Effect of the sulphurization conditions on the properties of Cu₂ZnSnS₄ thin films and solar cell performance

Solar cell: SLG/Mo/CZTS/CdS/i-ZnO/ITO Solar cell J-V curves Precursors Composition Morphology CuS **SnS**₂ T550t1m1 T530t2m20 8xZTC Best cell efficiency 3.1%. Cu/(Zn+Sn 8 periods of Zn/SnS₂/CuS layers Large grains [1] H. Katagiri, K. Jimbo, S. Yamada, T. Kamimura, W.S. Maw, T. Fukano, T. Ito, T. and densely Motohiro, Appl. Phys. Express 1 (2008) 041201. CL 175 ONTIT **RF-magnetron Sputtering**/ Sulphurized film **Chemical Bath Mo-coated SLG RF-magnetron Sputtering**

RTP

Deposition



M.G. Sousa PhD. Student Supervisor: Prof. A.F. da Cunha

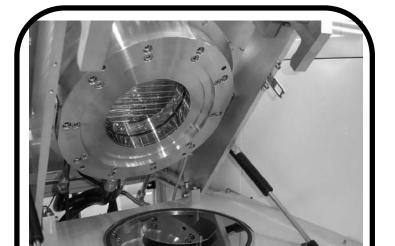
Objectives

We have studied the effect of several sulphurization parameters on the properties of Cu_2ZnSnS_4 thin films obtained through rapid thermal processing (RTP) of multiperiod precursors with 8 periods of Zn/SnS₂/CuS where Zn was thermally evaporated while SnS₂ and CuS were RF-magnetron sputtered. In this study we varied the heating rate, the time at maximum temperature, the maximum temperature and the amount of evaporated sulphur. The samples were characterized through scanning electron microscopy, energy dispersive spectroscopy, Raman diffraction, photoluminescence scattering spectroscopy, X-ray and I-V measurements.

