

Supporting Information

Actual partial pressure of Se vapor in a closed selenization system: quantitative estimation and impact on solution-processed, chalcogenide thin-film solar cells

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S1. Estimation of the actual partial pressure of Se vapor during selenization

1) Original model developed by Scragg.¹

When the reaction chamber is filled with nitrogen and sealed, n_N moles of nitrogen are contained in the total volume V_T . Before evaporation of Se, the number of moles of gas molecules, n_B , inside the container of volume V_B is given by:

$$n_B = n_N \frac{V_B}{V_T}$$

The number of moles of gas molecules outside the container, n_C , is given by:

$$n_C = n_N \frac{V_C}{V_T}$$

where V_C is the volume of the outside reaction chamber. Note that we conserve the total volume and number of gas molecules:

$$\begin{aligned} V_C + V_B &= V_T \\ n_C + n_B &= n_T \end{aligned}$$

After the Se has completely vaporized, the concentration of gas molecules inside the container has risen by an amount n_{Se} :

$$n'_B = n_N \frac{V_B}{V_T} + n_{Se}$$

The internal pressure is now greater than the external pressure. This causes a fraction F of the gas molecules inside the container to move out, after which the pressures are equal. Then, we have:

$$n_{B,eq} = (1 - F) \left(n_N \frac{V_B}{V_T} + n_{Se} \right)$$

and

$$n_{C,eq} = n_N \frac{V_C}{V_T} + F \left(n_N \frac{V_B}{V_T} + n_{Se} \right)$$

Now, writing the internal and external pressures after equilibration explicitly, and making them equal, we have:

$$P_B = RT \left(1 - F \right) \left(\frac{n_N}{V_T} + \frac{n_{Se}}{V_B} \right) = P_C = RT \left(\frac{n_N}{V_T} + F \left(\frac{n_N V_B}{V_T V_C} + \frac{n_{Se}}{V_C} \right) \right)$$

where R is the gas constant (8.314 J mol K⁻¹) and T is the selenization temperature. Rearranging for F and making the following substitutions of

$$P_{\text{Se,B}} = n_{\text{Se}} \frac{RT}{V_{\text{B}}}$$

which is the partial pressure of Se inside the container if all of the Se had remained inside it, and

$$P_{\text{N}} = n_{\text{N}} \frac{RT}{V_{\text{T}}} = P_{\text{N,RT}} \frac{T}{303}$$

where P_{N} is the background pressure of nitrogen at the selenization temperature and $P_{\text{N,RT}}$ is the P_{N} at room temperature; we then obtain

$$F = \frac{P_{\text{Se,B}}}{\left(\frac{V_{\text{B}}}{V_{\text{C}}} + 1\right) (P_{\text{Se,B}} + P_{\text{N}})}$$

We can now calculate the actual partial pressure of Se inside the container after equilibration, $P_{\text{Se,eqm}}$:

$$\frac{P_{\text{Se,eqm}}}{P_{\text{Se,B}}} = (1 - F) = \frac{P_{\text{N}} + \frac{P_{\text{Se,B}} V_{\text{B}}}{V_{\text{T}}}}{P_{\text{N}} + P_{\text{Se,B}}}$$

2) A new model modified by the authors

The authors modified the original model, focusing on the following two points. First, the original model did not consider the pressure exerted by the lid of the graphite box, which will definitely suppress the escape of the internal Se. Thus, the original equilibration equation of $P_{\text{B}} = P_{\text{C}}$ should be modified to

$$P_{\text{B}} = P_{\text{C}} + P_{\text{L}},$$

where P_{L} is the pressure originating from the weight of the lid.

The second issue is that, in actuality, some of Se vapor condenses on the wall of the outside chamber because the wall is water-cooled during the whole selenization process due to safety concerns. This will decrease P_{C} . The authors did observe a non-negligible quantity of solid Se condensed on the cold chamber wall after the selenization process. This is treated numerically by introducing an additional constant for the condensation ratio (C), determining what portion of the gas molecules in the outside chamber re-condense at the cold wall. In this case, we have:

$$n_{\text{B,eq}} = (1 - F) \left(n_{\text{N}} \frac{V_{\text{B}}}{V_{\text{T}}} + n_{\text{Se}} \right)$$

and

$$n_{\text{C,eq}} = (1 - C) \left(n_{\text{N}} \frac{V_{\text{C}}}{V_{\text{T}}} + F \left(n_{\text{N}} \frac{V_{\text{B}}}{V_{\text{T}}} + n_{\text{Se}} \right) \right)$$

Because nitrogen molecules do not “condense” at the cold wall, a pressure drop corresponding to the nitrogen gas occurs due to the temperature drop at the wall. However, to avoid this complexity in deriving equations, we treated both the Se and nitrogen molecules as “condensing” at the cold wall, resulting in a pressure drop of the outside chamber.

