Experimental study of the optical properties of Cu$_2$ZnSnS$_4$ thin film absorber layer for solar cell application

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Abstract. Cu$_2$ZnSnS$_4$ (CZTS) has become the subject of considerable interest due to its use as thin film solar cell material. Current thin film solar technologies based on CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) and CdTe photo-absorber materials use rare and expensive elements, such as In, Te, Ga and toxic Cd which severely limit the mass productions and deployment of solar cells. CZTS is an intrinsically p-type material with a large optical absorption coefficient ($\alpha = 10^4$ cm$^{-1}$) and exhibits a tunable direct optical band gap in the range between 1.49 to 1.51 eV. The CZTS thin films were deposited on soda lime glass by dip coating method with sulfurized Cu, Zn, Sn precursors and were characterized CZTS thin film as absorber layer of solar cell. The optical characterization has been performed by UV-Vis spectrometry in order to study the effect of Cu/(Zn+Sn) ratio on the absorption coefficient and the band gap energy of the prepared thin films. As the ratio is increased (0.4 to 0.7), the absorption coefficient increases slightly whereas the band gap energy decreases.

1. Introduction

The ability to combine cheap abundant materials with low cost and low power deposition techniques is attractive for large scale and sustainable Photovoltaic. The prime candidate is Cu$_2$ZnSnS$_4$ (CZTS), an abundant, cheap and non-toxic alternative of traditional solar cell elements. CZTS is an I$_2$-II-IV-VI$_4$ quaternary compound. From the chalcopyrite CIGS structure, CZTS can be obtained by substituting the trivalent In/Ga with a bivalent Zn and IV-valent Sn which forms in the kesterite structure [1]. CZTS is an intrinsically p-type material. Its large optical absorption coefficient ($\alpha = 10^4$ cm$^{-1}$) [2] and tunable direct optical band gap in the range of 1.49-1.51 eV [3], make it attractive as absorber layer material.

Several vacuum deposition processes, such as sputtering [4], co-evaporation [5] and pulsed laser deposition [6], have been studied for CZTS thin-film preparation. However, these processes usually use a high-cost, precise vacuum apparatus and technology. Chemical bath deposition processes, such as electroplating [7], spin coating [8], and spray pyrolysis [9], also have been applied as CZTS thin-film preparation processes instead of vacuum deposition process. Metal hydrates are often employed as low-cost raw materials for the chemical bath deposition. Katagari and coworkers have fabricated CZTS solar cells with the CZTS absorber layer prepared by sulfurizing electron-beam evaporated precursors [10]. The efficiency of the solar cell was 7%. The solar cell consisted of an Al/ZnO:Al/CdS/CZTS/Mo/soda-lime glass (substrate) structure. The estimated optical band gap energy was 1.51 eV. Ito and Nakazawa reported on the fabrication of CZTS thin films prepared by atomic beam sputtering [11]. Friedlmeirer et al deposited thin films by thermal evaporation [12]. Tanaka et al. reported on CZTS thin film fabrication prepared by co-evaporation [13]. Seol et al. prepared CZTS thin films by RF magnetron sputtering [14]. The examined optical band gap energy was 1.51 eV. However all these processes were done in vacuum and they were expensive.
In this report, CZTS thin films were prepared by dip coating method with sulfurized Cu, Zn, Sn precursors and the influence of Cu/(Zn+Sn) ratio on the absorption coefficient and the band gap energy of the prepared thin films were studied.

2. Experiment
Copper (II) acetate monohydrate, zinc (II) acetate dihydrate and tin (II) chloride dihydrate and thiourea were dissolved in 2-methoxyethanol to prepare the Cu, Zn and Sn precursors. The chemicals were stirred by magnetic stirrer at 65°C for 1 h to prepare the solution. Monoethanolamine was used as the stabilizer during the experiment. Soda Lime Glass substrates were first cleaned by ultrasonic bath for 45 minutes sequentially with methanol, acetone, de-ionized water and acetone. Then after drying the substrates they were dip coated in the solution for two or three minutes. After deposition by dip coating, all the films were dried at 250°C for 1 h to eliminate solvents. The coated glasses were sulfurized by annealing at 400°C in a hydrogen sulfide containing atmosphere for 1 h.

Four types of solution were prepared by varying the Cu/(Zn+Sn) ratio from 0.4 to 0.7. The ratio of Zn/Sn was kept constant (0.55). Table-1 lists the chemical composition of the prepared tin films. After fabrication, optical characterization has been performed by UV-VIS-Spectrometry to study the effect of Cu/(Zn+Sn) ratio on the absorption coefficient and band gap energy of the prepared thin films.

Table 1. Chemical compositions of sol-gel solutions and CZTS thin films

| Solution Name | Sample Name | Cu/(Zn+Sn) | Zn/Sn |
|---------------|-------------|------------|-------|
| Sol-1         | CZTS-1      | 0.4        | 0.55  |
| Sol-2         | CZTS-2      | 0.5        | 0.55  |
| Sol-3         | CZTS-3      | 0.6        | 0.55  |
| Sol-4         | CZTS-4      | 0.7        | 0.55  |

3. Result and discussion
To investigate the optical properties of the prepared thin films, the UV-Vis spectroscopy analysis was done with wavelength ranging from 300 to 800 nm. The absorption coefficient, \( \alpha \) was calculated from the measured absorbance data for different wavelength corresponding to different photon energy at room temperature. Fig. 1 shows the variation of \( \alpha \) with the photon energy \( h\nu \) for different CZTS thin films. The absorption coefficient increases with photon energy but at high photon energy, it starts to decrease. Here, CZTS-3 has the highest absorption coefficient (>1.5x10^4 cm\(^{-1}\)). CZTS-1 has the lowest absorption coefficient (~10^2 cm\(^{-1}\)). As the solution gets thicker the samples made from it achieves greater coefficient. CZTS-2, 3 and 4 have absorption coefficient greater than 10^5 cm\(^{-1}\) which is good for the absorber layer.
The dependence of absorption coefficient on the photon energy helps to study the band structure and the type of electron transition involved in absorption process. The direct transition energy band gap can be obtained by plotting \((\alpha h\nu)^2\) vs. \(h\nu\) curve and then extrapolating the linear portion of the curve to \((\alpha h\nu)^2 = 0\). In Fig. 2 \((\alpha h\nu)^2\) as function of \(h\nu\) is plotted to obtain band gap for different CZTS thin films.

From figure 2 it is clearly seen that as the Cu to (Zn+Sn) ratio increases the exhibited band gap energy of the thin films decreases. Ideal band gap of CZTS film is 1.5 eV. CZTS-1 and CZTS-2 thin films has band gap much higher than the ideal one. CZTS-3 has band gap of 1.72 which is also higher than 1.5 eV. CZTS-4 has the band gap close the ideal one. So considering all the optical properties determined by UV-Vis spectroscopy CZTS-4 is the best choice as absorber layer in solar cell.
4. Conclusion

CZTS thin film as absorber material in solar cell were fabricated from different concentrated metallic salt solutions with variation in the Cu/(Zn+Sn) ratio from 0.4 to 0.7. UV-Vis spectroscopy, confirms absorption coefficient of CZTS films in order of $10^4$ cm$^{-1}$. As Cu/(Zn+Sn) ratio increases we find that the absorption coefficient increases slightly, whereas band gap decreases from 1.83 to 1.49 eV. The films could be applicable as solar absorber layers in CZTS thin-film solar cell application.

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