Effect of selenization conditions on the growth and properties of $Cu_2ZnSn(S,Se)_4$ thin films

S. Ranjbar, M. R. Rajesh Menon , M. G. Sousa , P. A. Fernandes and A. F. da Cunha

I3N- Departamento de Física, Universidade de Aveiro, Portugal.

samaneh.ranjbar@ua.pt

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Abstract

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) is a potentially cost effective candidate for future thin film solar cells (TFSCs). We report the growth of CZTSSe using a hybrid process involving the sequential evaporation of Zn and sputtering of the sulfide precursors of Cu and Sn, followed by a selenization step. Two approaches for selenization were followed, one using a tubular furnace (TF) and the other using a Rapid Thermal Processor (RTP). SEM and EDS were employed to investigate the morphology and composition of the films. Structural analyses were done using XRD and Raman spectroscopy. Structural analyses revealed the formation of CZTSSe. The effects of annealing conditions on the morphological and structural properties of the films were investigated.

Experiment

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin films are prepared in two steps.

1. Zn was evaporated on Mo-coated glass and then SnS_2 and CuS were sputtered subsequently using an RF magnetron system to prepare $Zn/SnS_2/CuS$ precursors.
2. The precursors were selenized using two approaches.

2.a. A conventional Tubular Furnace (TF).

The precursors were selenized by placing them and Selenium pellets inside a graphite box within the TF.

2.b. A Rapid Thermal Processor (RTP).

2 µm thick layer of Se was deposited over the precursor after which they were annealed in an RTP Furnace.

The heating rate and annealing time were 1 ºC/s and 2 min, respectively.

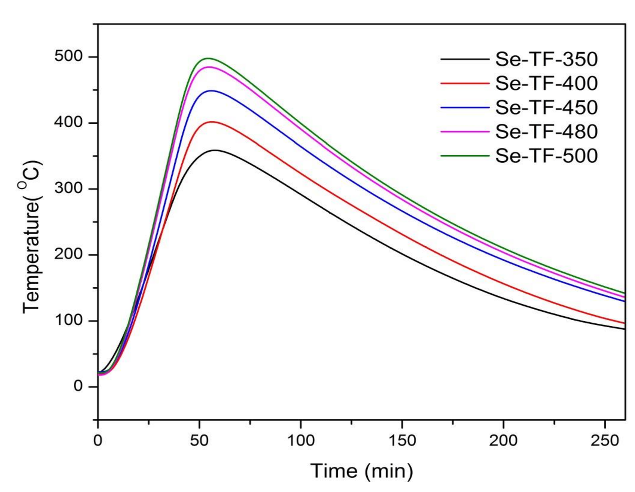

Fig.1. Temperature profile of samples selenized in TF.

Table 1. The samples are named according to the type of selenization method and their maximum temperature.

Sample	Se-TF-350	Se-TF-400	Se-TF-450	Se-TF-480	Se-TF-500	Se-RTP-400	Se-RTP-450	Se-RTP-500	Se-RTP-525
Method	Tubular Furnace	Tubular Furnace	Tubular Furnace	Tubular Furnace	Tubular Furnace	Rapid Thermal Processor	Rapid Thermal Processor	Rapid Thermal Processor	Rapid Thermal Processor
Temp (ºC)	350	400	450	480	500	400	450	500	525