Now, we can write the equations for the pressures inside and outside the graphite container as,

$$P_B = RT (1 - F) \left(\frac{n_N}{V_T} + \frac{n_{Se}}{V_B} \right)$$

and

$$P_C = RT(1 - C) \left(\frac{n_N}{V_T} + F \left(\frac{n_N V_B}{V_T V_C} + \frac{n_{Se}}{V_C} \right) \right)$$

Because $P_B = P_C + P_L$,

$$RT(1 - F) \left(\frac{n_N}{V_T} + \frac{n_{Se}}{V_B} \right) = RT(1 - C) \left(\frac{n_N}{V_T} + F \left(\frac{n_N V_B}{V_T V_C} + \frac{n_{Se}}{V_C} \right) \right) + P_L$$

Arranging the above equation using the relation of $P_{Se,B} = n_{Se} \frac{RT}{V_B}$ and $P_N = n_N \frac{RT}{V_T} = P_{N,RT} \frac{T}{303}$ yields

$$F = \frac{P_{Se,B} + C \cdot P_N - P_L}{(P_N + P_{Se,B}) \left((1 - C) \frac{V_B}{V_C} + 1 \right)}$$

Again, we can now calculate the actual partial pressure of Se inside the container after equilibration, $P_{Se,eqm}$, using F derived above:

$$\frac{P_{Se,eqm}}{P_{Se,B}} = (1 - F)$$

S2. Comparison between the original model and the modified model

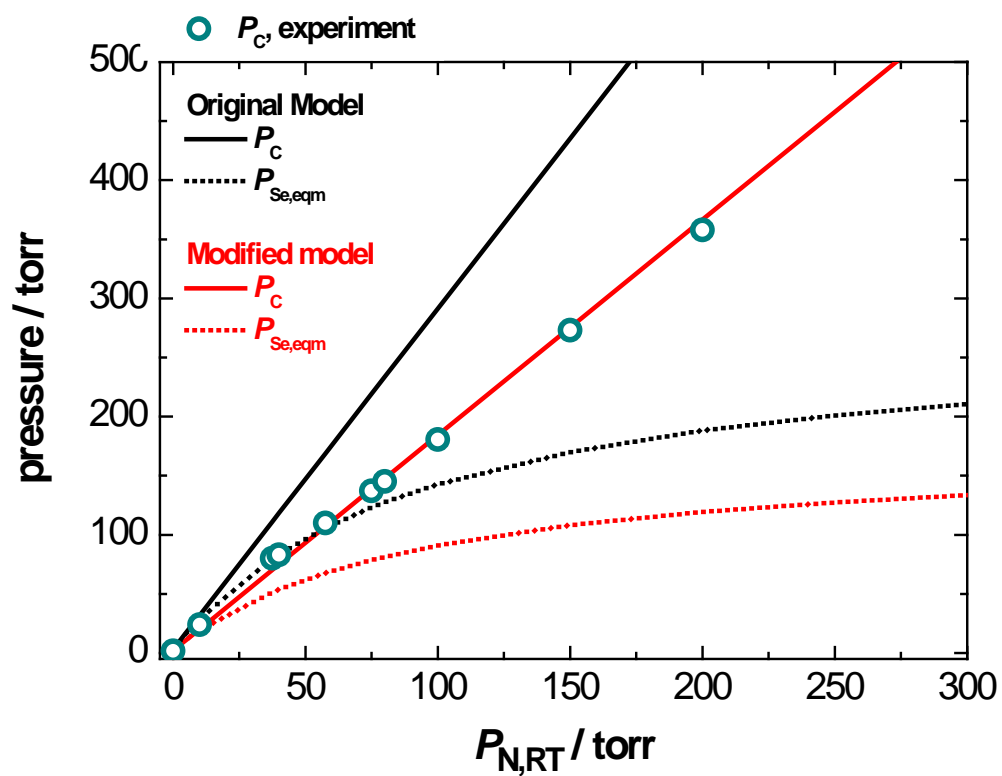


Fig. S2. P_C and $P_{Se,eqm}$ values, as function of $P_{N,RT}$, estimated from the original model (black) and the modified model (red). Experimentally measured P_C was presented as a green dots. The initial Se amount was fixed at 0.2 g and the selenization temperature was 600 °C

S3. Actual partial pressure of Se vapor ($P_{\text{Se,eqm}}$) vs. the initial Se amount

Table S3. Actual partial pressure of Se vapor ($P_{\text{Se,eqm}}$) as a function of the initial Se amount at various background pressures. The unit of $P_{\text{Se,eqm}}$ is torr.

