



PHD

An Investigation of Tin Chalcogenide Precursors and Thin Film Materials for Applications in Energy Harvesting Devices

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Appendix C: Supplementary Information for Chapters

A.C.1 – Supplementary Information for Chapter 2:

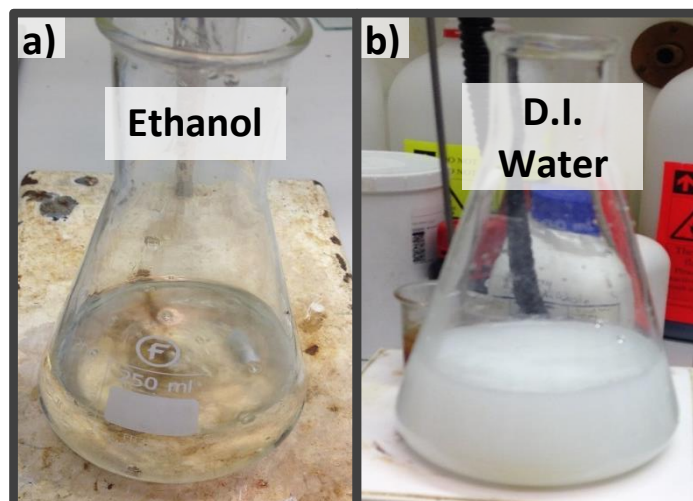


Figure C.1.1: Appearance of the resultant solutions consisting of the stannous chloride, TU, nitric acid and ammonium nitrate precursor mixtures in a) Ethanol or b) Deionised water.

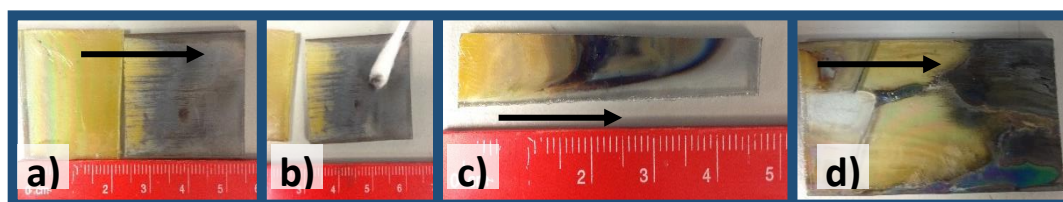


Figure C.1.2: Sections of films deposited at furnace temperature ≥ 475 °C, where there is a clear colour transition from yellow to grey (arrow represents the direction of the AACVD gas flow). Image b) shows the appearance of a cotton bud after gentle swiping of the grey film surface. This indicates the poor quality, and non-adherent properties of the powdery grey films generated in this section of these samples, which have been shown to consist of α -SnS.

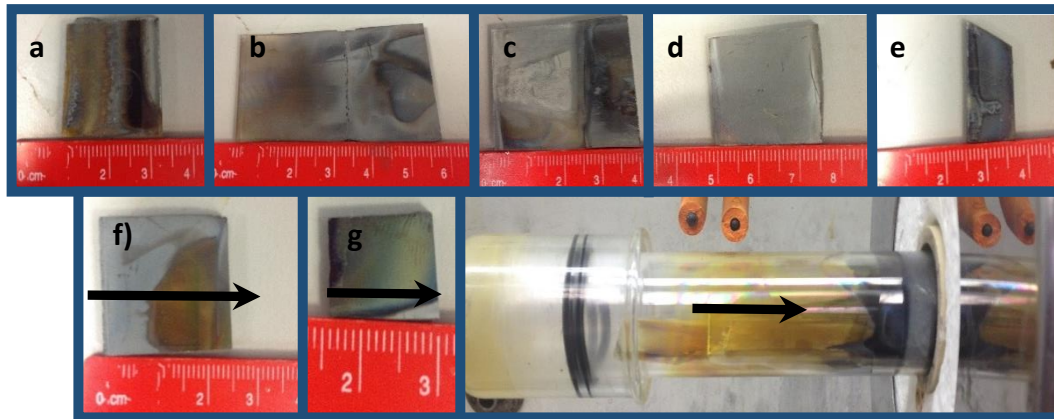


Figure C.1.3: Grey regions beyond the yellow to grey transition point further down the reactor (>10 cm). All grey film show heterogeneity in coverage, appearance and colour, with large crystallites being formed on various regions of the substrate. The films are poorly adhered to the surface. All films are a result of deposition at 475 and 575 °C using the 1 to 2 solution for 120 minutes. a) 475 °C deposition, this region was brown and grey in colour and had large grey crystallites on the surface in the central region. b) 475 °C deposition, very powdery film with regions of brown, grey and dark grey. c) 575 °C deposition, very powdery films with brown, grey and dark grey regions with variation of film coverage. d) 575 °C deposition, disperse coverage with powdery poorly adhered crystallites. e) 475 °C deposition, dark grey section with some regions of large dark grey crystals. f) 575 °C deposition, here we see a region with both a dark brown and grey films and the cause of this type of deposition maybe a result of gas flow dynamics and cooling effects during the deposition process, the brown region was smooth and adhered compared to powdery grey region. g) 475 °C deposition, shows a variation of colour from dark grey, grey, green, yellow/green and blue. h) Reactor after depositing at 575 °C, segment revealed when pull out the furnace, and presents the abrupt transition between yellow and grey material.