Morphological analysis

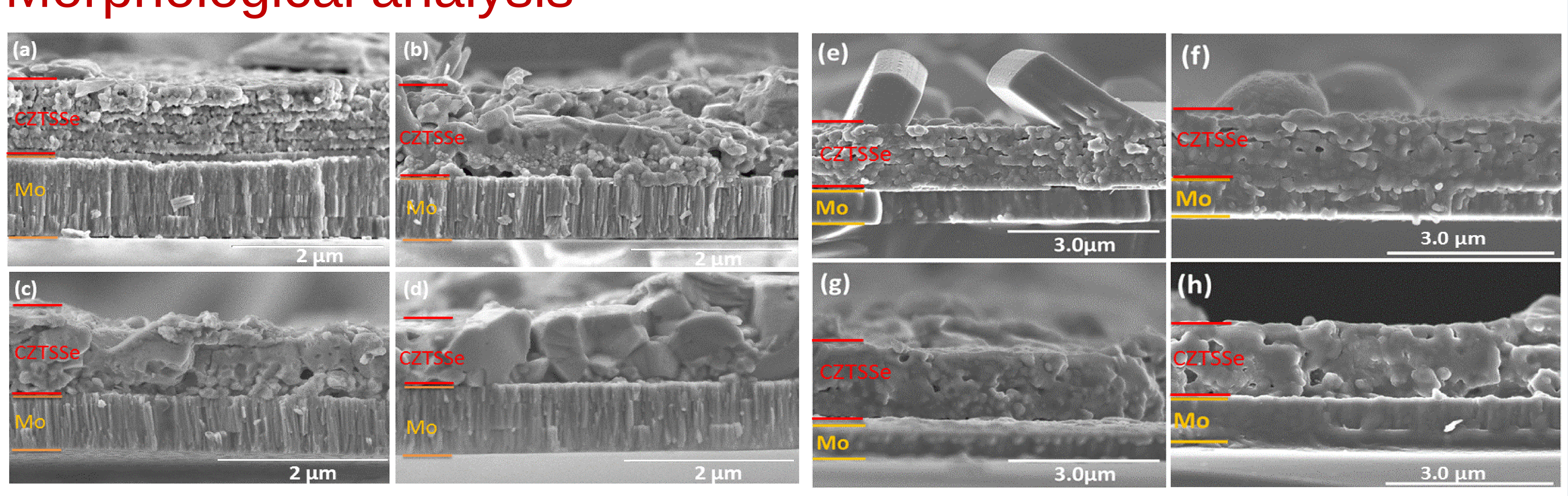

Fig.1. Cross-sectional SEM images of samples selenized in a tubular furnace (TF) and a rapid thermal processor (RTP) at various temperatures: (a) Se-TF-350, (b) Se-TF-450, (c) Se-TF-480, (d) Se-TF-500, (e) Se-RTP-400, (f) Se- RTP-450, (g) Se- RTP-500 and (h) Se- RTP-525.

- ❑ Temperature below 450 ºC is not enough for the full conversion of the precursors to CZTSSe, see Fig. (a) and (e).
- ❑ The grain size increased as the selenization temperature is increased.
- ❑ Compared to TF annealed samples, RTP annealed films are more uniform and smoother.

Table 2. Metal composition of the samples selenized using the tubular furnace (TF) at various temperatures.

Sample	[Cu]/[Zn]	[Cu]/[Sn]	[Zn]/[Sn]	[Cu]/([Zn]+[Sn])
Se-TF-350	2.66	2.31	0.87	1.24
Se-TF-400	2.03	1.9	0.93	0.98
Se-TF-450	1.34	2.02	1.51	0.81
Se-TF-480	2.04	3.5	1.71	1.29
Se-TF-500	2.27	3.23	1.42	1.33

Structural characterization

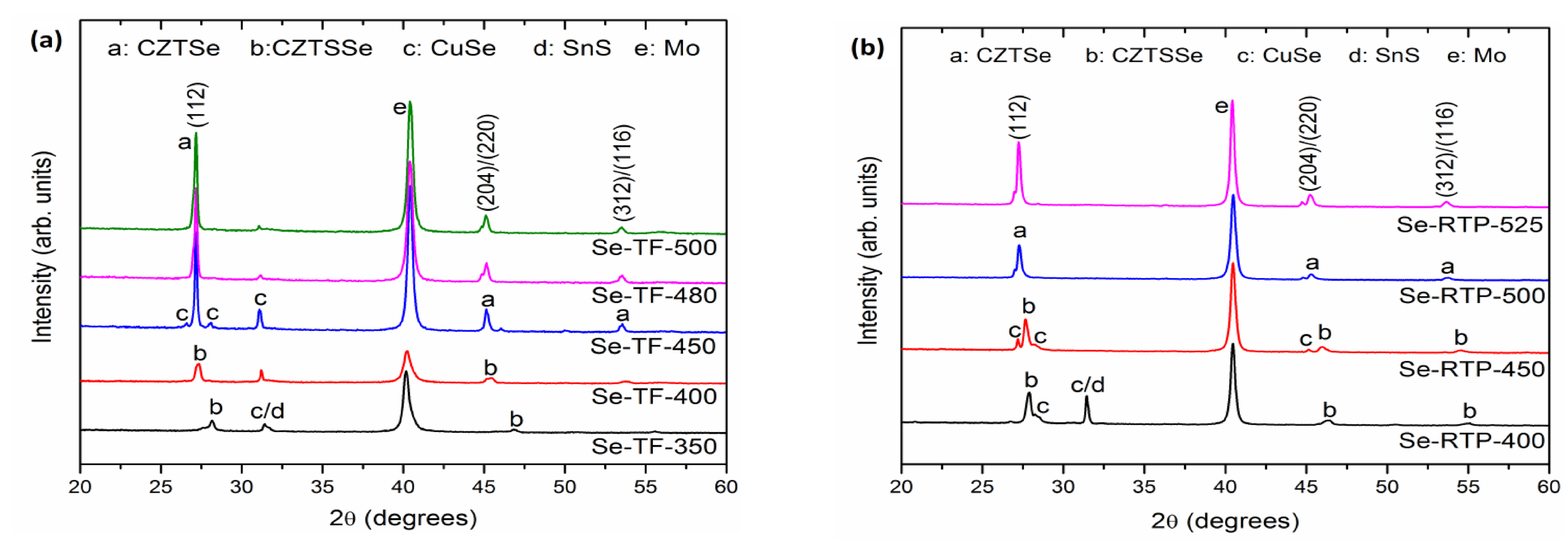

Fig.2. XRD patterns of samples selenized in (a) a TF and (b) a RTP, at various temperatures.

