

Growth and Characterization of single phase SnS thin films by sulphurization of sputtered sulphide precursors

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Motivation

Currently several materials are being developed with the aim of replacing $\text{CuIn}_{1-x}\text{Ga}_x(\text{S}_{1-y}\text{Se}_y)_2$ as absorber layer in thin film solar cells by compounds that do not involve the use of In. **One promising material is SnS.** Producing single phase SnS thin films has been a challenging task because additional phases such as SnS_2 , Sn_2S_3 tend to form. Therefore, finding the appropriate thermodynamic conditions is essential. Thin film solar cells based on SnS have shown substantial progress. Nevertheless, the latest reported cell results are still rather low with an efficiency of 2.4%.

In this work, we present a process to grow tin sulphide thin films by sulphurization of sulphide precursors prepared by RF magnetron sputtering. The sulphurization has been performed in a tubular furnace inside a graphite box and in a rapid thermal processing furnace.

The composition of the films was analysed by EDS. The structural analysis and the phase detection were performed by X-ray diffraction (XRD) and Raman scattering. The morphological characterization was made by Scanning electron microscopy (SEM). The optical properties were studied through spectrophotometry.

Tubular Furnace

ABSTRACT

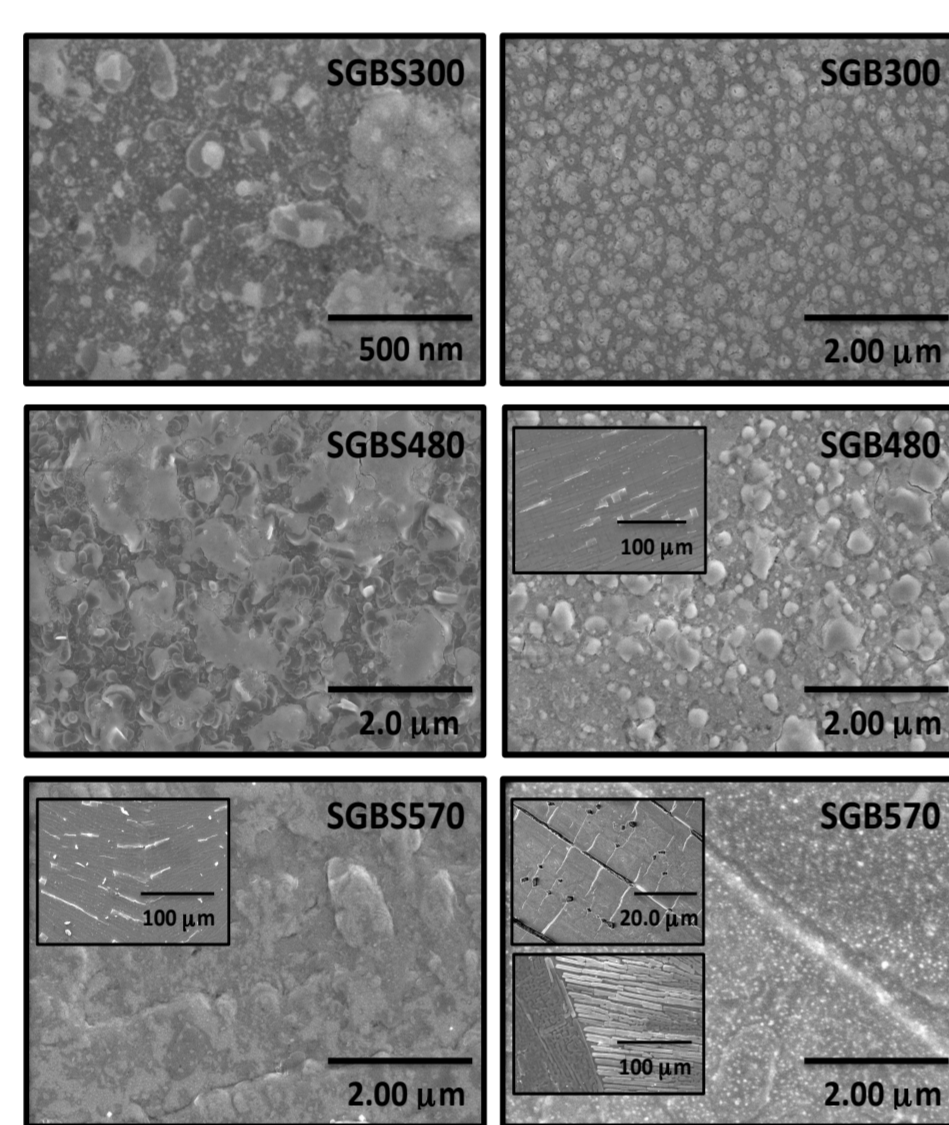
Single-phase SnS thin films have been grown on soda-lime glass substrates based on the sulphurization of RF-magnetron sputtered SnS_2 precursors. Two different approaches to sulphurization were compared and thoroughly studied.

