Deposition of Kesterite Cu$_2$ZnSnS$_4$ (CZTS) Thin Films by Spin Coating Technique for Solar Cell Application

Sanjay Kumar Swami, Anuj Kumar, Viresh Dutta*

Photovoltaic Laboratory Centre for Energy Studies, Indian Institute of Technology Delhi, HauzKhas, New Delhi, -110016, India

Abstract

The thin films of Cu$_2$ZnSnS$_4$ (CZTS) have been successfully deposited on soda lime glass by spin coating technique. CZTS films were prepared by spin coating of a solution prepared by dissolving of copper (II) chloride, zinc (II) chloride, tin (IV) chloride and Thiourea in 2-Methoxyethanol. The X-ray diffraction studies showed the formation of kesterite phase with the peaks corresponding to (112), (220) and (312) planes. Raman spectrum indicated the presence of principal kesterite peak at 333 cm$^{-1}$. SEM study showed that the surface of CZTS film was uniform. The electrical measurements showed the p-type conductivity, resistivity $\sim$0.014 $\Omega$·cm with carrier concentration $\sim$7.9$\times$10$^{19}$ cm$^{-3}$ and mobility $\sim$5.43 cm$^2$ V$^{-1}$s$^{-1}$ at room temperature. CZTS film showed optical absorbance of 10$^4$ cm$^{-1}$ with optical band gap of 1.5 eV. Thus, CZTS films can be made using a simple spin coating technique, but improvement in the film properties by post deposition needs to be done for making photovoltaic quality films.

Keywords: CZTS thin films; kesterite; spin coating; solar cell

1. Introduction

Cu$_2$ZnSnS$_4$ (CZTS) is one of the most promising absorber layer materials for low-cost thin film solar cells due to its semiconductor properties such as p-type conductivity, direct band gap and high absorption coefficient ($\geq$10$^5$ cm$^{-1}$), as well as the earth abundant and nontoxic constituent elements [1-3]. This semiconductor film can be regarded as an alternative to CIS and CIGS materials, in which the extremely expensive and resource limited Indium is replaced by cheap and abundant zinc (Zn) and tin. CZTS films have been deposited by physical vapour deposition methods like atom beam sputtering, thermal etc.

*Corresponding author. Tel.: +91-11-26591261; fax: +91-11-26591261.
E-mail address: vdutta@ces.iit.ac.in.
evaporation [4-5], sputtering and sequential evaporation, co-evaporation, multi-stage evaporation and pulsed laser deposition. Also chemical deposition methods like photo-chemical deposition, sol-gel [5], spray pyrolysis [6-7] and vapour-phase sulphurisation of E-B evaporated precursors [8] have been used. In this work we report CZTS thin film preparation by spin coating technique on soda lime glass substrate. By this inexpensive process the CZTS absorber layer can be prepared easily, which may be useful for solar cell application.

2. Experimental

Cu₂ZnSnS₄ thin films were deposited by spin coating technique starting with non aqueous solution containing cupric chloride (2M), zinc chloride (1M), stannic chloride (1M) and thiourea (8M) dissolved in 2-methoxy ethanol and few drops of monoethanolamine (MEA) were added. Clear yellow sol-gel was formed after being stirred at 50°C for several minutes. Milman’s spin coater-300 was used to deposit the CZTS film on properly cleaned soda lime glass substrate. The fabrication process of CZTS film by spin coating technique is shown by flow chart.

The films were investigated by studying their composition, structural, optical and electrical properties. X-ray diffractometer (Phillips X'PERT PRO) was used to record X-ray diffraction (XRD) patterns of the films. Spectral transmittance of the films was recorded in the wavelength range 400–1500 nm by using Perkin Elmer Lambda 1050 UV-VIS-NIR spectrophotometer. The microstructure and the surface morphology were observed using a Zeiss EVO-50 scanning electron microscope (SEM). The elemental composition was determined using energy dispersive spectrometer (EDS) system attached to the SEM. Electrical resistivity of the films at room temperature was determined with a Ecopia HMS-5000 Vander Pauw Hall effect measurement system and Raman spectrum was recorded at room temperature by
Renishaw InVia Raman microscope operating at excitation by 514.5 nm photons of 50 mW argon ion laser from Spectra Physics.

3. Result and discussion

3.1. Structure analysis

SEM image of CZTS film is shown in Fig. 2 which indicates that the film has uniform surface features over the entire area.

Fig. 2. Surface morphology of the CZTS thin films

The XRD spectrum shown in Fig. 3(a), with the peaks corresponding to the planes (112), (200), (220), (312) and (112), confirms the formation of CZTS phase with no other sulphide compounds present. The existence of kesterite film is also confirmed by the Raman peak (333 cm⁻¹) shown in (Fig. 3(b)). Hence both XRD and Raman studies confirm the formation of good quality CZTS film.

Fig. 3. (a) XRD pattern; (b) Raman spectrum of CZTS film
The EDX results shown in Table 1 confirm proper elemental composition in the spin coated film. Sulfurisation/selenisation treatment will be needed to achieve improvements in the compositional and structural properties.

Table 1. Elemental Composition of the spin-coated CZTS films

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>32.28</td>
</tr>
<tr>
<td>Zn</td>
<td>15.49</td>
</tr>
<tr>
<td>Sn</td>
<td>13.89</td>
</tr>
<tr>
<td>S</td>
<td>38.34</td>
</tr>
</tbody>
</table>

3.2. Optical properties

The transmittance spectrum of the films formed on glass substrate is analysed to obtain the absorption coefficient and the band-gap energy.

![Transmittance of CZTS film deposited by spin coating](image)

The absorption coefficient near the fundamental absorption edge is \(\sim 10^4 \text{ cm}^{-1}\). Band gap energy of 1.5 eV is obtained by extrapolating the straight part of the \((\alpha h\nu)^2/\nu h\nu\) plot. These optical properties show that spin coated CZTS films are well suited for solar cell application.

3.3. Electrical properties

Vander Pauw measurements indicates that CZTS thin film exhibits p-type conductivity with resistivity \(\sim 0.014 \Omega\cdot\text{cm}\), carrier concentration \(\sim 7.9\times10^{19} \text{ cm}^{-3}\) and mobility \(\sim 5.43 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}\) at room temperature.
4. Conclusion

Cu2ZnSnS4 thin film was successfully fabricated using spin coating technique. The results showed that a good quality kesterite polycrystalline structure had formed. The p-type CZTS film with resistivity ~0.014 Ω-cm, carrier concentration ~7.9×10^{19} cm^{-3} and mobility ~5.43 cm^{2} V^{-1}s^{-1} at room temperature, and a high absorption coefficient as 10^4 cm^{-1} achieved by this synthesis technique. The optical energy band-gap of the CZTS sample is about 1.5 eV, which is very close to the optimum value for a solar-cell. These results show that CZTS films could be easily prepared by this technology for the solar-cell application.

References