. Hence the study on low-temperature deposition of CZTS using suitable chemical synthesis becomes particularly significant.

Many groups have employed wet chemical methods for CZTS thin film depositions such as spray pyrolysis [5], Sol-gel [6], spin coating [7], electrodeposition [8], Successive Ionic Layer Adsorption and Reaction (SILAR) [9], dip coating [10] etc. to obtain device quality CZTS thin films. The record efficiency for CZTS based solar cell is achieved by slurry based coating using hydrazine as solvent [3]. However, hydrazine is highly toxic and hazardous, that has forced researchers to look for alternative solvents. Mau et al reported CZTS thin film deposition using copper acetate monohydrate, zinc acetate dihydrate and thiourea in water as well as ethanol solvents. The uniform CZTS thin films were obtained by sulfurizing the films at 500 °C in $\text{Ar} + \text{H}_2\text{S}$ ambient [11]. Chaudhuri et al reported CZTS thin film by dip coating using copper acetate, Zinc acetate, tin chloride and thiourea precursors dissolved in methanol. The deposition was followed by

thermolysis at 200 °C for 10 minutes [12]. Rajesh et al used $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, SnCl_2 and thiourea precursors dissolved in methanol. They added monoethanolamine as stabilizing agent. They reported uniform CZTS thin film formation by thermolysis at 200 °C for 1 hour [13]. Sun et al reported ethylene glycol as solvent and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , SnCl_2 and thiourea as precursors. The film was thermolysed at 200 °C followed by annealing in sulfur ambient at 500 °C for 30 minutes [14]. Later the same group reported CZTS film formation by using ethanol as solvent and thermolyzing it at 130 °C for 10 minutes [15].

Here we report a study on structural and optical properties of CZTS thin films grown by dip-coating using methanol as a solvent without adding any stabilizing agent or using hazardous chemical such as hydrazine. The dip coating is a simple, low-cost technique with feasibility to scale-up for commercial production. Mainly it consists of two steps; (i) dip casting of substrate into the precursor solution and (ii) thermolysis of the film. These steps are repeated multiple times in order to achieve the desired thickness. Moreover, during repetition of this process, voids and porosity may develop into the structure, which requires a post-growth annealing. We have systematically investigated the effects of annealing on the properties of the grown films.

EXPERIMENTAL

$\text{Cu}_2\text{ZnSnS}_4$ thin films have been deposited using the dip coating method. Prior to the deposition of CZTS, glass substrate was cleaned with Methanol, Acetone, Trichloroethylene and deionized (DI) water. The precursor solution for the dip-casting was prepared by dissolving CuCl_2 , ZnCl_2 , SnCl_2 and Thiourea in methanol. The glass substrate was dipped into this solution and then kept at 473 K for 20 minutes to promote thermolysis. In heat treatment process, the metal salts and thiourea decomposes and gives raise to formation of CZTS phase on the substrate. The film made with one and two dips are coded as 1d and 2d, respectively. These films were annealed in vacuum with and without sulfur ambient at three temperatures; 623 K, 723 K and 823 K. The films coated with one dip and annealed in sulfur ambient at 623 K, 723 K and 823 K, are coded as 1d3s, 1d4s, and 1d5s, respectively. Similarly, films deposited with one dip and annealed in absence of sulfur ambient at 623 K, 723 K and 823 K, are coded as 1d3a, 1d4a, and 1d5a, respectively. Also, films coated with two dip and annealed in sulfur ambient at 623 K, 723 K and 823 K, are coded as 2d3s, 2d4s, and 2d5s, respectively. Similarly, films deposited with two dip and annealed in absence of sulfur ambient at 623 K, 723 K and 823 K, are coded as 2d3a, 2d4a, and 2d5a, respectively. As-deposited and annealed films were

characterized using X-Ray diffraction technique (XRD), Raman scattering spectroscopy, scanning electron microscopy and diffused reflection spectroscopy.