The two series of identical precursors were sulphurized in the same furnace, inside a graphite box with and without elemental sulphur evaporation. Different maximum sulphurization temperatures, in the range 300°C to 570°C, were tested.

Sulphurization of SnS_2 precursors in a graphite box with and without sulphur vapour at high temperature produces SnS films which appear to be single-phase from the structural analysis. The studies show that the direct absorption transitions of SnS are at 1.41 eV and 1.68 eV for sulphurization in graphite box with and without elemental sulphur evaporation, respectively. The indirect absorption transition values varied from 1.49 eV to 1.37 eV.

RESULTS

Sample	Composition Ratios			Precursor thick (nm)	Final thick (nm)
	Sn (at.%)	S (at.%)	[Sn]/[S]		
SGBS300	4.24	6.30	0.68	256.0	
SGBS400	5.23	7.24	0.72	224.0	
SGBS570	3.62	3.92	0.92	220.1	
SGB300	4.93	6.91	0.71	~320	316.1
SGB480	2.80	2.20	1.26		387.1
SGB570	3.75	2.38	1.57		302.7



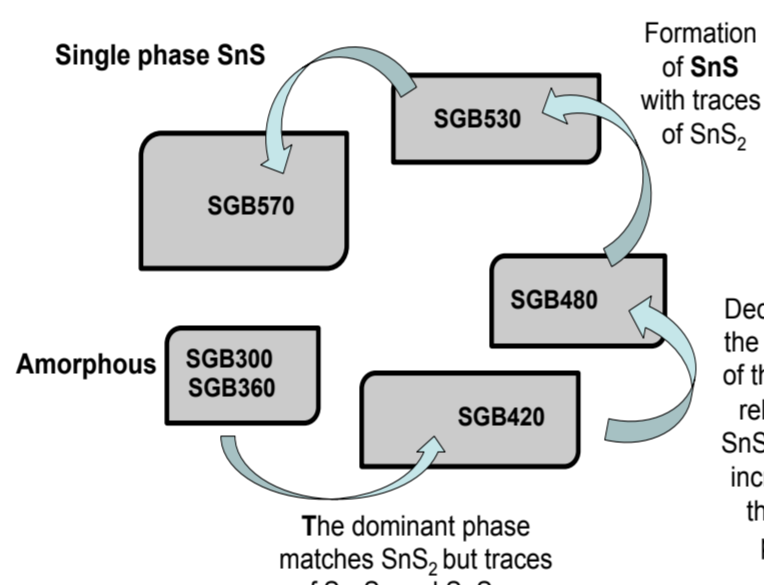
SEMEDS Hitachi SU-70 equipped with a Rontec EDS system operated at an acceleration voltage of 4.0 kV

COMPOSITION

- The Sn/S ratio increased with increasing the sulphurization temperature;
- For SGB300 to SGB570 the composition ratios increased from 0.6 at 300 °C to near stoichiometric at 570 °C;
- SGB300 has Sn/S ratio below 1 and SGB400 and SGB570 present a ratio higher than 1. These latter results suggest that the samples are tin rich;
- The samples sulphurized in a graphite box at higher temperatures were predominantly SnS;
- Considerable material losses are observed in experiments with graphite box.