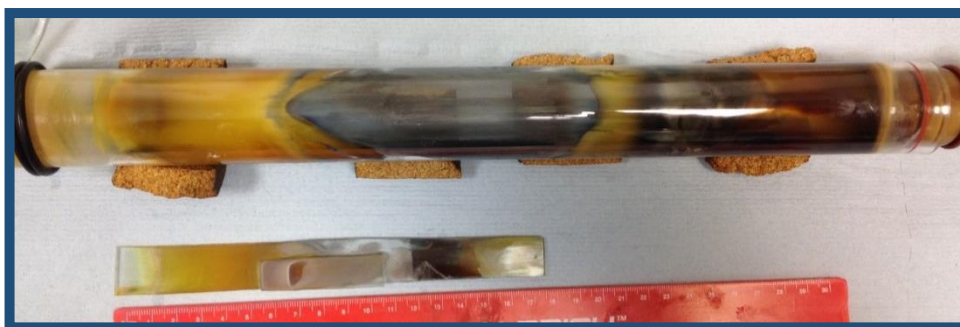


Figure C.1.4: Entire reactor colour and substrate appearance after deposition 6 (dep. 6) consisting of a 0.1 M solution with 1:2 (Sn²⁺:TU) deposited at 475°C for 120 min.

Deposition Time (min)	Deposition Temperature (°C)	Sn:S	C (at. %)	O (at. %)	
a)	10	375	1:1.86	7.08	73.67
b)	20	375	1:1.82	3.29	14.83
c)	30	375	1:1.87	11.40	5.10
d)	120	275	1:1.98	6.97	9.09
e)	120	375	1:1.92	7.29	35.33
f)	120	475	1:1.67	4.50	2.07
g)	120	575 (yellow)	1:1.72	2.54	15.23
h)	120	575 (Grey)	1:1.24	5.50	6.50
i)	CBD 7min	70°C	Cd:S = 1:0.95	15.05	10.01

EDS data for films deposited onto glass using the 1 to 2 solution.

Table C.1: Tabulated EDAX data for spectra presented in Figure C.15.

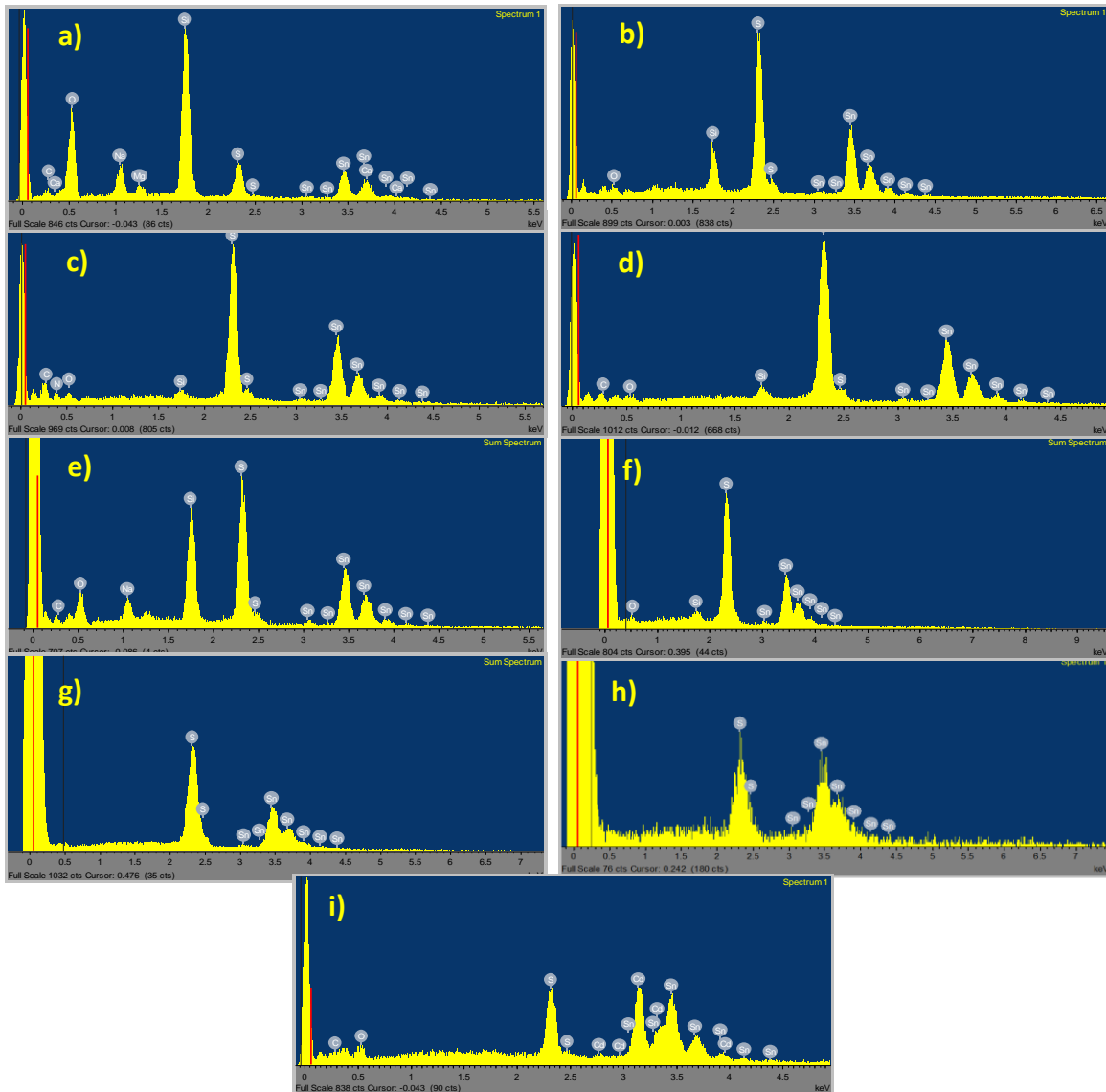


Figure C.1.5: Table of data and EDS Spectra for films deposited onto glass substrates using the 1 to 2 solution under various deposition conditions. An EDS spectra of the CdS sample deposited by CBD is also included.