RESULTS AND DISCUSSIONS

A. Structural Properties

The structural properties of the deposited CZTS thin film samples were studied using Bruker's X-ray diffractometer (XRD) with Cu K α radiation [$\lambda = 1.54056$ Å]. Figure 1 shows X-ray diffractograms of as-deposited samples as well as samples annealed in absence of sulfur ambient samples. As seen from the figure 1 (a), the as-deposited sample exhibit a broad peak near 2θ value 28.5° , that corresponds to diffraction from (112) plane of CZTS [16]. However, the peak is quite convoluted with a hump generally observed at lower angles and there are no other distinct peaks, which indicates that the as-deposited film is amorphous in nature. Annealing the film at 623 K results in appearance of broad but clearly observable peaks (figure 1 (b)) at the expected 2θ value of about 28.5° , 47° , and 56° , that correspond to diffraction from plane (112), (220) and (312), respectively, for CZTS. Similar trend is observed for the films deposited with two dips, as evident from figure 1(e) and 1(f). However, on increasing the annealing temperature beyond 723 K, the secondary phases start appearing in both the cases, i.e. one dip and two dips. As manifested by figure 1(c), 1(d), the film deposited with one dip starts showing the presence of SnS, Cu₃SnS₄, Cu₂SnS₃, and CuS on annealing at 723K and 823K. The film deposited with two dips also behaves similarly, as evident from figure 1(e) and 1(f), exhibiting the presence of diffraction peaks from SnS₂, CuS and Cu₂SnS₃ on annealing at 723K and 823K, respectively. Thus, it is clear that the annealing at higher temperature in absence of sulfur ambient leads to formation of secondary parasitic phases in CZTS films. To overcome this problem, the films are annealed in presence of excess sulfur. Figure 2 shows XRD patterns of the films deposited with one dip and two dips followed by annealing in the sulfur ambience. In the sulphur ambience, increasing the annealing temperature from 623 K to 823 K cause these peaks to get sharper and stronger with decreased full width half maxima (FWHM), indicating the growth of larger grains in the films.

The average grain size of the crystallites has been calculated using Scherrer's formula,

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where, constant k is a shape factor usually = 0.94,

β is full-width at half maximum (FWHM) of the peak.

Using the size of crystallites, the dislocation density can be found using,

$$\delta = \frac{1}{D^2} \quad (2)$$

The micro strain in the film can be calculated by using the equation,

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

The observed values for the peak about 28.5° are mentioned in the Table I.

The intensity of the diffraction peak, which is seen at $2\theta=28.5^\circ$, increases as the annealing temperature increases from 623 K to 823 K for 1 dip and 2 dip, suggesting increase in annealing temperature in sulfur ambient can improve the crystallinity of the CZTS films. Moreover, the full width at half maximum (FWHM) of the films decreases as the annealing temperature increases, and it indicated that the grains grew with increase in temperature. The clear decrease in the dislocation density and strain is observed with increase in the annealing temperature suggests improvement in crystallinity with increasing annealing temperature. Similarly, as the number of dips increases from 1 to 2, for sample 2d3s, 2d4s and 2d5s, the FWHM of the film decreases and grain size increases. However, the peaks in case of two dips are slightly narrower and stronger in comparison to the corresponding sample grown using 1 dip. This is mainly due to increased thickness of the films with two dips.

Here, it is important to note that the XRD patterns of CZTS, CTS (copper tin sulphide) and β -ZnS are very similar and the angle differences in the major peaks are within the instrument accuracy. The XRD peaks from (1 1 2), (2 0 0), (2 0 4) and (3 1 2) planes of CZTS coincide with the XRD peaks from (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of β -ZnS respectively [17]. These facts make the XRD identification of CZTS a difficult task and may result in wrong interpretation if the peaks are due to ZnS and CTS phases. Hence, to check the presence of these secondary phases, Raman spectroscopy was performed on the as-deposited as well as annealed samples using LabRAM HR 800 made Raman spectrometer through excitation wavelength of 488 nm. Figure 3 shows Raman spectra of all samples deposited by dip coating followed by annealing.

