Effect of Cu and Sn concentration on the performance of all-sprayed CZTS solar cell

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Abstract. Cu\textsubscript{2}ZnSnS\textsubscript{4}/In\textsubscript{2}S\textsubscript{3} thin film solar cell was prepared using chemical spray pyrolysis. Influence of variation in copper concentration in precursor solution on the properties of CZTS thin films was monitored. Concentration of copper was found to have essential role in adjusting composition and crystallinity of CZTS thin films. Junction was fabricated using CZTS as absorber layer and spray pyrolysed In\textsubscript{2}S\textsubscript{3} as buffer layer. Two sets of devices were prepared, one by varying copper concentration and the other by varying tin concentration in the precursor solution for the deposition of CZTS thin films. For both sets, In\textsubscript{2}S\textsubscript{3} thin films were deposited as buffer layer and Ag electrodes were used for taking contacts. All the performance parameters were found to have dependence on the concentration of Cu and Sn. For getting maximum conversion efficiency, the sprayed CZTS absorber layer should have elemental ratio of Cu:Zn:Sn:S= 2.5:1:0.7:12 in the precursor solution. Maximum efficiency obtained was 1.85 \%.

1. Introduction

The high demand for solar energy triggered recent research works in the direction of developing low cost solar cells using earth abundant materials. Even though the solar cells based on copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) draw much attention due to their high photo electric conversion efficiency [1]; however scarcity / high cost of indium and gallium and also the poisonous nature of cadmium and tellurium limit their large scale application in future. Copper zinc tin sulphide (CZTS) thin film, consisting of relatively cheap Zn and Sn, is found to be more suitable for large scale applications. CZTS has attractive physical properties, such as direct band gap (\textasciitilde 1.5 eV), high optical absorption coefficient (>10\textsuperscript{-4} cm\textsuperscript{-1}) and low thermal conductivity. Theoretical calculations have shown that conversion efficiency as high as 32.2 \% [2] is possible for CZTS thin film solar cells. The maximum efficiency reported so far is 11\% for Cu\textsubscript{2}ZnSnS\textsubscript{4} based solar cell [1]. So far, a number of deposition techniques have been employed to prepare CZTS thin films, such as sputtering [3], thermal evaporation [4], pulsed laser deposition [5], electrodeposition [6], hydrothermal method [7], sol-gel method [8], SILAR method [9] and Chemical spray pyrolysis [10]. In this report, we studied effect of Cu and Sn concentrations on the performance parameters of spray pyrolysed CZTS/In\textsubscript{2}S\textsubscript{3} solar cell.

2. Experimental details

2.1. Preparation of CZTS films

CZTS thin films were deposited on cleaned soda lime glass substrates using indigenously developed chemical spray pyrolysis unit [11]. Precursors used were copper chloride (CuCl\textsubscript{2}.2H\textsubscript{2}O), zinc acetate
(Zn(CH₃COO)₂), stannic chloride (SnCl₄.5H₂O) and thiourea (CS(NH₂)₂). Precursors of Cu, Zn and S were dissolved in water to get desired molarity while the precursor of Sn was first dissolved in few drops of concentrated HCl, to avoid precipitation, and then water was added to make desired molar solution. The pH of final precursor solution was kept at 3.2. The precursor solution was then sprayed on to preheated soda lime glass substrates. To prepare samples having different Cu concentration, the molarity of CuCl₂ was varied as 0.0175, 0.02, 0.0225 and 0.025 M, keeping concentrations of ‘Zn’, ‘Sn’ and ‘S’ at 0.01, 0.01 and 0.12 M respectively. Substrate temperature, spray rate and volume of solution were fixed at 350°C, 8ml/min and 60 ml respectively. CZTS thin films thus prepared were named as CZTS:1.75C, CZTS:2C, CZTS:2.25C & CZTS:2.5C in accordance with ‘Cu’ concentration.

Film thickness was measured using Dektak-6M stylus profilometer. X-ray diffraction (XRD) measurements were carried out employing Rigaku (D.Max.C) X-ray diffractometer (having CuKα (λ=1.5405 Å) radiation and Ni filter operated at 30 kV and 20 mA). Raman studies were carried out in the back scattering mode at room temperature using micro Raman system of Jobin Yvon Horiba LABRAM-HR with spectral resolution of 1 cm⁻¹. Argon ion laser of wavelength 488 nm was used as the excitation source. Elemental composition of the films was determined using energy dispersive X-ray (EDAX) analyzer attached to the SEM.

2.2 Junction fabrication

Glass plates coated with ITO (thickness 200 nm, optical transmission 82% and electrical resistivity 2.25×10⁻⁴Ωcm) were used as the substrate for junction fabrication. Four junctions were prepared with the aforementioned CZTS layers. In₂S₃ layer of thickness 500 nm was deposited over CZTS layer. After deposition of In₂S₃, optimum quantity of metallic ‘In’ [12] is diffused over the multilayer structure. This was followed by the deposition of silver electrodes of area 3mm² over In₂S₃ layer, as top electrode. The prepared junctions were named as CZTS:1.75C, CZTS:2C, CZTS:2.25C & CZTS:2.5C in accordance with the CZTS layer that goes in to fabrication.

