Absorber thin films of Cu$_2$ZnSnS$_4$ from chemically deposited binary compounds

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Chemical bath deposition is an easily scalable process for obtaining thin films of metal chalcogenides of binary compositions on surfaces of any geometry. We have reported the deposition of thin films of both wide and narrow-gap semiconductor metal chalcogenides [1] and subsequently solar cells using chemically deposited SnS as absorbers in CdS/SnS structures, open circuit voltages, $V_{oc}$, of up to 400 mV and short circuit current densities, $J_{sc}$, of up to 3.1 mA/cm$^2$ with a fill factor of 0.37 and conversion efficiency of 0.57% are also reported earlier [2]. In the case of solar cells using Sb$_2$S$_3$ thin films, $V_{oc}$ is 670 mV, $J_{sc}$ is up to 5 mA/cm$^2$ and efficiency of conversion $\eta$, about 1% [3].

In recent years, thin films of quaternary and pentanary semiconductors Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSn(S/Se)$_4$ (CZTSSe) incorporating tin chalcogenides have emerged as promising candidate absorber materials that have an advantage of being chemicals composed of more abundant elements than the chalcopyrite absorber CuIn(Ga)Se$_2$. Thin film solar cells with conversion efficiencies, $\eta$, of 6.7% [4] using CZTS as absorber and >10% [5] using CZTSSe absorber in structures of glass/Mo/CZTS(CZTSSe)/CdS/ZnO are reported. Co-sputtering of ZnS, SnS, Cu, followed by sulfurization in N$_2$+H$_2$S at 580°C [4] and spin-coating of solutions that contain the sulfides and selenides of the metal ions in N$_2$+H$_2$S at 580°C were the methods reported for the preparation of the absorber films for these cells.

We previously reported on thermal processing at 350 - 400°C under N$_2$ of chemically deposited SnS-CuS thin films of different thickness ratios to obtain thin films of ternary compounds Cu$_2$SnS$_3$ and Cu$_4$Sn$_3$S$_4$ with optical band gap $E_g$ of 0.95 - 1.2 eV and p-type conductivities suitable as absorbers in solar cells. In the present work, we used a similar approach to obtain thin films of Cu$_2$ZnSnS$_4$ (CZTS) by processing sequentially deposited thin films of binary compounds, SnS, CuS, and ZnS. Chemical baths reported in [1] are used for obtaining thin films of the binary compounds. The films of the quaternary semiconductor show tetragonal structure with crystallite diameter of 17 nm, p-type conductivity of $\sim$ 10$^3$ (ohm cm)$^{-1}$ with photosensitivity and $E_g$ 1.4 eV. The paper will deal with the preferred sequence of deposition of component films, conditions of thermal processing and intermediate stages forming thin films of CZTS, and the results on solar cells incorporating these layers. The use of an evaporated metal layer on a CuS-SnS-ZnS stack to improve the structural, optical and electrical properties of the films will also be presented.