**Solution-processed chalcogenide thin film solar cells**

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The photovoltaic technology based on polycrystalline thin films of Cu(In,Ga)Se2 (CIGS) has shown a steady progress within the last decade by reaching the record conversion efficiency of 20.8% on glass substrates in 2013 [1] thus surpassing the highest efficiency for the market-dominating poly-Si technology [2]. What is remarkable, that efficiencies as high as 20.4% are also achievable for CIGS solar cells on flexible polymer substrates as demonstrated by Empa [3]. Related chalcogenide absorbers kesterites which comprise compounds Cu$_2$ZnSnS$_4$ (CZTS), Cu$_2$ZnSnSe$_4$ (CZTSe) and their alloys are less efficient than CIGS cells but can eventually offer lower manufacturing costs starting from abundant and non-toxic materials. The currently highest efficiency of 12.6% was reported by IBM for an absorber processed by non-vacuum solution approach using hydrazine as solvent [4]. The non-vacuum deposition from true solutions or nanoparticle dispersions are expected to eventually lower the capital investment for the manufacturing equipment, increase the material utilization and enable a fast roll-2-roll processing on flexible substrates [5]. For industrial acceptance, however, no losses in conversion efficiency can be tolerated regardless the absorber material, which imposes big challenges in the non-vacuum deposition research [6].

Three research developments are presented to highlight important challenges for the non-vacuum-processed chalcogenide solar cells. A solution-based route for the CIGS absorber layers is discussed, which employs binder-free solutions of metal salts in non-toxic, alcohol solvents [7]. By coordinating metal cations in carboxylic chelate complexes by in-situ redox-reactions it is possible to obtain liquid-coated precursor that can be later crystallized in the polycrystalline absorber. Despite the low-boiling-point nature of the solvents, a residual carbon-rich layer is observed between the CIGS and metal back contact. Fabricated solar cells exhibit active area efficiencies of up to 7.7%.

For the CZTSSe absorbers, the solution chemistry has been modified to metal salt solutions in dimethyl sulfoxide with a chalcogen source but no organic binders [8]. A frequently observed drawback of the chemical solution processing – poor crystallinity of the chalcogenide absorber – can be overcome by employing a sodium-containing reactive agent. A massive improvement in grain growth in the presence of sodium is explained by an enhanced surface chemisorption of selenium molecules and the formation of liquid Na$_2$Sex phases during reactive annealing of the precursor. By adjusting the sodium precursor quantity, it is possible to tune doping levels and gradients to maximize the collection of photogenerated carriers in thin film CZTSSe solar cells with up to 6% efficiency.

Finally, a novel solution approach for obtaining highly transparent and conducting ZnO:Al (AZO) layers to be used as front contacts in thin film solar cells is highlighted [9]. Different morphologies from AZO nanorods towards densely packed films are accomplished by altering the aqueous solution chemistry. Using metallic Al as a continuous and controllable doping source allows the fabrication of AZO thin films with tunable doping gradients and doping concentrations. Excellent optoelectronic properties are achieved at process temperatures not exceeding 85 °C, which allows using temperature-sensitive and non-conductive substrates. The aqueous solution grown AZO as front electrical contact in a CIGS thin film solar cell is an excellent application for this low temperature process since the underlying p-CIGS/
n-CdS heterojunction can rapidly degrade when heated above 150 °C. The highest solar cell efficiency with the solution-grown AZO contacts was 14.7%, indicating a feasibility of a fully non-vacuum processed chalcogenide thin film solar cell in the nearest future.