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 $Cu(In,Ga)Se_2$ 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 Cu_2ZnSnS_4 (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**.

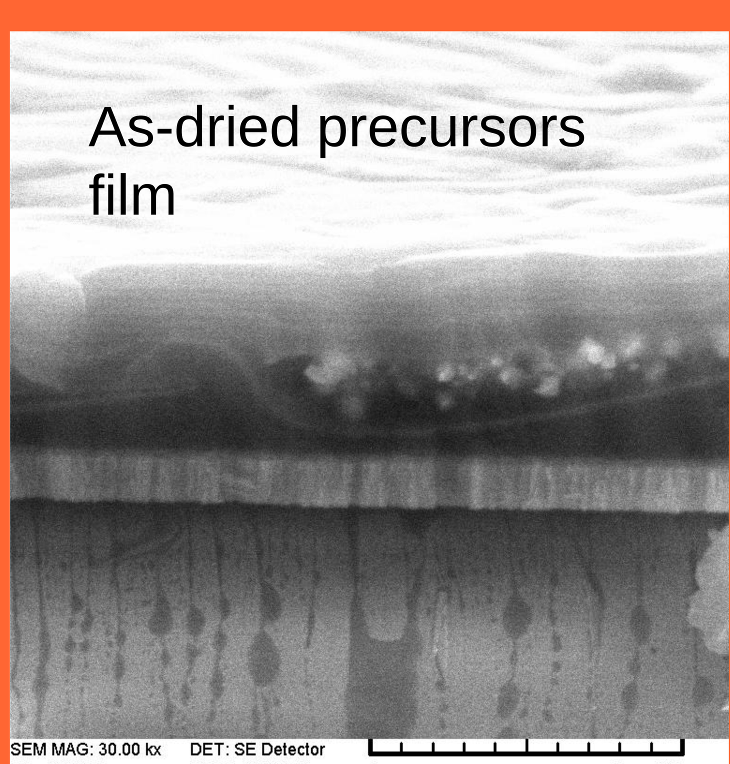
EXPERIMENTAL

$Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $SnCl_4{\cdot}5H_2O$ were dissolved in 2-metoxyethanol. To avoid their precipitation monoethanolamine (MEA) was added. The resulting solution was spin-coated at 3000 rpm on a molibdenum 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 elementar sulphur at 500-550 °C in Ar flow for 1 h. Different salts concentrations have been tested to reach a stoichometric composition for sulphurized samples.

Compositional ratios in the initial solution, in the as-dried deposited layers and in sulphurized sample. Values obtained from EDS measurements

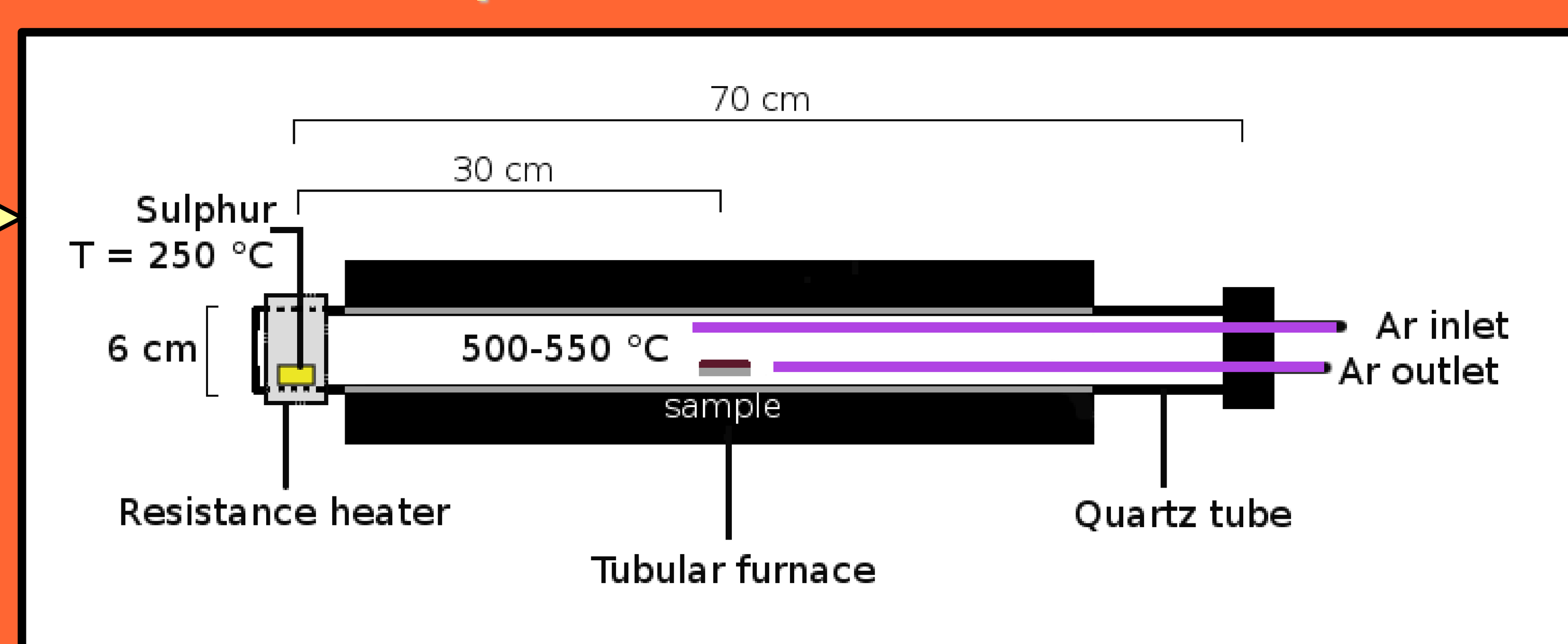
PRECURSORS SOLUTION		AS-DRIED FILM		SULPHURIZED SAMPLE		
Cu/(Zn+Sn)	Zn/Sn	Cu/(Zn+Sn)	Zn/Sn	Cu/(Zn+Sn)	Zn/Sn	S/metals
0.87	1.35	0.68	1.67	0.99	1.01	1.03