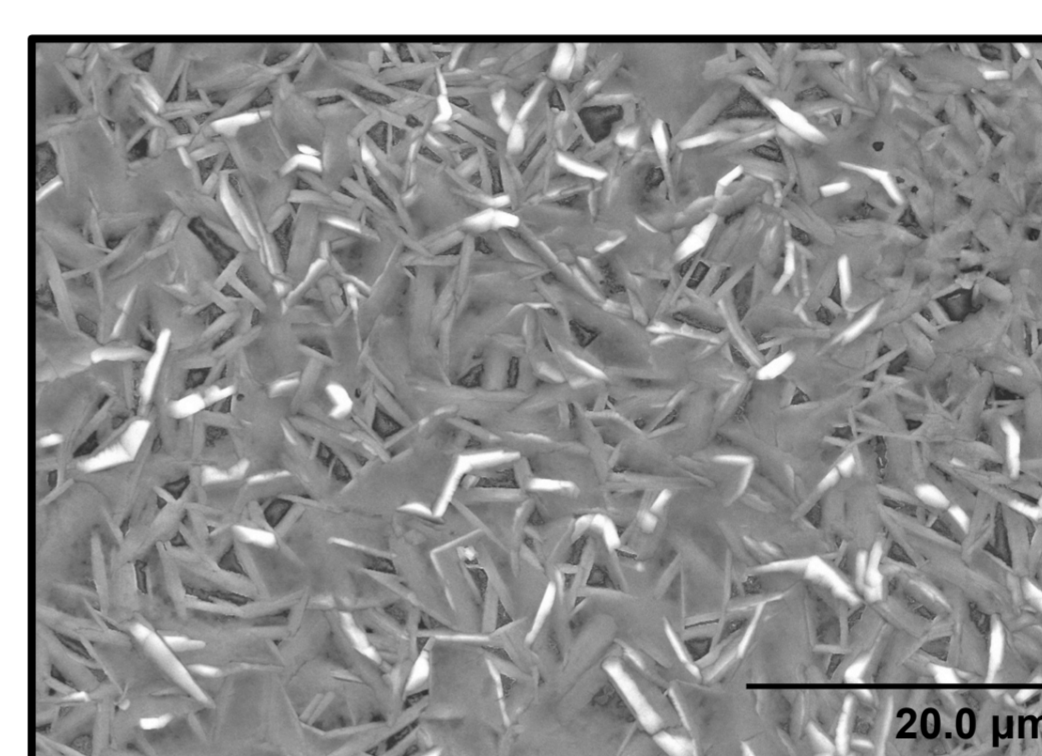
MORPHOLOGY

- The samples sulphurized at lower temperatures exhibited small grain structure uniformly distributed and good coverage of the substrate surface;
- A dense structure can be observed;
- Voids and cracks were found in the samples SGB570 and SGB570;
- As the maximum sulphurization temperature increased from 300 °C to 480 °C, the surface roughness increased;
- Increased further the temperature, from 480 °C to 570 °C, the surface roughness decreased.



MORPHOLOGICAL

SCANNING ELECTRON MICROSCOPY



SEM analysis reveals disk-like grains morphologies.

ENERGY DISPERSIVE X-RAY SPECTROSCOPY

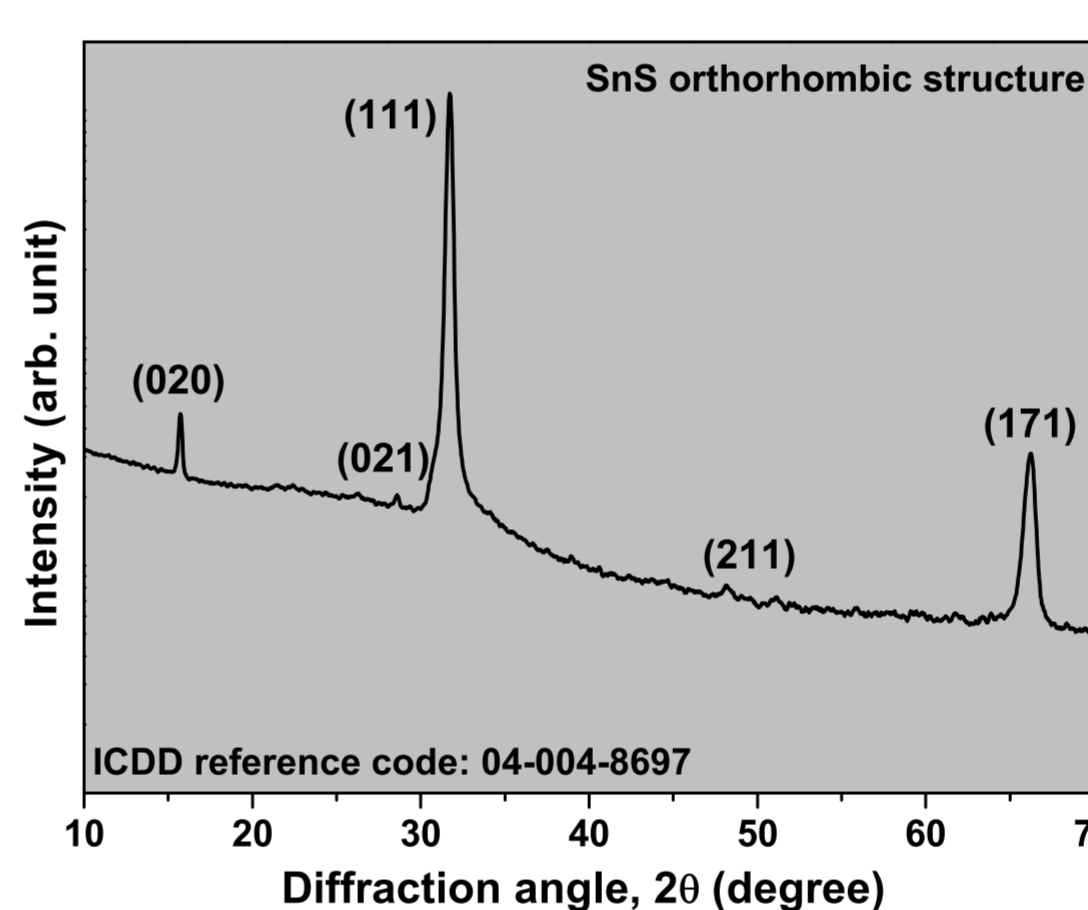
Sn (at.%)	S (at.%)	[Sn]/[S]
5.60	6.41	0.87