		Se amount / g			
		0.05	0.1	0.15	0.2
$P_{\text{N,RT}} /$ torr	4×10^{-3}	1.71	2.22	2.73	3.24
	0.4	2.35	2.88	3.39	3.90
	4	7.39	8.39	9.09	9.69
	10	14.08	16.92	18.40	19.44
	40	28.01	41.01	48.65	53.78
	100	35.66	59.91	77.52	90.94
	400	41.43	78.47	111.70	141.93

S4. Actual partial pressure of Se vapor ($P_{\text{Se,eqm}}$) vs. the background pressure at room temperature

Table S4. Actual partial pressure of Se vapor ($P_{\text{Se,eqm}}$) as a function of the background pressure at room temperature ($P_{\text{N,RT}}$) with different initial amounts of Se. The unit of $P_{\text{Se,eqm}}$ is torr.

		Background pressure at RT ($P_{\text{N,RT}}$) / torr									
		4×10^{-3}	0.04	0.4	4	40	80	100	150	200	400
Se amount / g	0.1	2.22	2.28	2.87	8.39	41.01	55.57	59.91	66.91	71.08	78.47
	0.2	3.24	3.29	3.90	9.69	53.78	81.37	90.94	108.07	119.42	141.94
	0.3	4.26	4.32	4.92	10.80	60.41	96/54	110.16	136.12	154.54	194.39

S5. XRD data for the films selenized with different amounts of Se

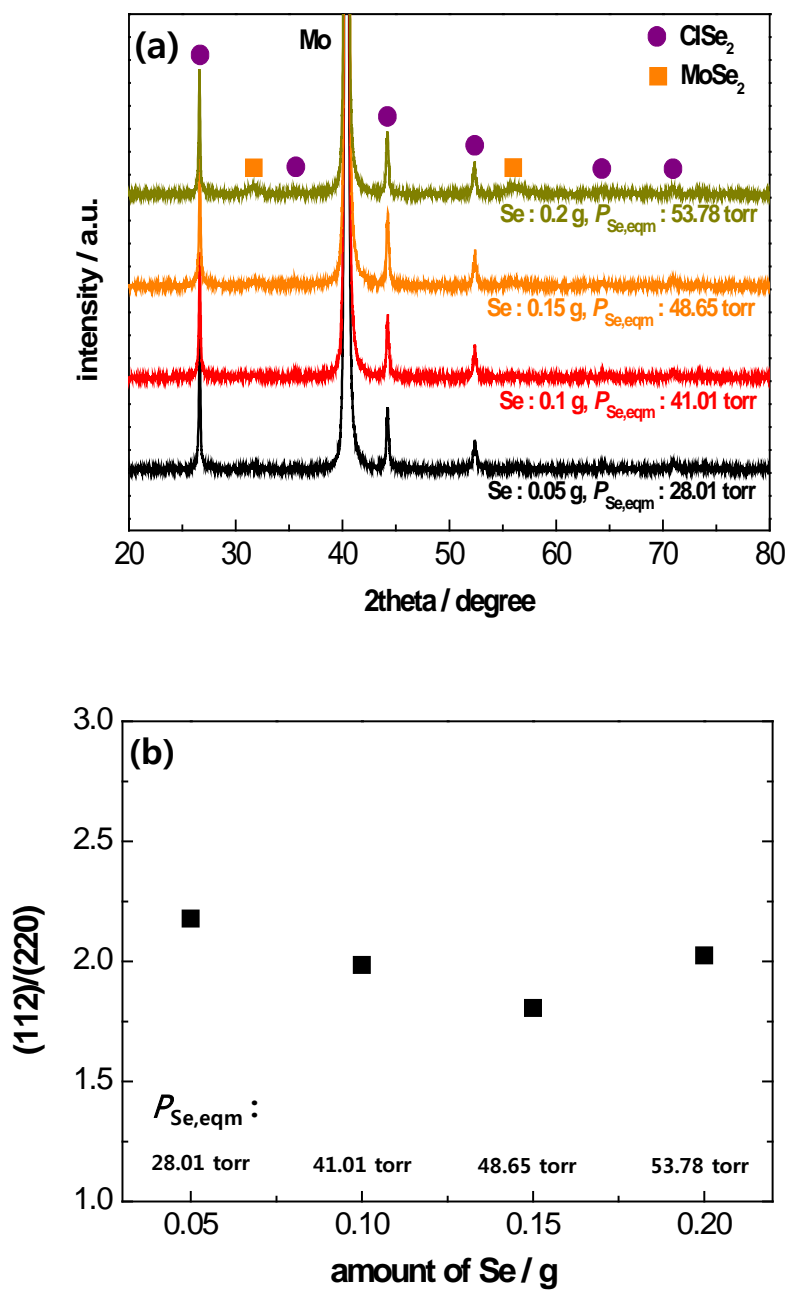


Fig. S5. (a) XRD patterns of the films selenized with different amounts Se, and (b) the intensity ratio of the (112) and (220) peaks. $P_{\text{N,RT}}$ was 40 torr for all cases.