Evaporation process

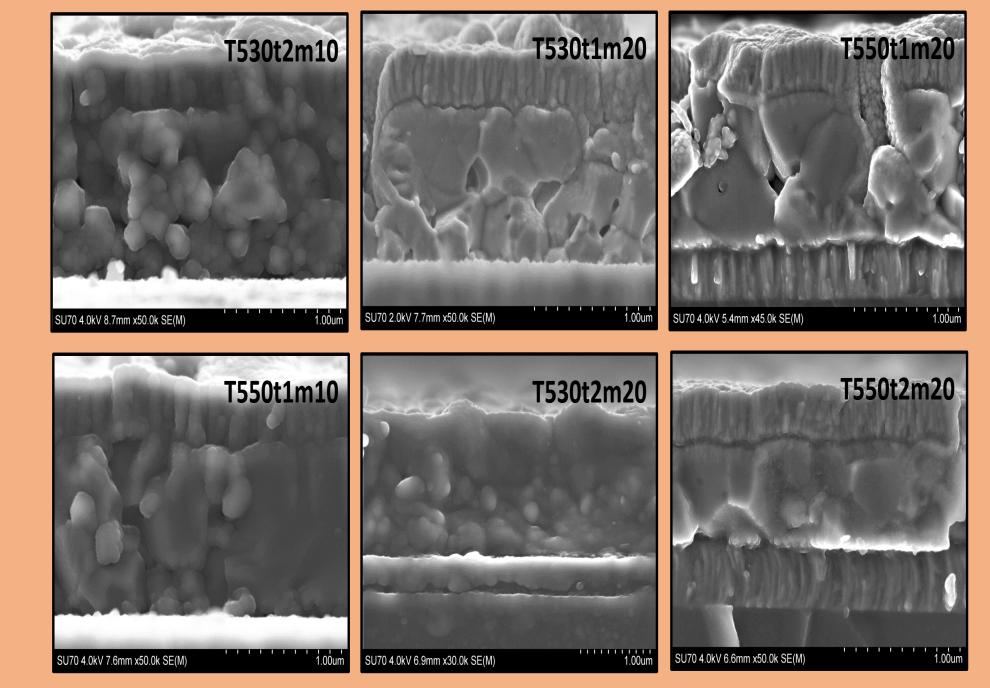
Methods and techniques

Rapid Thermal Processing Furnace



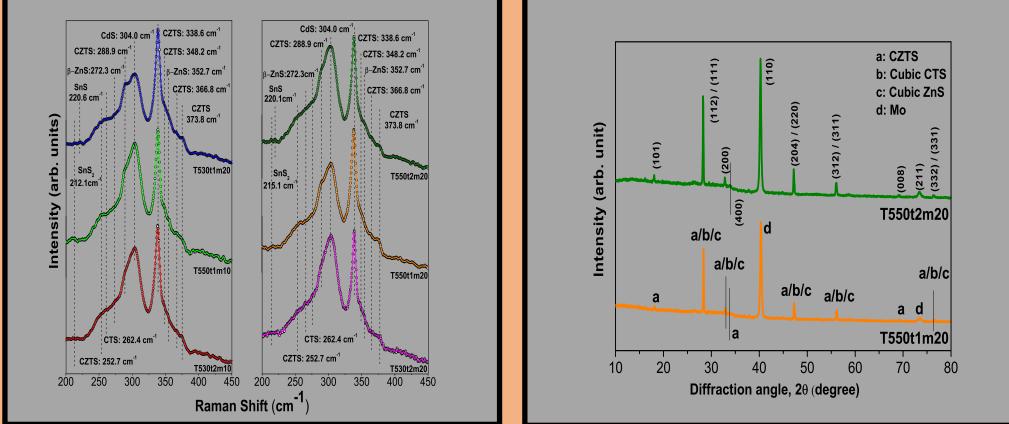
The sulphurization was performed in the RTP furnace at an overall pressure of 1 atm consisting of partial pressure of 95% N_2 +5% H_2 and sulphur vapour resulting from the evaporation of elemental

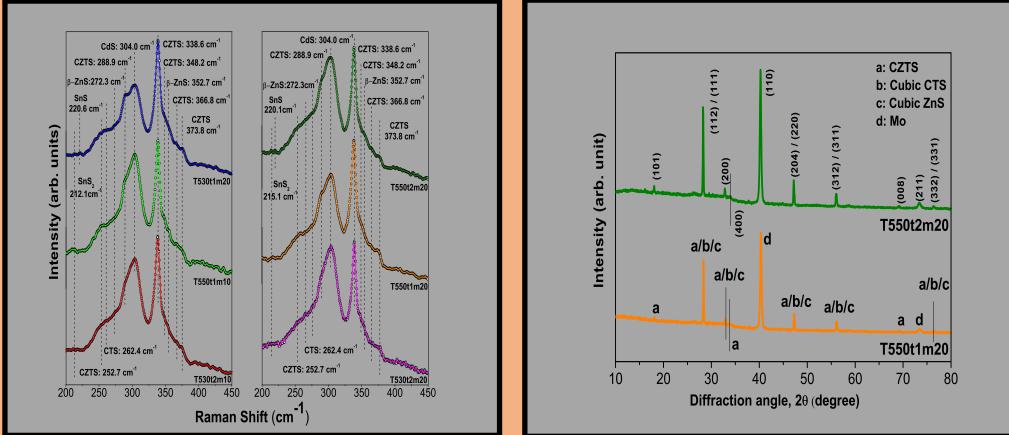
SEM/EDS Hitach SU-70 equipped with a Rontec EDS system operated at an acceleration voltage of 4.0 KV



RAMAN LabRam Horiba, HR800 UV spectometer, 532 nm excitation laser

packed







sulphur pieces placed near the sample under treatment. This process was carried out with the samples inside a graphite susceptor covered with a quartz lid and illuminated from the top.

