Absorber thin films of Cu_2ZnSnS_4 from chemically deposited binary compounds

Maricela Rebeca Aragón-Silva, D. Becerra, M. T. S. Nair, P. K. Nair
Department of Solar Energy Materials, Centro de Investigación en Energía
Universidad Nacional Autónoma de México
Temixco, Morelos-62580, Mexico, MEXICO
mtsn@cie.unam.mx

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 tin and antimony chalgaogenides as absorber materials [2, 3]. Using chemically deposited thin films of 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 upto 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_2S_3 thin films, V_{oc} is 670 mV, J_{sc} is up to 5 mA/cm^2 and efficiency of conversion Ƞ, about 1% [3].

In recent years, thin films of quaternary and pentanary semiconductors Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSn(S/Se)_4$ (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, Ƞ, of 6.7% [4] using CZTS as absorber and >10% [5] using CZTSSe absorber in structures of glass/Mo/CZTS(or CZTSSe)/CdS/ZnO are reported. Co-sputtering of ZnS, SnS, Cu, followed by sulfurization in N_2+H_2S at 580^{o}C [4] and spin-coating of solutions that contain the sulfides and selenides of the metal ions in N_2H_4 followed by annealing at 540 ^{o}C were the methods reported for the preparation of the absorber films for these cells.

We previously reported on thermal processing at 350 - 400 ^{o}C under N_2 of chemically deposited SnS-CuS thin films of different thickness ratios to obtain thin films of ternary compounds Cu_2SnS_3 and Cu_4SnS_4 [6] 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_2ZnSnS_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 ~ 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.

[1] Nair et. al., *Sol. Energy Mater. Sol. Cells* 52 (1998) 313
[2] Avellaneda et. al., *Thin Solid Films* **517** (2009) 2500: Nair et. al., *ECS Transactions* 41 (4) 177-183 (2011)
[3] Messina et al, *Thin Solid Films* 517 (2009) 2503–2507; Nair et al, *ECS Transactions*, 41 (4) 149-156 (2011)
[4] H. Katagiri et. al., *Thin Solid Films* 517 (2009) 2455
[5] Barkhouse et al *Prog. Photovolt: Res. Appl.* 2012; 20:6–11
[6] David Avellaneda et al. *J. Electrochem Soc.* **157 (**2010) D346