The sample tended towards a stoichiometric ratio 1:1

SEM/EDS Hitachi SU-70 with a Rontec EDS system operated at an acceleration voltage of 4.0 kV

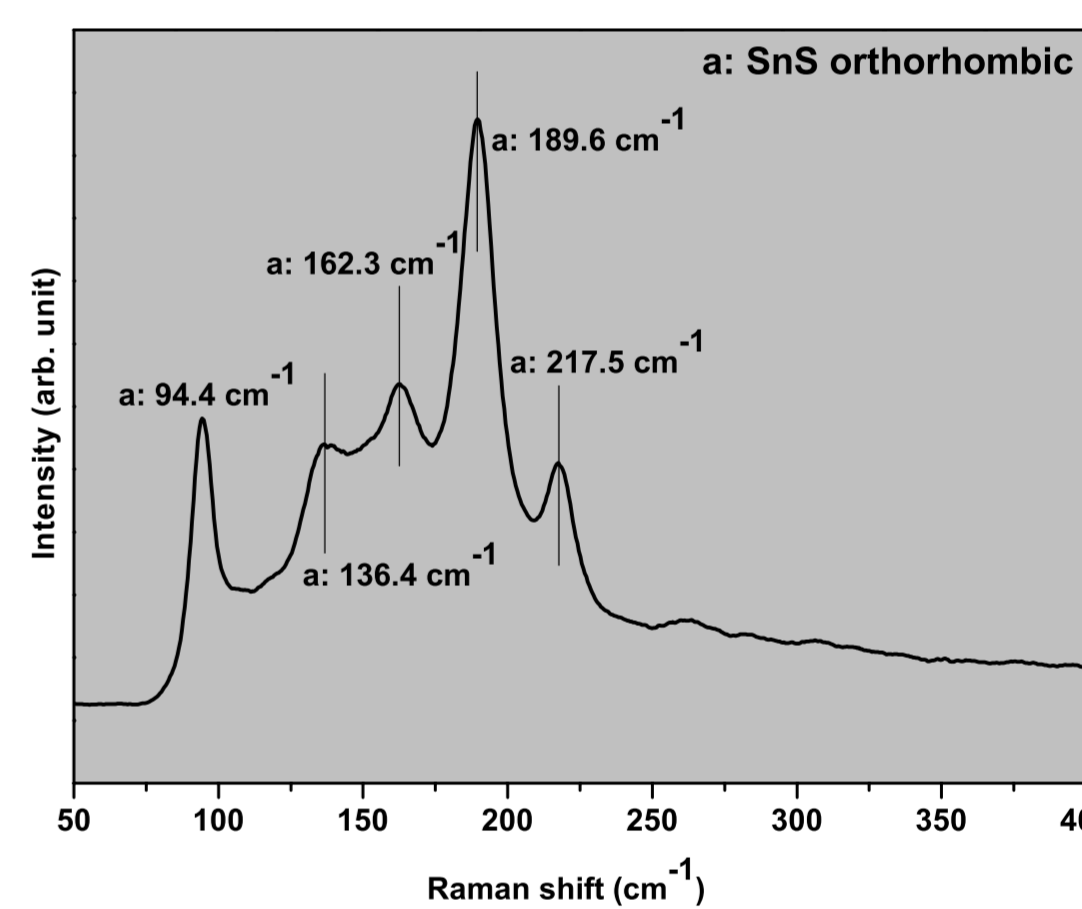
STRUCTURAL

X-RAY DIFFRACTION



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

RAMAN SPECTROSCOPY

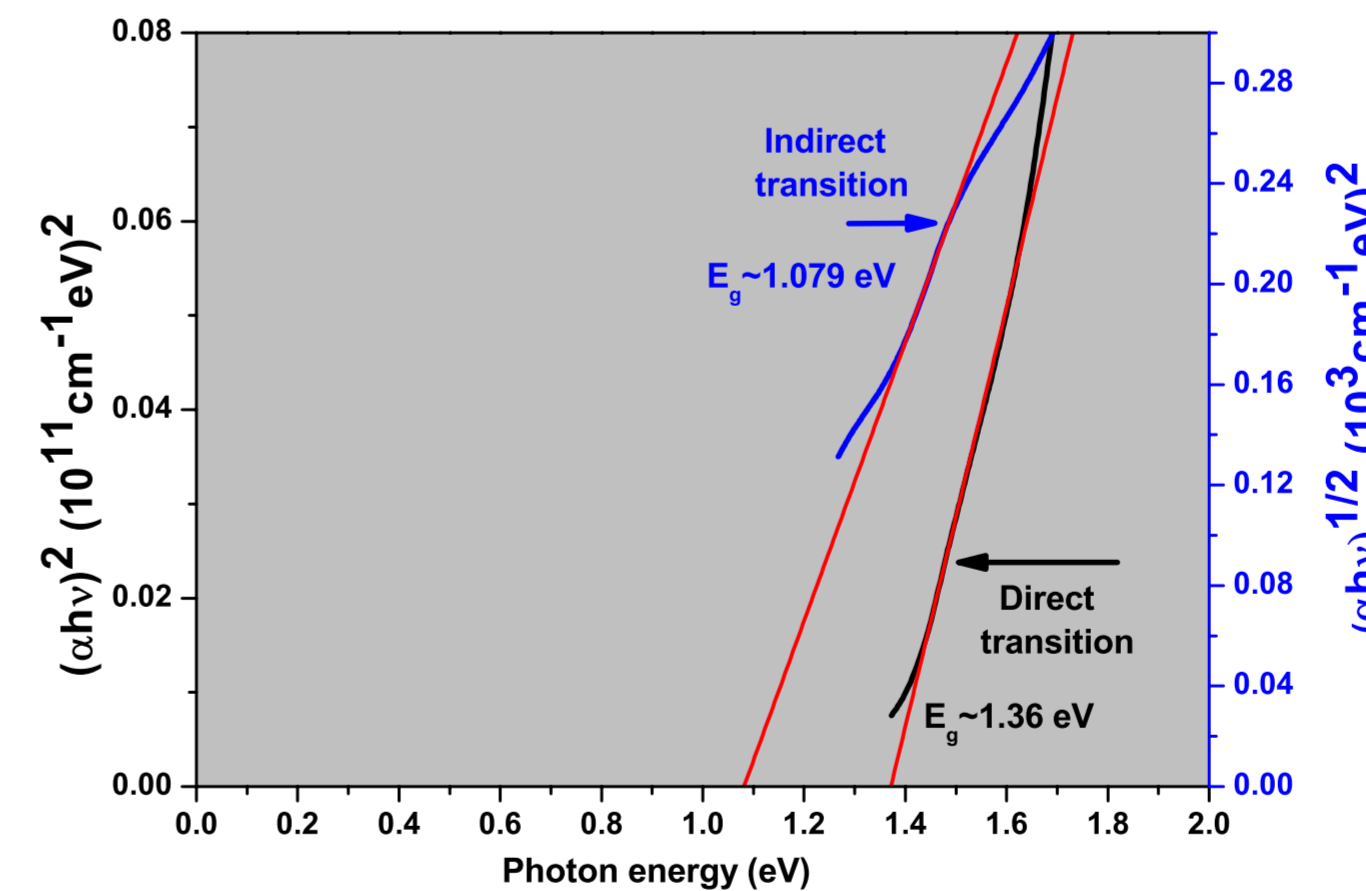


RAMAN LabRam Horiba, HR800 UV spectrometer, 532 nm excitation laser

The samples are composed of the orthorhombic-SnS phase. The peaks are sharp which suggests that the samples have good crystalline quality.

The raman spectrum shows peaks at 94.4 cm^{-1} , 162.3 cm^{-1} , 189.6 cm^{-1} and 217.5 cm^{-1} which are assigned to the SnS phase.

