CZTS: a non-vacuum deposition method

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INTRODUCTION
The research in thin film solar cells has been dominated by light absorber materials based on chalcogenides CdTe and Cu(In,Ga)Se2 in the last decades. Both the toxicity of cadmium and the scarce availability of indium lead towards the development of a material which constituents are earth-abundant and relatively harmless. Polycrystalline CuZnSnSx (CZTS) is a semiconductor with a bandgap between 1.40 and 1.50 eV and an absorption coefficient higher than 10^4 cm^-1, thus suitable for being employed as a thin film light absorber.

Kesterite-type CZTS material showing the highest energy conversion efficiency (η) is synthesized mostly via vacuum-based methods such as sputtering or evaporation of metals (or metal sulphides) onto the suitable substrate. These techniques have the advantage of easily controlling the chemical composition and phase profile in the thin films and normally have good reproducibility. However, the real low-cost potential of kesterites could be more efficiently exploited if combined with a scalable, non-vacuum deposition method.

Starting from a sol-gel recipe proposed by Tanaka et al. [1] this work aims at fabricating CZTS using less expensive metallic precursors spin-coated on a rigid substrate. The annealing step was conducted using elemental sulphur rather than hydrogen sulphide, in order to develop a safer sulphurization method.

EXPERIMENTAL
Cu(NO3)2·3H2O, Zn(NO3)2·6H2O, SnCl2·5H2O were dissolved in 2-methoxyethanol. To avoid their precipitation monoethanolamine (MEA) was added. The resulting solution was spin-coated at 3000 rpm on a molybdenum thin layer covering a soda-lime glass (SLG). Samples were dried in air at 300 °C and the deposition step was repeated several times in order to achieve the suitable thickness. After the precursors deposition, samples were annealed with elemental sulphur at 500-550 °C in Ar flow for 1 h. Different salts concentrations have been tested to reach a stoichiometric composition for sulphurized samples.

The Raman spectra of sulphurized samples reveal the presence of the CZTS kesterite phase, but they also show other species are present in the annealed films. PL measurements showed that samples emit at room temperature, but none of the emission matches with the CZTS energy gap.

One of the most likely secondary phase contained in these samples is Cu2SnS3 (CTS). CTS exists in several crystal structures most of which are semiconductors with bandgap varying from 1.35 to 0.95 eV [2].

PROBLEMS
- Uneven coating of the surface once sulphurized
- Presence of secondary phases (CTS)

POSSIBLE SOLUTIONS/FUTURE EFFORTS
- Sulphurizing at higher temperatures (to promote the solid state reaction CTS+ZnS→CZTS) [4]
- Optimization of solution viscosity, deposition rate and drying time/temperatures to improve substrate covering (also switching to dip-coating or knife deposition techniques)

References