Earth-abundant chalcogenide thin films with tuneable bandgap for Photovoltaic applications.

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Identifying new low cost and low environmental impact energy sources is becoming an imperative need of civil society. More widespread use of renewable energy is, indeed, mandatory to meet the global energy demand, which is expected to be 28 TW in 2050. Silicon solar cells are the most mature renewable technology and rule the photovoltaic (PV) market, but chalcogenide-based thin-film devices, mainly $Cu(In,Ga)Se_2$ and CdTe, have matched them in performance. Above all, chalcogenide-based PV is versatile: flexible devices have already been produced. However, the recent sharp drop in silicon modules' price and the limited availability of some elements employed have focused the scientific community's attention on cheap and abundant materials on Earth. In this context, Cu_2ZnSnS_4 (CZTS) has been extensively investigated over the past ten years.[1] Here, we present the synthesis and the characterization of Earth-abundant chalcogenide thin-films with tunable bandgap, leading to well-defined phases of Cu_2XYS_4 (with X = Zn, Fe; Y = Sn, Ge). We propose a straightforward and cheap synthesis method based on the sol-gel technique. The thin films are produced thanks to a direct drop-casting of the precursor solution, followed by a gelation process and heat treatment in argon atmosphere to generate the desired crystalline phase of the quaternary alloy.[2] UV-Vis, μ-Raman, XRD and EDX spectroscopy measurements have characterized the so-synthesized layers, their morphology was studied by SEM imaging, proving the excellent quality of the material. The optical bandgaps of the presented compounds (CZTS, Fe-substituted CZTS, Ge-substituted CZTS) range from 1.4 to 2.1 eV, depending on the combination of the chosen metal precursors, making them suitable to be employed as stand-alone devices or as top solar cells in tandem architecture with various bottom cells. Promising single-junction prototypes of working devices have been produced, even employing semi-transparent substrates.[3-5] Another exciting alternative to the most studied CZTS is Cu_2MnSnS_4 (CMTS), a p-type semiconductor with Earth-abundant and low-cost elements. Manganese is cheaper (2$/kg vs 2,7$/kg) and has a higher occurrence in the Earth's crust than zinc (440ppm mean vs 65ppm mean), leading to the more economical and environmental sustainability of CMTS in respect of CZTS.[1, 6, 7] Here, we also report the CMTS thin films grown by a two-step deposition process (sputtering, followed by high-temperature annealing in sulphur vapours), produced in collaboration with the industrial partner in the research project. The CMTS-based solar cells reached a record efficiency of about 1% and an open-circuit voltage exceeding 400 mV. Photoluminescence measurements allowed us to identify the detrimental defects acting in working conditions, suggesting paths to improve the photovoltaic properties.

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