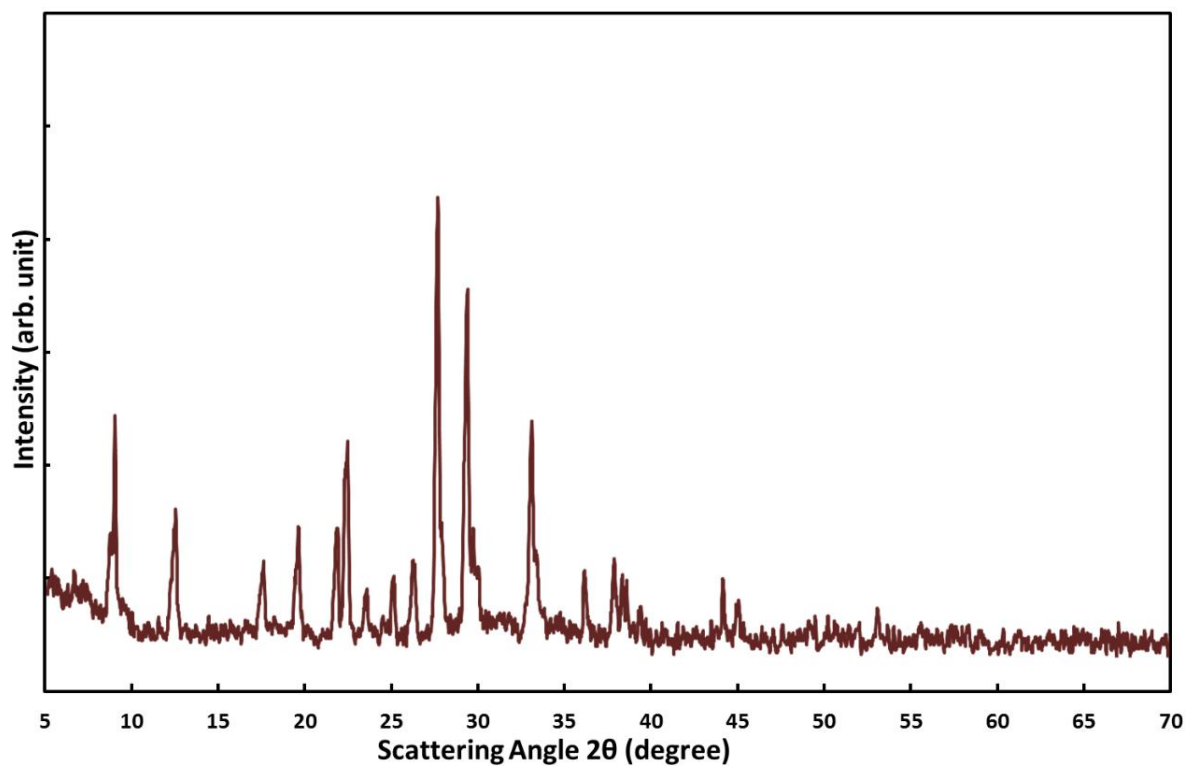


Figure C.1.6: XRD pattern of the dried yellow precipitate formed when thiourea was added to an ethanol solution of SnCl_2 , HNO_3 and NH_4NO_3 at a 1:4 (Sn:TU) ratio.

A.C.2 – Supplementary Information for Chapter 3:



Figure C.2.1: Photo of Compound 1.

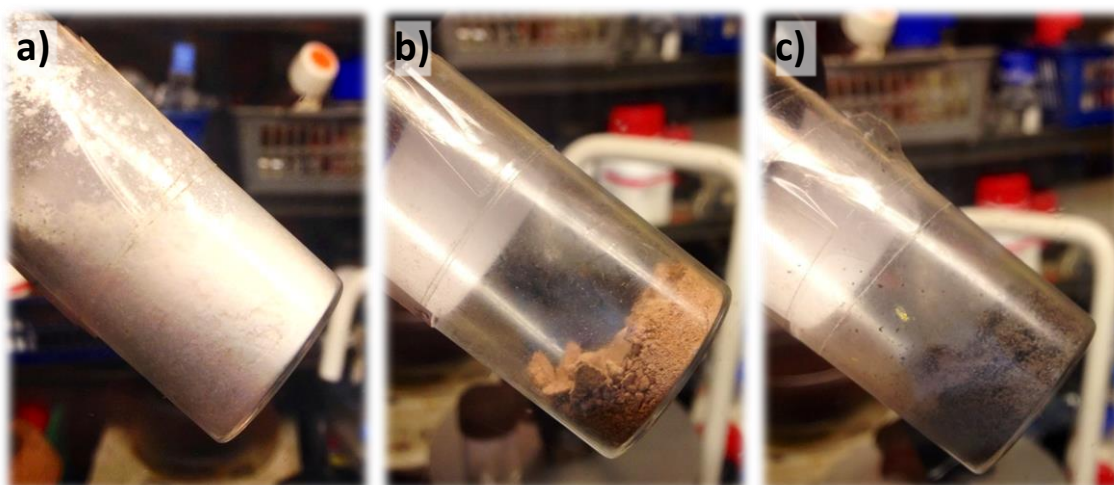


Figure C.2.2: Photo of Compound 2 when stored at RT in an argon filled glovebox. a) 1 hour, b) 2 days and c) 1 week after isolation and storage.

