

### Optimization of growth parameters of photoactive $\text{Cu}_2\text{ZnSnS}_4$

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$\text{Cu}_2\text{ZnSnS}_4$  (CZTS) is a promising candidate for application in low-cost and environmentally friendly thin film solar cells due to its optoelectronics properties. It is a perfect absorber material for photovoltaic applications due to its high absorption coefficient ( $>10^4 \text{ cm}^{-1}$ ) and direct optical band gap (1.4 - 1.5 eV). Among the CZTS preparation techniques, electrodeposition of Cu, Sn and Zn stack layers followed by sulphurisation in  $\text{H}_2\text{S}$  is an attractive technique because of its simplicity, low cost and easy to control stoichiometry. In this investigation, optimization of growth parameters in order to obtain photoactive CZTS thin films by sulphurisation of electrodeposited Cu, Sn and Zn stack layers has been investigated. Cu thin film was electrodeposited on Mo substrate at  $-0.89 \text{ V}$  Vs Ag/AgCl electrode in an electrochemical cell containing 0.4 M  $\text{CuSO}_4$ , 3 M lactic acid and NaOH at pH 11. Deposition of Sn thin film on Mo/Cu electrode was carried out at  $-1.2 \text{ V}$  Vs Ag/AgCl in an electrochemical cell containing 0.055 M, 2.25 M NaOH and 8 ml of sorbitol. Zn thin film was electrodeposited on Mo/Cu/Sn at  $-1.2 \text{ V}$  Vs Ag/AgCl in an electrochemical cell containing 0.2 M  $\text{ZnSO}_4$ . Deposition parameters of Cu, Sn and Zn have been obtained by voltammograms. In order to grow CZTS, Mo/Cu/Sn/Zn thin film electrodes were annealed at  $550 \text{ }^\circ\text{C}$  for 60 min in  $\text{H}_2\text{S}$ . Sulphurisation process was carried out at different temperatures and durations using set of identical Mo/Cu/Sn/Zn thin film electrodes and thereby optimized temperature and duration of the sulphurisation. Atomic ratios of initial Cu, Sn and Zn layers could be crucial parameters in determining properties of CZTS thin films. Therefore, atomic ratios of Cu/Sn/Zn layers were optimized by changing Cu, Sn and Zn deposition duration. Various combinations of deposition durations were carried out and optimized by monitoring the dark and light I-V measurements in a PEC containing 0.1 M sodium acetate. Dark and light I-V characteristics revealed that the best photoactive CZTS films can be grown by depositing Cu for 20 min, Sn for 10 sec and Zn for 10 sec. Results further showed that photoconductivity of CZTS thin films is p-type. It is evident from reflectance measurements that the band gap of the CZTS films is 1.5 eV. In conclusion, it is found that the highest photoactive p-CZTS thin films can be grown by sulphurisation of electrodeposited Cu, Sn and Zn stack layers on Mo substrate using  $\text{H}_2\text{S}$  at  $550 \text{ }^\circ\text{C}$  for 60 min. Cu: Sn: Zn ratios of the stack layers are the crucial parameters in determining photoactive CZTS thin films. The methodology developed in this study will be further investigated in order to develop the materials for wider applications.

**Keywords:**  $\text{Cu}_2\text{ZnSnS}_4$ , Cu/Sn/Zn stack layers, Electrodeposition, I-V characteristics

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