To study effect of Sn Concentration on performance parameters of CZTS/In₂S₃ junction, concentration of ‘Sn’ in the precursor solution for CZTS layer was varied from 0.009 M to 0.006 M in steps of 0.001 M, keeping concentration of ‘Cu’, ‘Zn’ and ‘S’ at 0.025, 0.01 and 0.12 M respectively. All other spray parameters were maintained the same as for previous trials. Finally junction was fabricated with the same conditions as the previous ones. The devices were named as CZTS:0.9Sn, CZTS:0.8Sn, CZTS:0.7Sn and CZTS:0.6Sn. Illuminated J–V characteristics of these devices were measured using Source Measure Unit PXI-1033 (National Instruments). During measurements, devices were illuminated with the help of Class AAA Solar Simulator (PET Photo Emission Tech. Inc. USA).

3. Results and discussion

3.1 Characterization of CZTS thin films

3.1.1 Structural analysis using X-ray diffraction

XRD measurements were performed in all the deposited films and the diffractograms are presented in figure 1. Peaks corresponding to (112), (200), (220) and (312) planes were detected indicating the polycrystalline nature of the film. But the dominant peak corresponds to the (112) diffraction line of the kesterite structure of CZTS. Crystallite size in these films was determined from the broadening of the most intense peak (112) in the XRD pattern, using Scherer formula. There were no notable peaks related to secondary phases from XRD; however existence of binary or ternary sulfides such as ZnS, Cu₂S, and Cu₂SnS₃ cannot be ruled out just because they are absent in XRD pattern because they have diffraction patterns similar to CZTS owing to their similar zinc blend-type structures. To distinguish the CZTS phase from other sulfides very precisely, Raman analysis was done.
3.1.2 Structural analysis using Raman spectra.
Surface Raman scattering analysis (figure 2) was performed since additional information on possible secondary phases can be obtained. All films showed strong peak at 333 cm\(^{-1}\) which is attributed to the ‘A1 mode’ of CZTS and is related with vibration of ‘S’ atoms. There is a small shift in peak position to lower energies with respect to the reported value 338 cm\(^{-1}\). This peak is but related to CZTS since XRD measurements confirm the presence of CZTS. The second peak of CZTS at 287 cm\(^{-1}\) is also present in all the samples, but its intensity is very small compared to the peak at 338 cm\(^{-1}\).

Advantage of Raman spectra over XRD pattern in analyzing the presence of secondary phases is that, in Raman spectra, peaks corresponding to secondary phases are not present in the vicinity of peaks corresponding to CZTS. Intensity of peaks corresponding to CZTS increases with increase in ‘Cu’ concentration up to 0.0225 M, beyond which intensity decreases. Formation of secondary phases is initiated when ‘Cu’ concentration is raised to 0.025 M. The peak at 475 cm\(^{-1}\) (very low intensity; only for sample CZTS:2.5C) indicates formation of Cu\(_x\)S phase. Even from Raman analysis, presence of ZnS and other sulfides could not be detected.
Figure 2. Raman spectra of CZTS thin films prepared by varying copper concentration in the precursor solution.

3.1.3 Compositional analysis.
Elemental composition of CZTS films deposited with different ‘Cu’ concentration in the precursor solution on glass substrates is shown in Table 1. As expected, there is proportionate increase in atomic concentration of ‘Cu’ in the films when ‘Cu’ concentration is increased in the precursor solution. When concentration of ‘Cu’ in the solution is varied, it affects atomic concentration of not only ‘Cu’ but also ‘Zn’, ‘Sn’ and ‘S’ in the films. Even though there is slight decrease in sulfur concentration, there is no systematic variation in the case of ‘Zn’ and ‘Sn’. The $\frac{\text{Cu}}{(\text{Zn} + \text{Sn})}$ ratio in the film increased from 0.75 to 0.92 with increase in ‘Cu’ concentration. Katagiri et al. [13] had reported that solar cells with high conversion efficiencies are possible with CZTS films which are slightly Cu-deficient i.e. when $\left(\frac{\text{Cu}}{(\text{Zn} + \text{Sn})}\right) \sim 0.9$.