A.C.3 – Supplementary Information for Chapter 4:

Additional SEM Images:

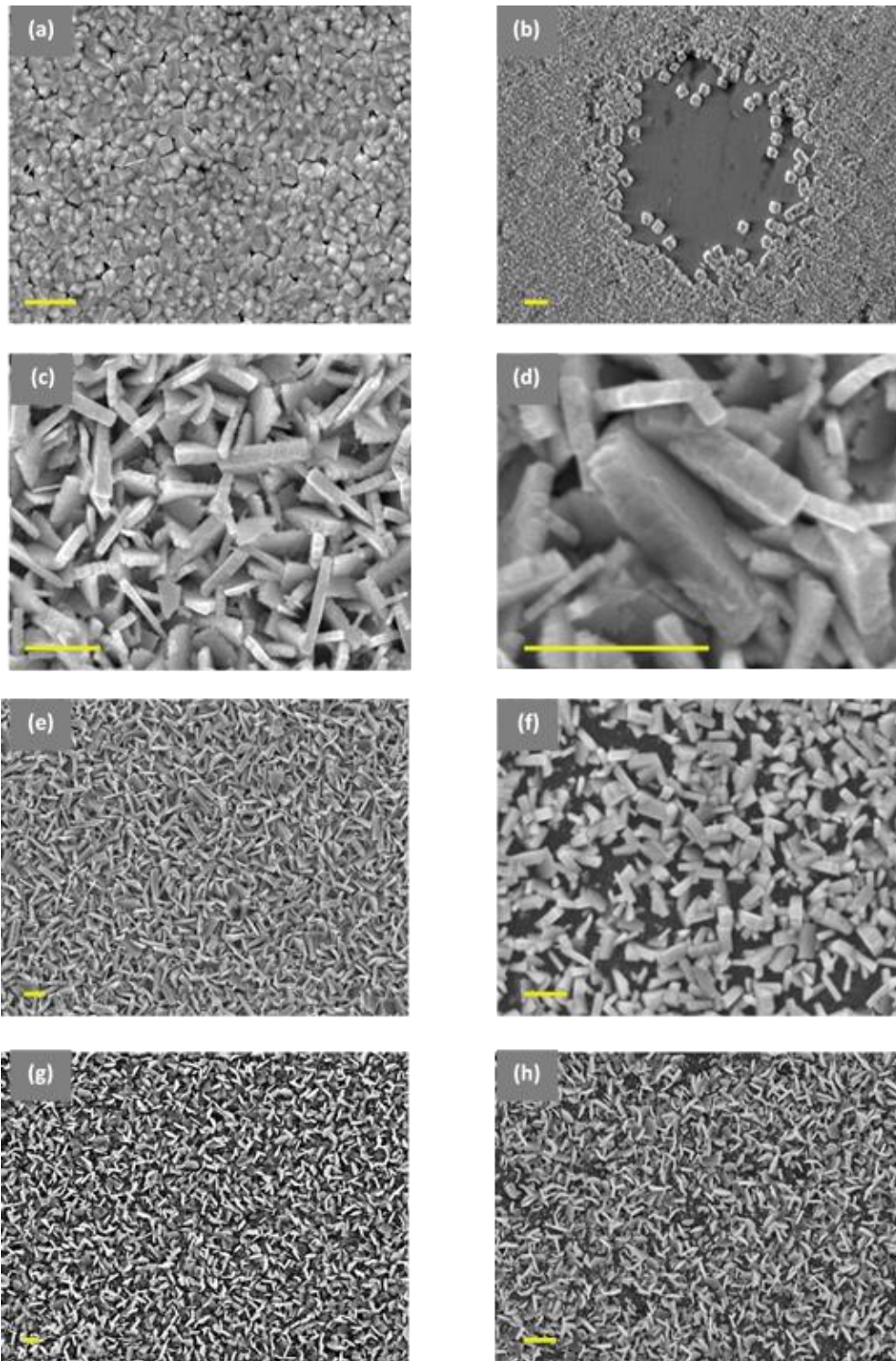


Figure C.3.1: SEM images of SnS films deposited at different temperatures onto silicon substrates. The scale bar is set for 2 μm . (a,b) Cubic-SnS deposited at 300 °C, (b) shows a scratched region of the Cubic-SnS film, (c,d,e) α -SnS films deposited at 375 °C, (f) α -SnS film deposited at 400 °C, (g) α -SnS film deposited at 450 °C and (h) α -SnS film deposited at 500 °C.

EDAX Spectra for SnS films deposited from Precursor 1

	Deposition Time (min)	Deposition Temperature (°C)	Sn:S	C (at. %)	O (at. %)
b)	40	300 (Cubic)	1:0.94	7.30	4.7
c)	40	350	1:1.00	4.13	4.5
d)	40	375	1:0.96	6.4	7.2
e)	40	400	1:0.95	4.6	3.3
f)	40	450	1:0.87	6.3	4.3