- ❑ Considering the amount of peak shift with respect to that of pure CZTSe, the $[S]/([S]+[Se])$ ratio is estimated.

Table 3. (112) peak position, FWHM and crystallite size of samples selenized in a TF and RTP at various temperatures.

Selenization Temperature (ºC)	(112) peak position (°)	FWHM (°)	Crystallite size (nm)	[S]/([S]+[Se])(%)
Se-TF-350	28.16	0.38	21.5	78
Se-TF-400	27.3	0.3	27.2	10
Se-TF-450	27.17	0.15	54.5	< 1
Se-TF-480	27.17	0.14	58.4	< 1
Se-TF-500	27.17	0.14	58.4	< 1
Se-RTP-400	27.87	0.28	29.6	55
Se-RTP-450	27.68	0.25	33.1	41
Se-RTP-500	27.28	0.2	41.3	9
Se-RTP-525	27.25	0.18	45.9	7

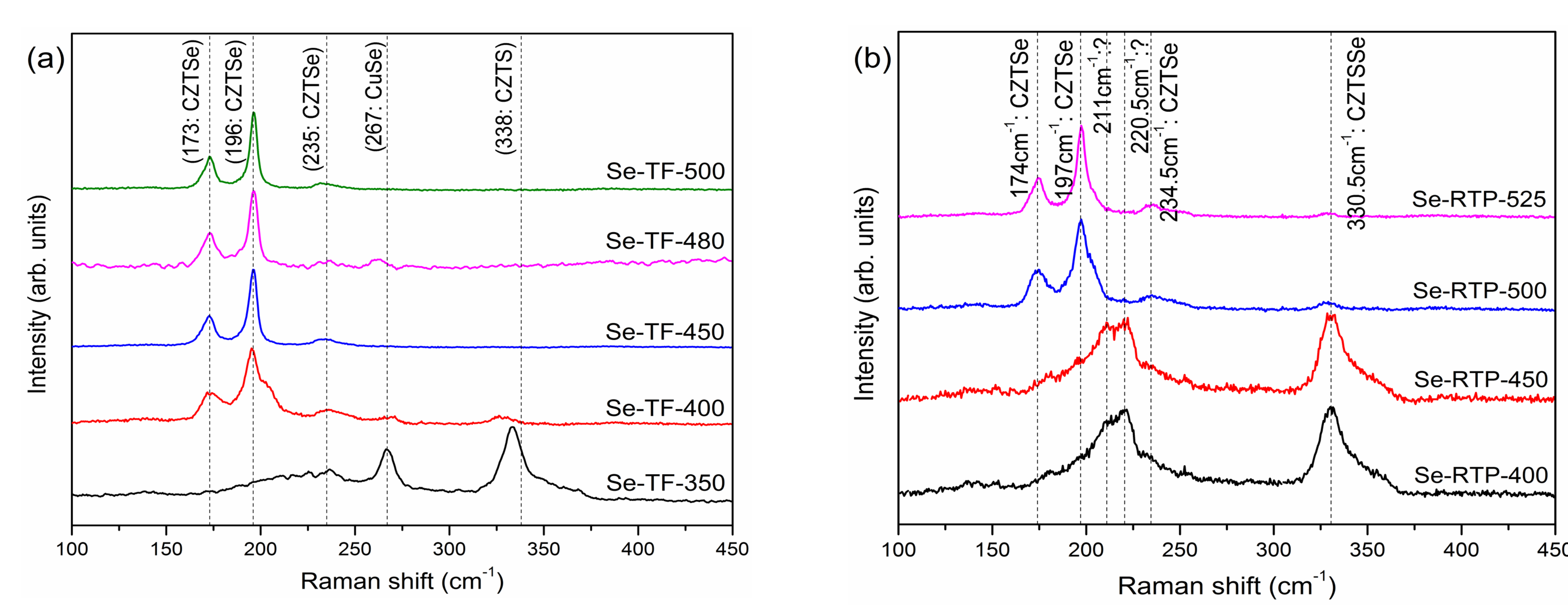

Fig.3. Raman spectra of samples selenized (a) using a TF and (b) a RTP , at various temperatures.

- ❑ The samples annealed at lower temperatures shows a bimodal behavior with peaks corresponding to A1 vibrational modes of CZTSe (196 cm^{-1}) and CZTS (338 cm^{-1}).
- ❑ The A1 mode vibrations of CZTSe are shifted to higher wavenumbers whereas that of CZTS is shifted to lower wavenumbers.
- ❑ At higher temperatures the spectra consist of only three peaks at 173, 196 and 235 cm^{-1} characteristic of CZTSe.

Conclusion

The effect of selenization temperature on the structural and morphological properties of CZTSSe thin films obtained through the selenization of $Zn/SnS_2/CuS$ precursors using a conventional tubular furnace (TF) and a rapid thermal processor (RTP) was studied. The results suggest that RTP selenization method could have some advantages over the TF in obtaining smooth, uniform and compact films of CZTSSe at much shorter selenization time, they also point to the fact that a minimum annealing temperature of 450 ºC is essential for obtaining compact films.

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