Table 1. Compositional analysis of CZTS thin films prepared by varying copper concentration in the precursor solution.

| Sample   | Cu (at.%) | Zn (at.%) | Sn (at.%) | S (at.%) | Cl (at.%) | $\frac{\text{Cu}}{(\text{Zn} + \text{Sn})}$ | $\frac{\text{Zn}}{\text{Sn}}$ | $\frac{\text{S}}{\text{metal}}$ |
|----------|-----------|-----------|-----------|----------|-----------|---------------------------------|----------------|----------------|
| CZTS:1.75C | 22.3      | 15.5      | 14.3      | 44.6     | 3.3       | 0.75                            | 1.1            | 0.86          |
| CZTS:2C   | 23.1      | 12.2      | 17        | 44.1     | 3.6       | 0.79                            | 0.72           | 0.84          |
| CZTS:2.25C | 25.3      | 13.1      | 15.5      | 43.3     | 2.8       | 0.88                            | 0.85           | 0.80          |
| CZTS:2.5C  | 26.4      | 12.7      | 16.1      | 41.6     | 3.2       | 0.92                            | 0.79           | 0.75          |
3.2 Characterization of CZTS/In$_2$S$_3$ Junction

3.2.1 Junction prepared by varying Cu concentration

The J-V characteristics of the devices are shown in figure 3. $V_{oc}$ is almost the same for all the devices whereas $J_{sc}$ increased steadily with increase in ‘Cu’ concentration. As with $J_{sc}$, there is significant improvement in $FF$ also. Increase in $J_{sc}$ and $FF$ may be due to the reduction in resistance of CZTS layer with increase in ‘Cu’ concentration. Maximum efficiency that we obtained from the set of devices was 1.6 % and it was for the device having a ‘Cu’ concentration of 0.025 M in the precursor solution. The cell parameters of the devices prepared using CZTS layer having different ‘Cu’ concentration is given in table 2.

![Figure 3. J-V characteristics of CZTS/In$_2$S$_3$ heterojunction prepared using CZTS layer having different ‘Cu’ concentration.](image)

**Table 2.** Performance parameters of the CZTS/In$_2$S$_3$ heterojunction prepared using CZTS layer having different ‘Cu’ concentration.

| Device name | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | $FF$ (%) | $\eta$ (%) | $R_s$ ($\Omega$ cm$^2$) | $R_{sh}$ ($\Omega$ cm$^2$) |
|-------------|--------------|---------------------|----------|-----------|----------------|-------------------|
| CZTS:1.75C  | 447          | 5.9                 | 40       | 1.07      | 23             | 186               |
| CZTS:2C     | 426          | 6.5                 | 42       | 1.16      | 18             | 198               |
| CZTS:2.25C  | 434          | 7.4                 | 42       | 1.35      | 17             | 258               |
| CZTS:2.5C   | 426          | 7.7                 | 49       | 1.6       | 11             | 216               |

3.2.2 Junction prepared by varying Sn concentration

J-V characteristics of these devices are shown in figure 4. As in the earlier case, there is not much variation in $V_{oc}$. But $J_{sc}$ and $FF$ increased up to 0.007M of ‘Sn’ concentration and then decreased. Efficiency also was maximum for device CZTS:0.7Sn. The maximum conversion efficiency achieved was 1.85 %. Series resistance of the devices, calculated from the inverse slope of the J-V characteristics at the open circuit voltage point, was minimum for CZTS: 0.7Sn and value obtained was 10 $\Omega$ cm$^2$. Performance parameters of the devices are tabulated in table 3.
Figure 4. J-V characteristics of the CZTS/In\textsubscript{2}S\textsubscript{3} heterojunction prepared by using CZTS layer deposited by varying the ‘Sn’ concentration

Table 3. Performance parameters of the CZTS/In\textsubscript{2}S\textsubscript{3} heterojunctions prepared by using CZTS layer deposited by varying the ‘Sn’ concentration

| Device name | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm\textsuperscript{2}) | FF (%) | $\eta$ (%) | $R_s$ (\Omega.cm\textsuperscript{2}) | $R_{sh}$ (\Omega.cm\textsuperscript{2}) |
|-------------|---------------|-------------------------------|--------|------------|-----------------|-----------------|
| CZTS:0.9Sn  | 447           | 7.1                           | 49     | 1.55       | 12              | 242             |
| CZTS:0.8Sn  | 411           | 7.7                           | 51     | 1.61       | 11              | 265             |
| CZTS:0.7Sn  | 430           | 8.3                           | 52     | 1.85       | 10              | 252             |
| CZTS:0.6Sn  | 445           | 7.3                           | 48     | 1.57       | 14              | 219             |

3.3 Conclusion

From the various studies done so far, on CZTS absorber layer, ratio of various constituent elements in precursor solution was optimised. For getting maximum conversion efficiency, the sprayed CZTS absorber layer should have elemental ratio of Cu:Zn:Sn:S= 2.5:1:0.7:12 in the precursor solution. Maximum efficiency obtained was 1.85% with fill factor of 52%.

Theoretical calculations have shown that conversion efficiency can be as high as 32.2% [2] for CZTS thin film solar cells. One of the ways to reach higher conversion efficiency is to use nano-structural CZTS [14], like nano-structural thin films or nanowire array, etc. For search of the best intrinsic characteristics and limits of nano-structural CZTS solar cells it is possible to initiated studies of single nanowire heterostructures as stand-alone and active photovoltaic elements. Usage the principle of bottom-up design allows us to find nanomaterial parameters, which is the most important solar cell performance, including chemical/dopant composition, diode junction structure, size, and morphology [15]. Recently the method, which provide such possibility was created [16]. Such future study gives the possibility to reach theoretical conversion efficiency for CZTS solar cell.
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