Table C.3.1: Tabulated EDAX data for spectra presented Figure C.3.2

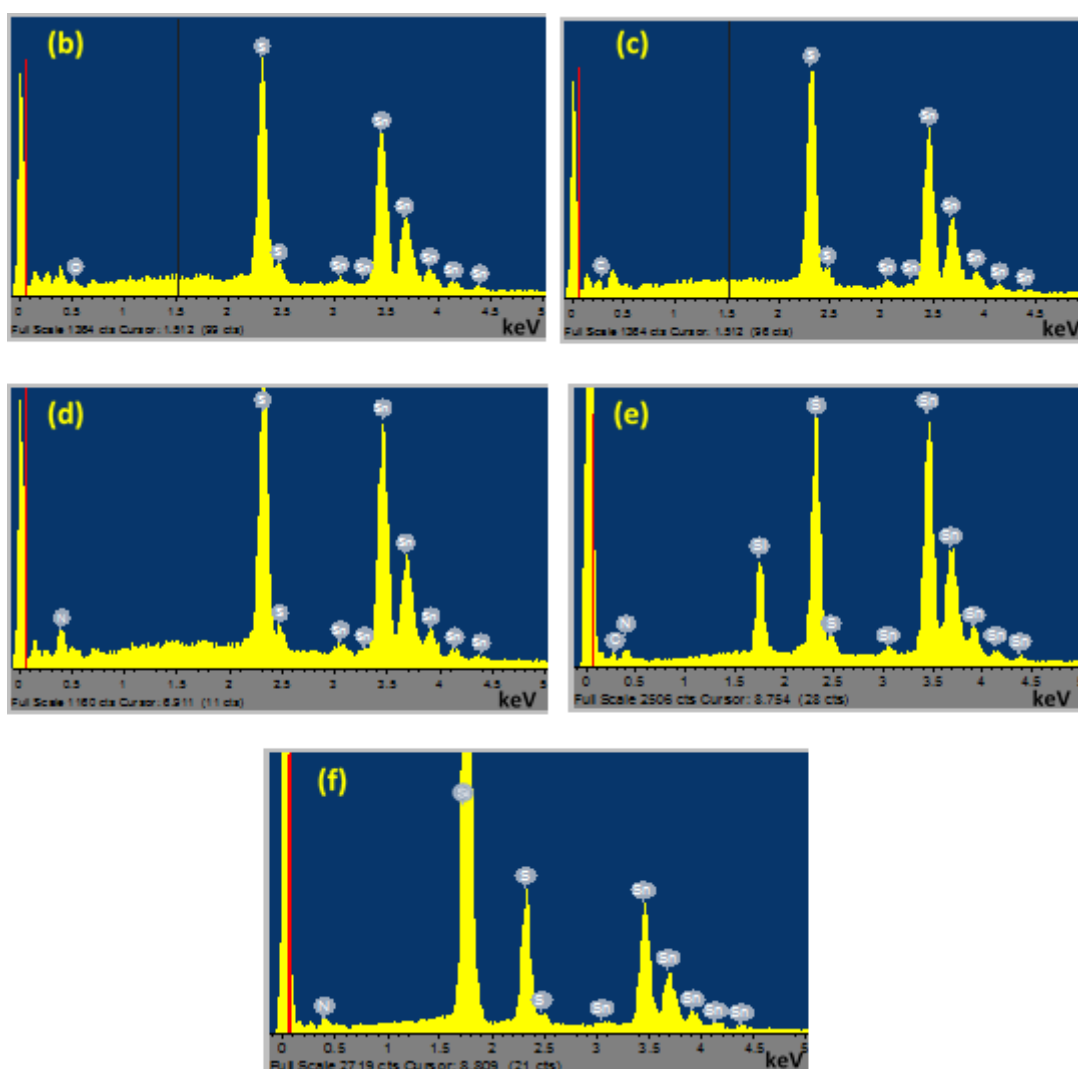


Figure C.3.2: EDAX spectra for SnS films deposited onto silicon substrates using precursor (1) at (b) 300, (c) 350, (d) 375, (e) 400 and (f) 450 °C.

EDAX Spectra for SnS films deposited from Precursor 2

	Deposition Time (min)	Deposition Temperature (°C)	Sn:S	C (at. %)	O (at. %)
b)	40	150	0.99:1	2.30	0.23
c)	40	175	1:0.97	1.23	1.45
d)	40	200	1:0.99	0.44	2.30
e)	40	250	1:0.97	3.33	2.50
f)	40	300	1:0.84	7.77	4.56

Table C.3.2: Tabulated EDAX data for spectra presented Figure C.3.3.