OPTICAL



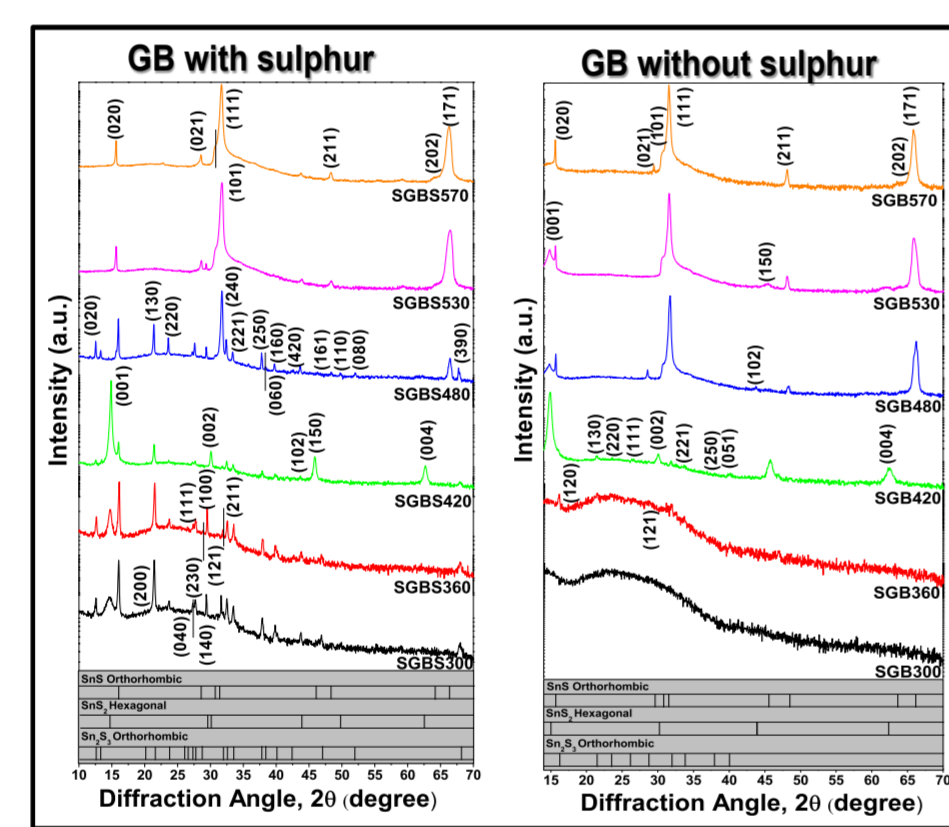
BAND GAP Shimadzu UV3600 spectrophotometer

The results show an indirect transition energy of 1.07 eV and an direct transition energy of 1.36 eV. These values are in good agreement with the 1.07 eV predicted for the indirect transition of SnS [1] which follows the discussion above present in the structural analysis.

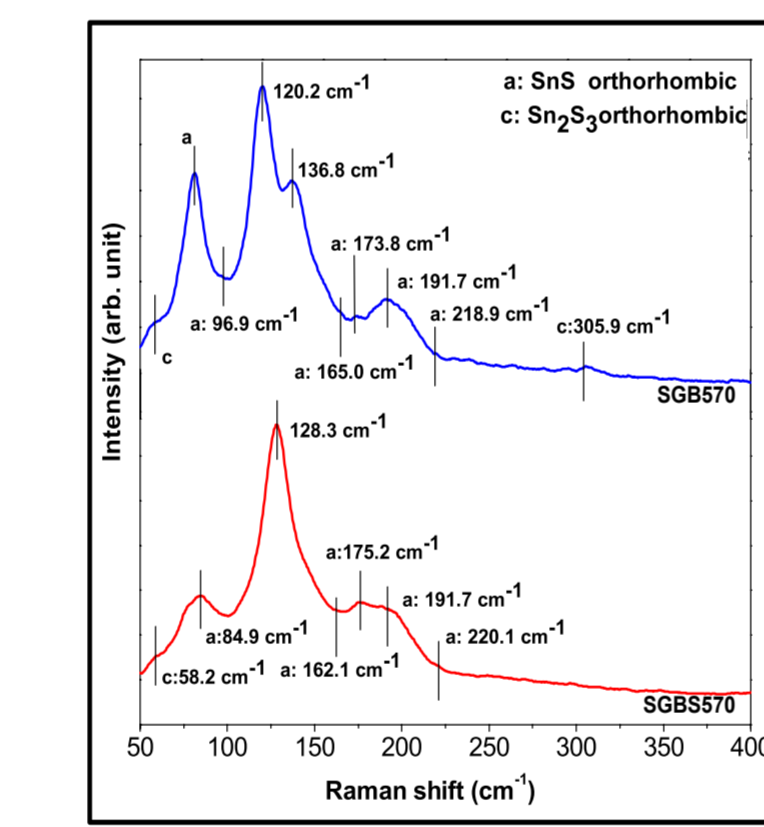
[1] J. Vidal, S. Lany, M. Avezac, A. Zunger, A. Zakutayev, J. Francis, J. Tate, Appl. Phys. Lett. 100 (2012) 032104

The structural analysis' results show that the formation of different Sn_2S_3 phases with the change of the maximum temperature and the sulphurization approach may be interpreted as the result of different dissociation reactions:

- $2\text{SnS}_2(s) = \text{Sn}_2\text{S}_3(s) + \text{S}(g)$
- $\text{SnS}_2(s) = \text{SnS}(s) + \text{S}(g)$
- $\begin{cases} \text{Sn}_2\text{S}_3(s) \rightarrow 2\text{SnS}(s) + \text{S}(g) \\ \text{Sn}_2\text{S}_3(s) + \text{SnS}_2(s) \rightarrow 3\text{SnS}(s) + \text{S}(g) \end{cases}$



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



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

Phases	SGBS300	SGBS480	SGBS570
SnS	84.9 cm^{-1}	84.9 cm^{-1}	84.9 cm^{-1}
SnS ₂	162.1 cm^{-1}	162.1 cm^{-1}	162.1 cm^{-1}
β-Sn	191.7 cm^{-1}	191.7 cm^{-1}	191.7 cm^{-1}
SnS ₂	220.1 cm^{-1}	220.1 cm^{-1}	220.1 cm^{-1}

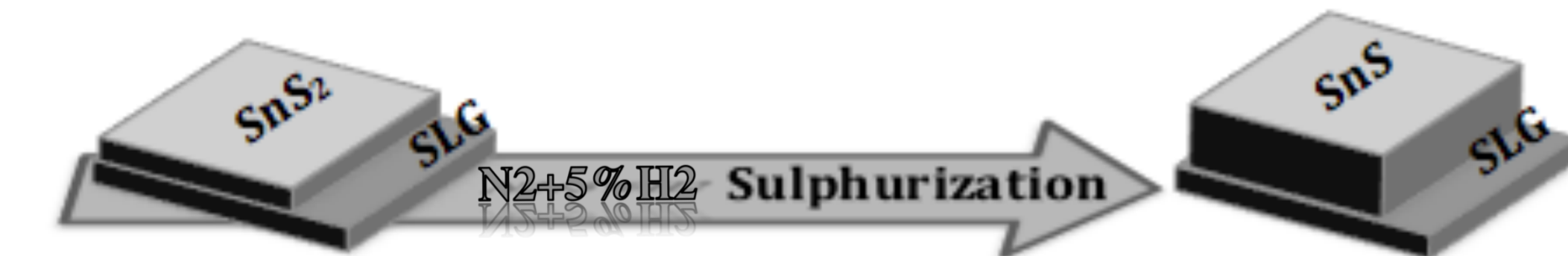
CONCLUSION

- Different attempts to produce single-phase SnS thin films with orthorhombic structure;
- Sulphurization of SnS_2 precursors in a GB which pieces of sulphur were evaporated produces at highest sulphurization temperature of 570 °C films predominantly formed by SnS phase but with residual amounts of Sn_2S_3 as well as a thin top layer of β-Sn;
- Sulphurization in a GB without sulphur evaporation the films appear to be single phase SnS phase and again capped by a thin layer of β-Sn.