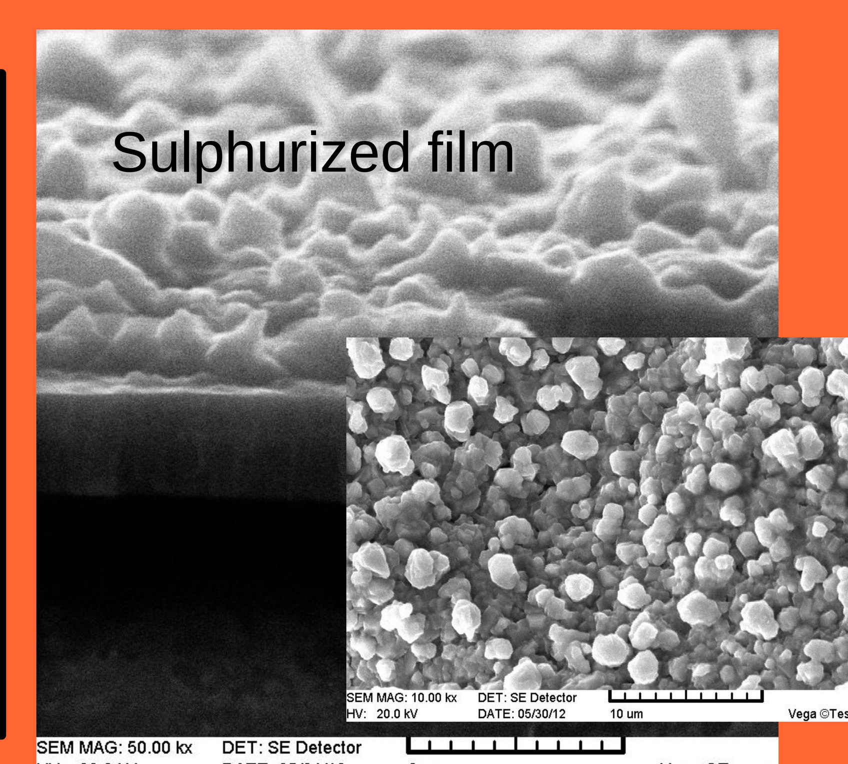
Sulphurization scheme

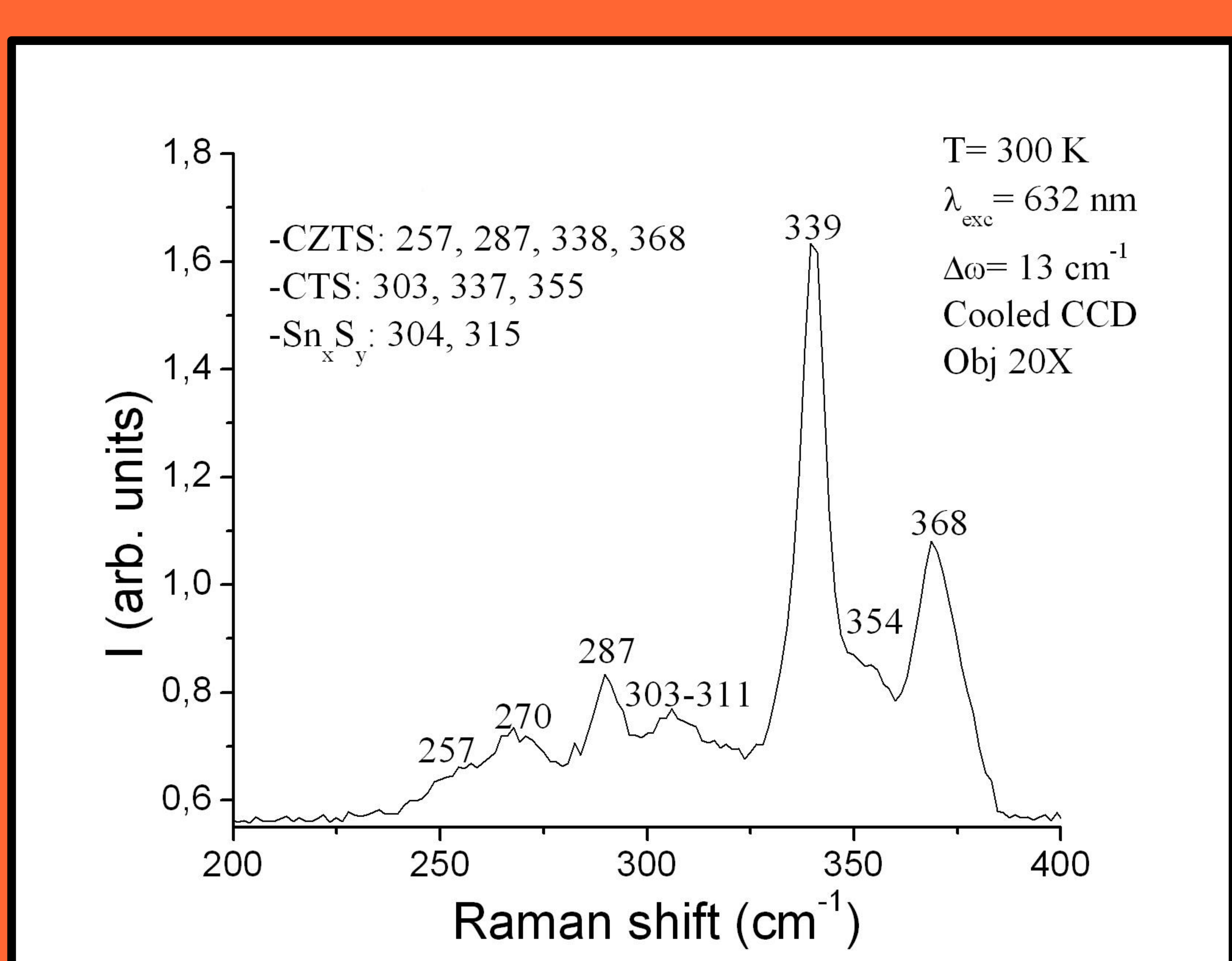


Mo layer (850 nm)

SLG (2 mm)







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 Cu_2SnS_3 (CTS). CTS exists in several crystal structures most of which are semiconductors with bandgap varying from 1.35 to 0.95 eV [2].

Raman scattering peaks expected from CZTS and other related binary and ternary sulphides (cm^{-1}) [3]

CZTS	SnS_2	SnS	ZnS	Cu_2S	Cu_2SnS_3 Tetragonal	Cu_2SnS_3 cubic	Cu_3SnS_4
266	315	164	278	264	336	295-303	295
288		192	351	475	351	355	318
338		218					
368-374							

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

[1] K. Tanaka, M. Oonuki, N. Moritake, H. Uchiki, Solar Energy Materials & Solar Cells 93 (2009) 583–587 [2] Y.-T. Zhai, S. Chen, J.-H. Yang, H.-J. Xiang, X.-G. Gong, A. Walsh, J. Kang, S.-H. Wei, Physical Review B 84 (2011) 075213 [3] A.-J. Cheng, M. Manno, A. Khare, C. Leighton, S. A. Campbell, E. S. Aydil, *Journal* of Vacuum Science & Technology A 29 (2011) 51203 [4] R. Schurr, A. Hölzing, S. Jost, R. Hock, T. Voβ, J. Schulze, A. Kirbs, A. Ennaoui, M. Lux-Steiner, A. Weber, I. Kötschau, H.-W. Schock, Thin Solid Films 517 (2009) 2465.