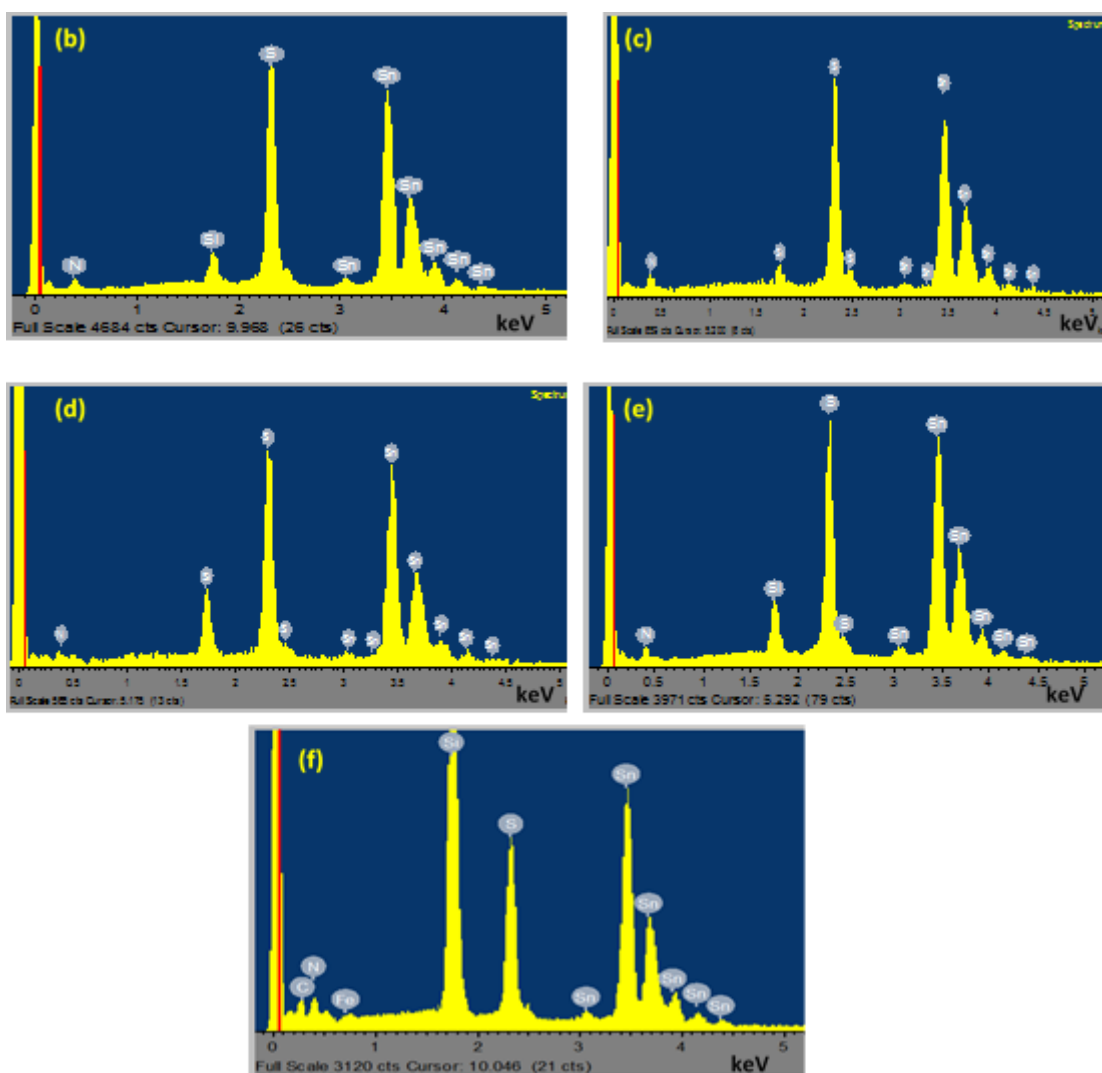


Figure C.3.3: EDAX spectra for SnS films deposited onto silicon substrates using precursor (2) at (b) 150, (c) 175, (d) 200, (e) 250 and (f) 300 °C.

EDAX Spectra for Sulphur Annealed α -SnS films deposited from Precursor 1 at 375 °C

Deposition Temperature (°C)	Anneal Time (min)	Anneal Temperature	Sn:S	C (at. %)	O (at. %)
375	40	300	1:1.5	8.88	0.45

EDAX Data for SnS films anneal in a sulphur rich atmosphere under N₂

Table C.3.3: Tabulated EDAX data for spectra presented Figure C.3.4.

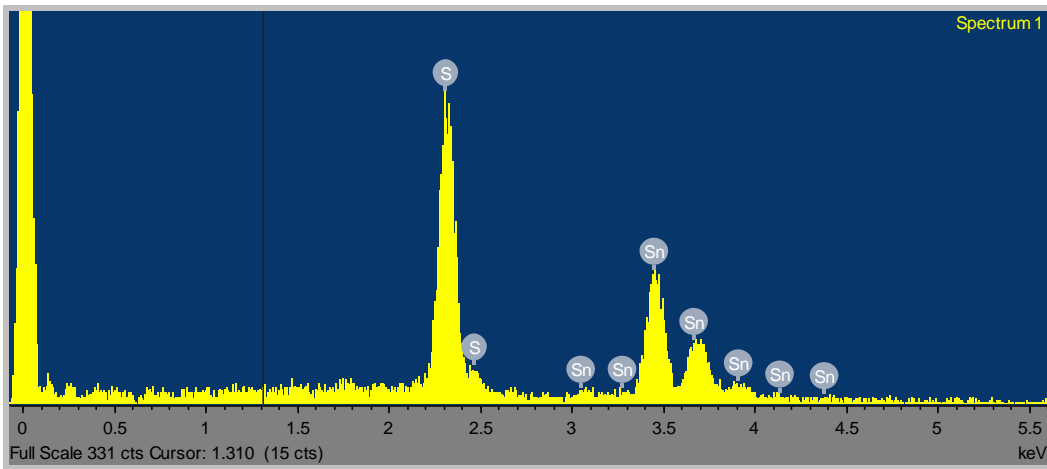


Figure C.3.4: EDAX spectra of α -SnS films after sulphur annealing for 30 min at 300 °C.

A.C.4 – Supplementary Information for Chapter 5:

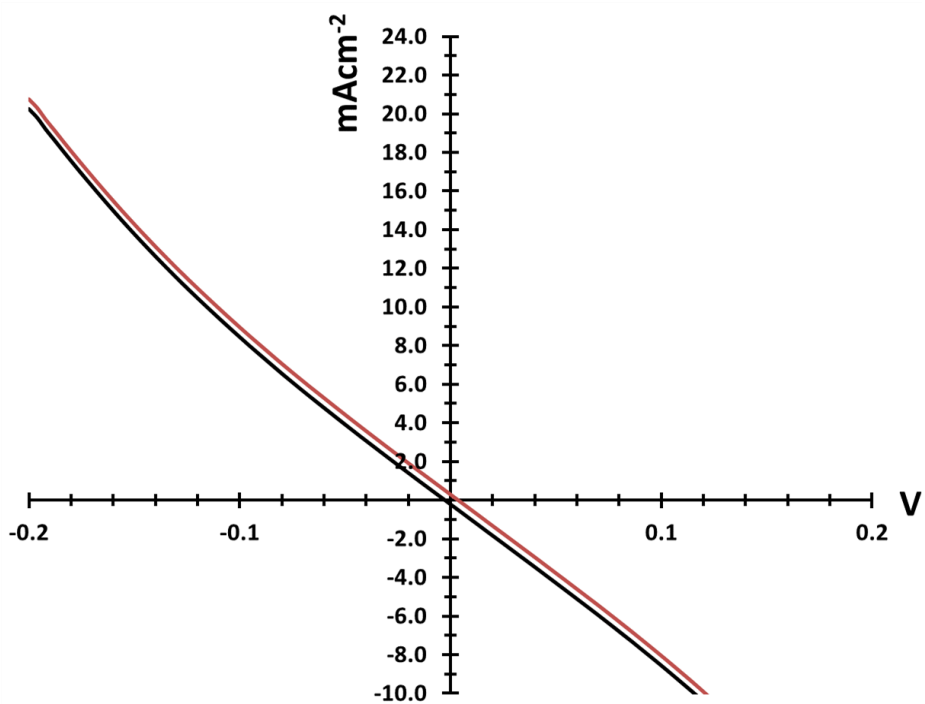


Figure C.4.1: Typical dark (Black) and illuminated (Red) J-V curves for the device with Mo/ α -SnS/Zn(O,S)/i-ZnO/ITO structure, representative of all the shunted devices using CBD Zn(O,S) as a buffer layer.

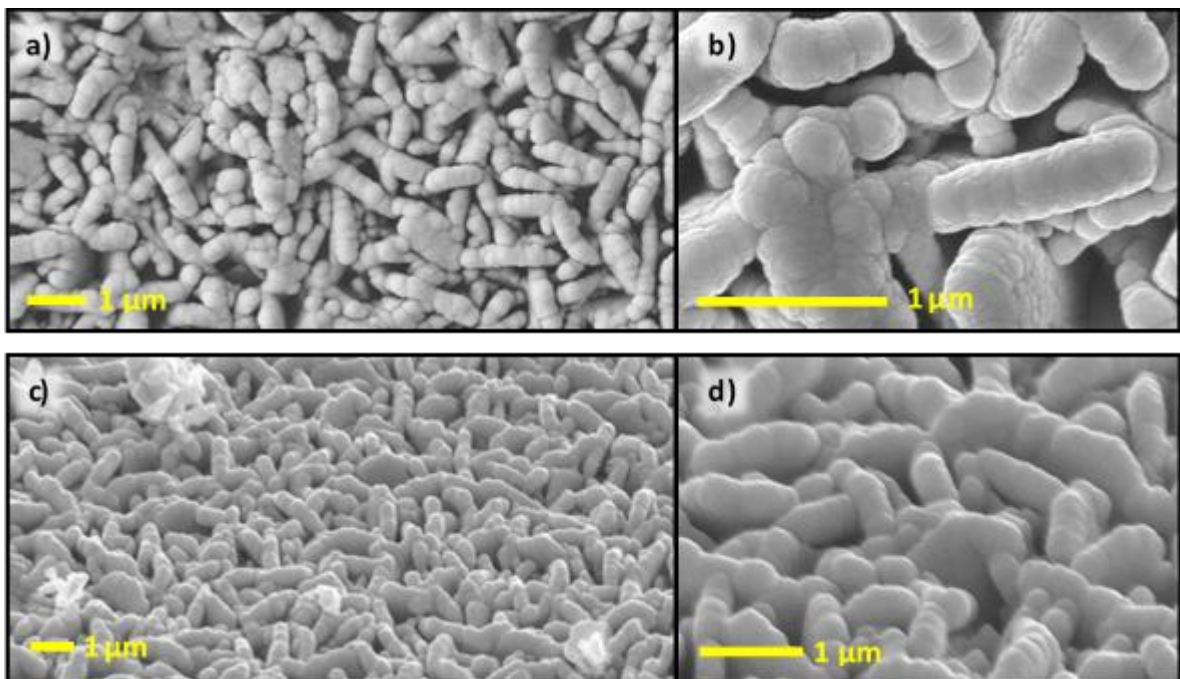


Figure C.4.2: SEM images of a device with the Mo/ α -SnS/Zn(O,S)/i-ZnO/ITO structure. a) Top down view of the ITO layer at 5 k mag and b) at 40 k mag. c) 45° viewing angle of the ITO rough surface formed by deposition onto the α -SnS crystallites at 4 k mag and d) at 20 k mag.

A.C.5 – Supplementary Information for Chapter 6:

Table C.5.1: Tabulated EDAX data for spectra presented Figures C.5.1 and C.5.2.

Temperature (Substrate)	Sn (atm %)	C (atm %)	O (atm %)	Si (atm %)
Precursor (13)				
(a) 300 °C (Silicon)	56.36	18.92	14.36	10.36
(b) 400 °C (Silicon)	44.32	22.12	20.33	13.23
Precursor (14)				
(c) 300 °C (Silicon)	27.19	10.00	7.48	55.33
(d) 400 °C (Silicon)	55.41	15.56	22.22	6.83
Sn:Se (Atomic ratio)				
Precursor (14=Se)				
(e) 400 °C (Glass)	1:0.78	4.20	60.37	17.12
(f) 400 °C (Silicon)	1:0.95	7.89	4.56	40.31
Sn:Te (Atomic ratio)				
Precursor (14=Te)				
(g) 400 °C (Silicon)	1:0.98	8.69	32.01	11.75