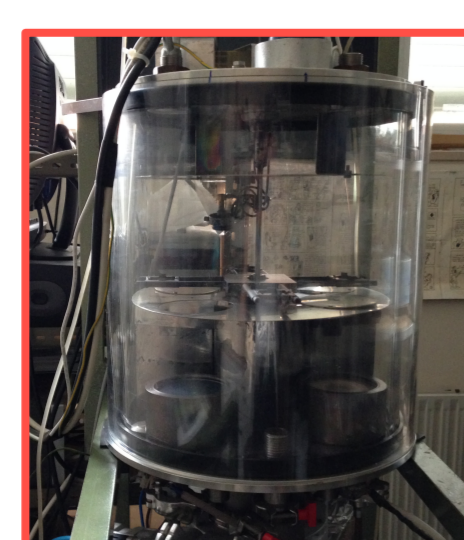
GROWTH METHOD

Sulphurization of

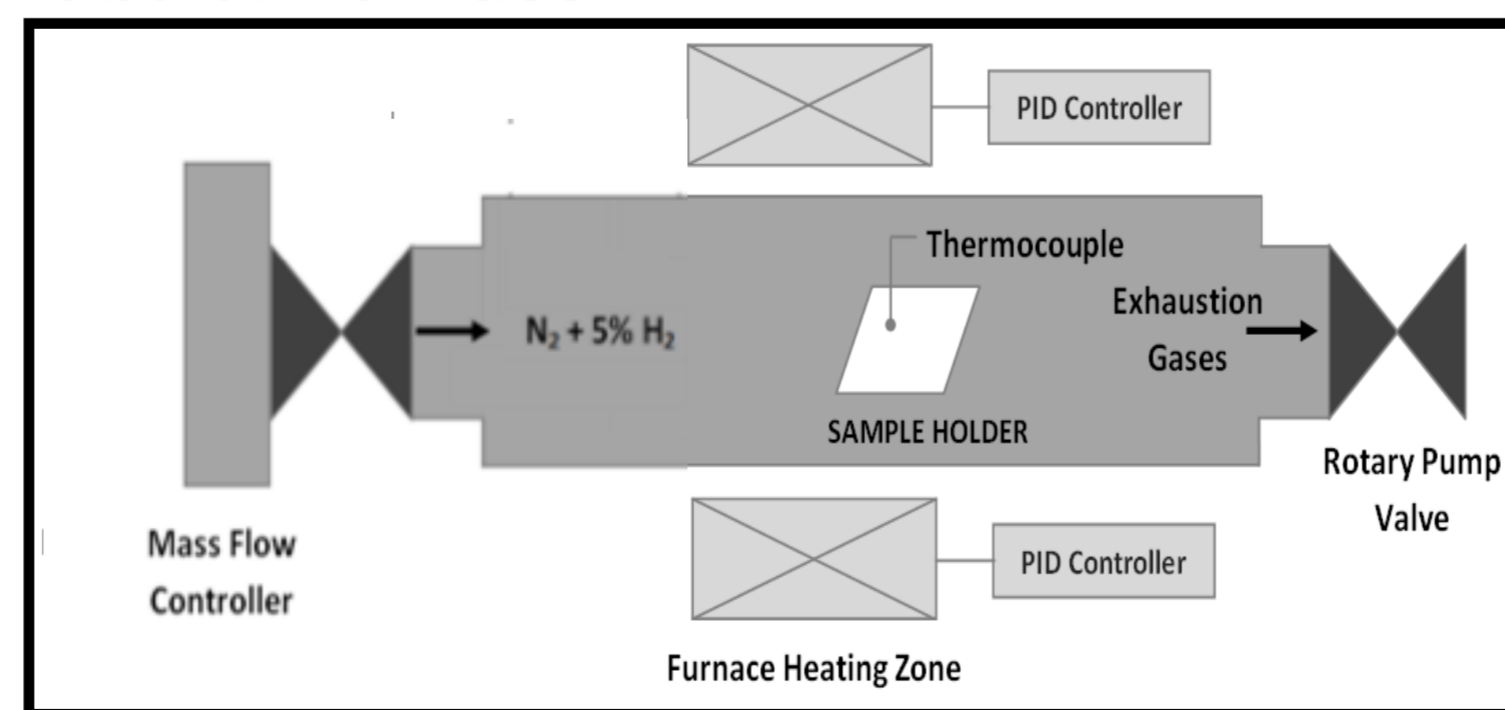
RF-magnetron sputtered SnS_2 precursors



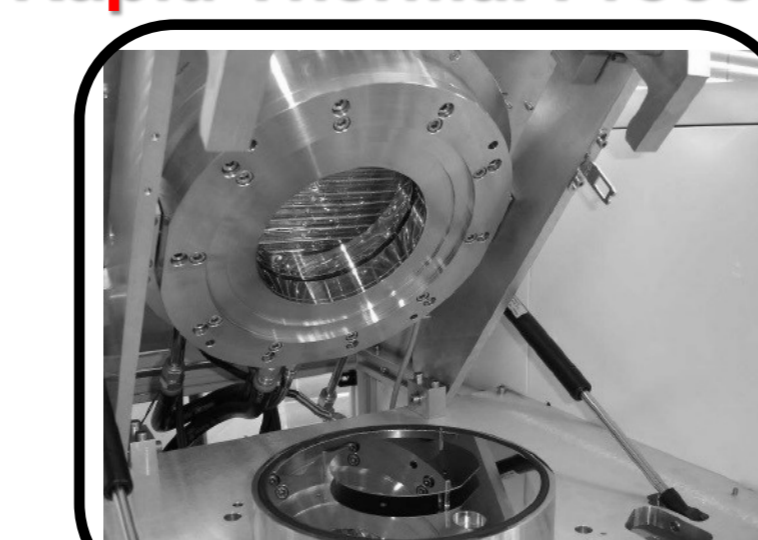
The SnS_2 precursor layers were deposited by RF-magnetron sputtering on soda lime glass (SLG) substrates.



Tubular Furnace



Rapid Thermal Processing Furnace



Such a system allows very fast heating/cooling ramp rate and very short sulphurization times are possible.

Conclusions

In the case of sulphurization in a tubular furnace the films closest to pure SnS have been obtained at annealing temperature of 570 °C for 15 minutes.

In the case of sulphurization in the rapid thermal processing furnace the best results were obtained again for an annealing temperature of 570 °C but for 5 minutes.

For the films sulphurized in the tubular furnace besides the dominant phase of SnS a top layer of β-Sn was also identified.

The sulphurization in the rapid thermal processing furnace allowed an almost complete elimination of the β-Sn layer and the films showed better crystallinity.

ACKNOWLEDGMENTS

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