As seen from figure 3(a), a broad but feeble peak is observed for the as deposited film at about 333 cm^{-1} , which corresponds to A symmetry mode of CZTS [9]. The A symmetry modes result from symmetric

vibrations of only anion lattice and are responsible for the strongest lines observed in the experimental Raman spectra of CZTS. This peak gets stronger and narrower as the films are annealed at higher temperatures. Moreover, as the number of dip increases from 1 dip to 2 dip, intensity of this peak increases which is similar to the trend observed in the XRD profiles again probably due to increased thickness. However, in XRD as well as Raman data. There are no significant changes in features between the films grown with one dip and two dips followed by annealing which indicate that the number of dips can be increased to increase the thickness without affecting the quality of the films. We checked this trend even for the films grown using three dips using XRD and Raman scattering (data not shown here) and the results were consistent. Further, absence of any distinct peak at 352 cm^{-1} , 314 cm^{-1} , 318 cm^{-1} or 473 cm^{-1} in all the films confirm the absence of secondary parasitic phases such as ZnS, SnS₂, CTS and Cu_xS in the films [17]. This was also re-confirmed by Raman scattering obtained by exciting the samples at 785 nm (all data not shown here).

It is important to note that the light penetration depth is inversely proportional to the absorption coefficient. For Raman spectroscopy, we performed back scattering configuration. It is known that the penetration depth (d) is inversely proportional to the of the absorption coefficient (α) [17]. i.e.

$$d \sim \frac{1}{2\alpha} \quad (4)$$

Using this equation and knowing α , the penetration depth of the excitation wavelength used in Raman scattering spectroscopy can be approximately estimated. As the excitation wavelength varies, the penetration depth of laser light in film also varies. Obviously with increase in excitation wavelength, the laser penetration depth increases. For the excitation wavelength of 488 nm, the penetration depth of laser in the film is about 150 nm, whereas if we increase the excitation wavelength 785 nm, then the penetration depth is about 400 nm [17]. To observe the effect of excitation wavelength, the data of samples 1d5s and 2d5s are compared here with 785 nm excitation wavelengths.

Figure 4(a) and 4(b) and shows the Raman spectra of the 1d5s and 2d5s films taken at excitation wavelength of 488 nm. Figure 4(c) and 4(d) shows the Raman spectra of the 1d5s and 2d5s films taken at excitation wavelength of 785 nm. For CZTS material, the major Raman peak is observed in the range of 330 to 338 cm^{-1} , which corresponds to A symmetry mode of CZTS and it includes motion of anions (sulfur) only. In case of the 488 nm excitation wavelength, the identical Raman peak is observed at about 333 cm^{-1} . However, for the

case of 785 nm excitation wavelength, the major peak is observed at about 338 cm^{-1} . As mentioned earlier, the penetration depth is higher for the 785 nm excitation wavelength; the more information of the structure can be extracted. As a result, one more split peak observed for the excitation wavelength of 785 nm at 366 and 374 cm^{-1} corresponding to B(TO) and B(LO) modes of CZTS. The B mode of CZTS corresponds to the movements of cations in Z direction. Similar results are also observed by Fernandes et al. Thus, Raman scattering with two different excitation wavelengths confirmed the characteristics signature of dominant CZTS phase with absence of other binary parasitic phases the in the film.

In order to obtain the thickness of the films and substantiate the effects of number of dips, crosssectional scanning electron microscopy was performed on samples using Philips made XL 30 ESEM. Figure 5 shows the crosssectional SEM images for sample 1d5s (a) and 2d5s (b). The crosssectional SEM images show that the average thickness of the film deposited by one dip and annealed at 823 K is about $1.5\text{ }\mu\text{m}$. For the film deposited with two dips, the thickness of the film increases to about $3.0\text{ }\mu\text{m}$, as expected.