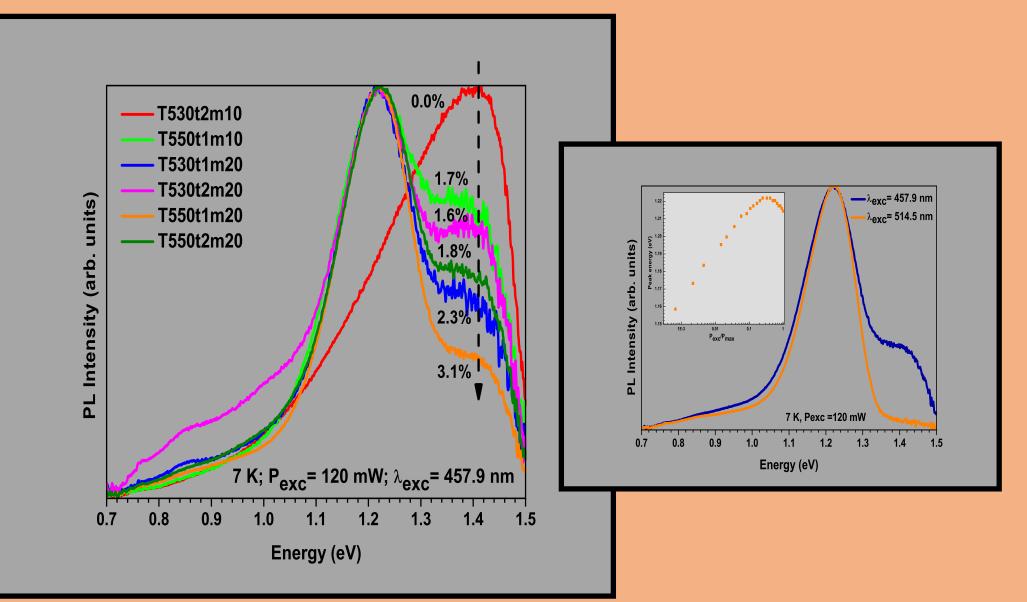
X'Pert MPD Philips PW 3710 system equipped with a CuK source XRD

Results

- □ These studies reveal that the samples sulphurized at higher temperature, shorter times and higher amount of evaporated sulphur exhibited larger grain sizes;
- □ The structural analysis based on Raman scattering and XRD did not reveal clear differences between the CZTS films;
- □ The cell results hint toward the detrimental effect of long sulphurization times and the positive effect of higher sulphur vapour pressure and higher sulphurization temperature;
- □ Photoluminescence spectroscopy studies showed an asymmetric broad band which occurs in the range of 1.0-1.4 eV.
 - The highest cell efficiency obtained in this study was 3.1%.

Sample	V _{oc} (mV)	J _{sc} (mAcm⁻²)	FF (%)	Efficiency (%)
T530t2m10	29.4	1.4	22.3	0.0
T550t1m10	462.4	9.3	40.8	1.7
T530t1m20	476.9	11.2	42.4	2.3
T530t2m20	471.2	9.5	36.3	1.6
T550t1m20	496.7	15.1	42.5	3.1
T550t2m20	435.8	11.2	37.1	1.8

PL Bruker IFS 66v FTIR spectometer, equipped with a Ge diode detector



J-V measurements with a home assembled system



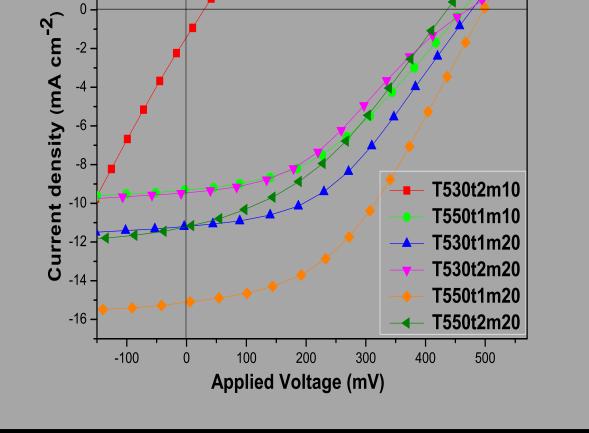
Publications

M.G.Sousa, A.F. da Cunha, P.A. Fernandes, J.P. Teixeira, R.A.Sousa and J.P.Leitão, Effect of rapid thermal processing conditions on the properties of Cu₂ZnSnS₄ thin films and solar cell performance, Sol. Energy Mater Sol. Cells 126 (2014) 101-106;

M.G.Sousa, A.F. da Cunha and P.A. Fernandes, Annealing of RF-magnetron sputtered SnS₂ precursors as a new route for single phase SnS thin films, J. Alloys Compd. 592 (2014) 80-85;

M.G.Sousa, A.F da Cunha, P.M.P.Salomé, P.A.Fernandes, J.P. Teixeira and J.P.Leitão, Cu₂ZnSnS₄ absorber layers

obtained through sulphurization of metallic precursors: Graphite box versus Sulphur Flux, Thin Solid Films 535



(2013) 27-30.



TUTE FOR DSTRUCTURES, DMODELLING AND DFABRICATION





ACKNOWLEDGMENTS

The authors acknowledge the financial support from the portuguese science foundation (FCT), through the grants technology PTDC/CTM-MET/113486/2009, Pest-C/CTM/LA0025/2011 **RECI/FIS**and NAN/0183/2012.