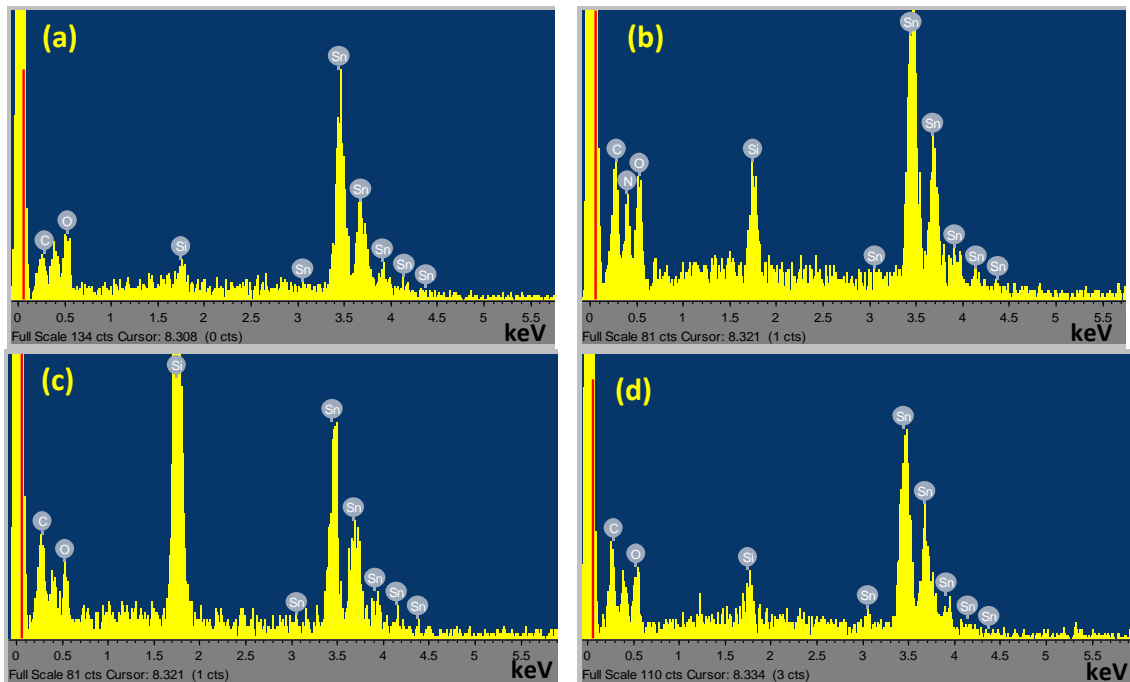


Figure C.5.1: EDAX spectra of Sn films deposited from precursor (13) at a) 300 or b) 400 °C and precursor 14 at a) 300 or b) 400 °C, with a deposition time of 40 min.

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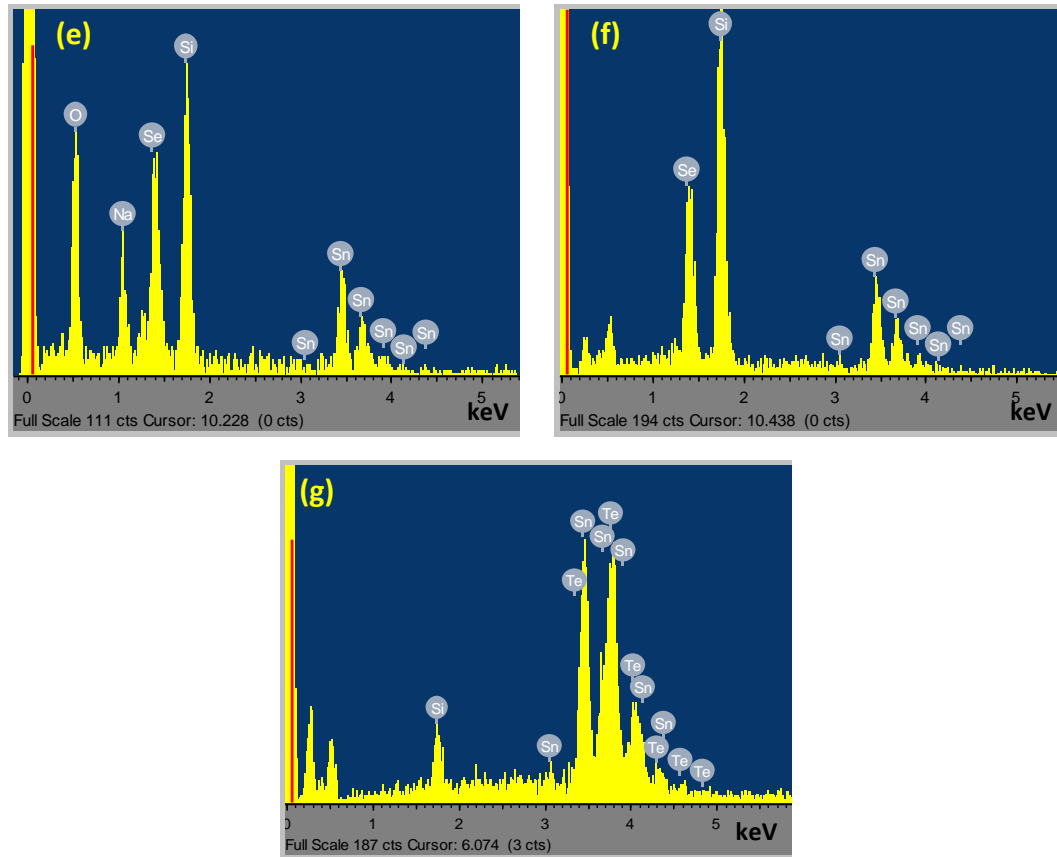


Figure C.5.2: EDAX spectra of e-f) α -SnSe or g) SnTe films deposited from precursor (14=Se) at 400 °C onto e) glass or f) silicon or from g) precursor (14=Te) at 400 °C onto silicon, with a deposition time of 40 min.