B. Optical Properties

In order to study the optical properties of the samples, we experimentally measured the diffused reflectance spectra of all the samples. Figure 6 and 7 show the tauc plot for the thin films deposited by one-dip and 2 dip coating followed by annealing in sulfur environment at different temperatures.

As seen from the figure 6 and 7, the film annealed at 623 K does not have a sharp absorption edge and the absorption starts rising from photon energy of about 1.2 eV. This may result from the band-tail absorptions since the film annealed at 623 K contains smaller grains with poorer crystallinity as evident from the XRD data. Further, the films may contain large number of defects as the smaller crystallites lead to large grain-boundaries area. The film prepared with 1 dip and annealed at 723 K does not exhibit the sharp absorption edge. But, the film annealed at 823 K and the film prepared with 2 dip and annealed at 723 K and 823 K show much sharper absorption edge. All these films show a steep rise in absorption at photon energy of about 1.4 eV and the value of band-gap obtained from the tauc plot is estimated to be about 1.43 eV in all three cases, which is very close to the optimum value for the semiconductor material as an absorber in solar-cells. The absorption coefficient is also found to be high in these films making them suitable for thin film absorbers.

CONCLUSION

We have investigated the deposition CZTS thin films using dip coating method followed by annealing in presence of sulfur atmosphere at different temperatures. The deposited films were characterized by XRD, Raman spectroscopy and UV–visible spectroscopy. The film with 2 dip, annealed at 823 K in sulfur ambient exhibits sharp peaks from (112), (220) and (312) planes in XRD, which confirms the good quality Kesterite structure of CZTS phase. The SEM image reveals that the film thickness for 2d5s is about 3.0 μm respectively. The band gap of this film is found to be 1.43 eV, which is close to the optimum value of the band gap required for the absorber material in thin film solar cell.

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FIGURE CAPTIONS

Figure 1.XRD profiles of (a) 1d (b) 1d3a (c) 1d4a (d) 1d5a (e) 2d (f) 2d3a (g) 2d4a (h) 2d5a.

Figure 2.XRD profiles of (a) 1d3s (b) 1d4s (c) 1d5s (d) 2d3s (e) 2d4s (f) 2d5s.

Figure 3. Raman spectra of CZTS thin films deposited by dip coating (a) 1d, (b) 1d3s, (c) 1d4s, (d) 1d5s, (e) 2d, (f) 2d3s, (g) 2d4s, (h) 2d5s.

Figure 4. Raman spectra of CZTS thin films deposited by dip coating with excitation wavelength 488 nm :(a) 1d5s, (b) 2d5s and with excitation wavelength 785 nm: (c) 1d5s (d) 2d5s.

Figure 5. Cross sectional Scanning Electron Microscopic images of 1d5s and 2d5s.

Figure 6. Plot of $(h\nu F(R))^2$ as function of Energy for CZTS thin films prepared with 1 dip followed by annealing in presence of sulfur.

Figure 7. Plot of $(h\nu F(R))^2$ as function of Energy for CZTS thin films prepared with 2 dip followed by annealing in presence of sulfur.

LIST OF TABLES

Table I. Structural parameters of CZTS thin films.

Table I. Structural parameters of CZTS thin films.

Sample	FWHM (degree)	Grain size (nm)	Dislocation density $10^{15}(\text{lines}/\text{m}^2)$	Micro strain
1d3s	2.6959	3.18	98.88	0.0463
1d4s	1.2200	7.02	20.29	0.0210
1d5s	0.1598	53.6	0.348	0.0027
2d3s	1.5109	5.67	31.10	0.0260
2d4s	0.6837	12.53	6.369	0.0117
2d5s	0.1491	57.44	0.303	0.0026

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7