S6. Comparison of the effects of $P_{Se,eqm}$, resulted from different combination of the Se amount and $P_{N,RT}$, on the film and device properties

Table S6. The amount of Se, $P_{N,RT}$ and resulting $P_{Se,eqm}$ values for the case A and B.

	A	B
amount of Se / g	0.2	0.08
$P_{N,RT}$ / torr	40	400
$P_{Se,eqm}$ / torr	53.8	60.0

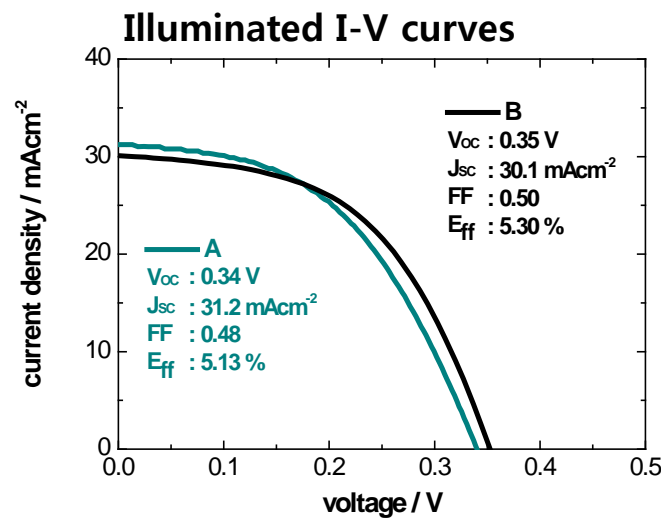
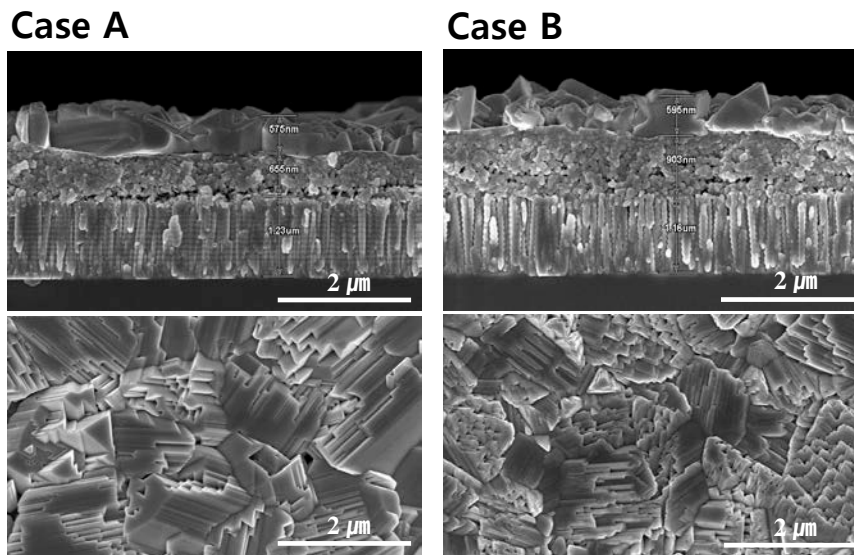


Fig. S6. SEM images of the selenized films and light illuminated I-V curves of the devices for Case A and B.

S7. Diode parameters and parasitic resistances vs. the amount of Se

Table S7. Detailed diode parameters and parasitic resistances extracted from devices built with CISE thin films selenized with different amounts of Se. $P_{N,RT}$ was 40 torr for all cases.

	Se amount / g			
	0.05	0.1	0.15	0.2
$J_0 / \text{mA cm}^{-2}$	0.033	0.048	0.118	0.085
$R_{SH} / \Omega \text{ cm}^2$	407.1	391.7	196.4	268.8
$R_S / \Omega \text{ cm}^2$	1.68	1.62	1.70	1.38
$K / \text{mA cm}^{-2} \text{ V}^{-m}$	3.092	3.375	5.416	4.258
m	3.144	3.276	3.157	3.310
A	1.60	1.65	1.96	1.74

S8. XRD data for the films selenized under different background pressures

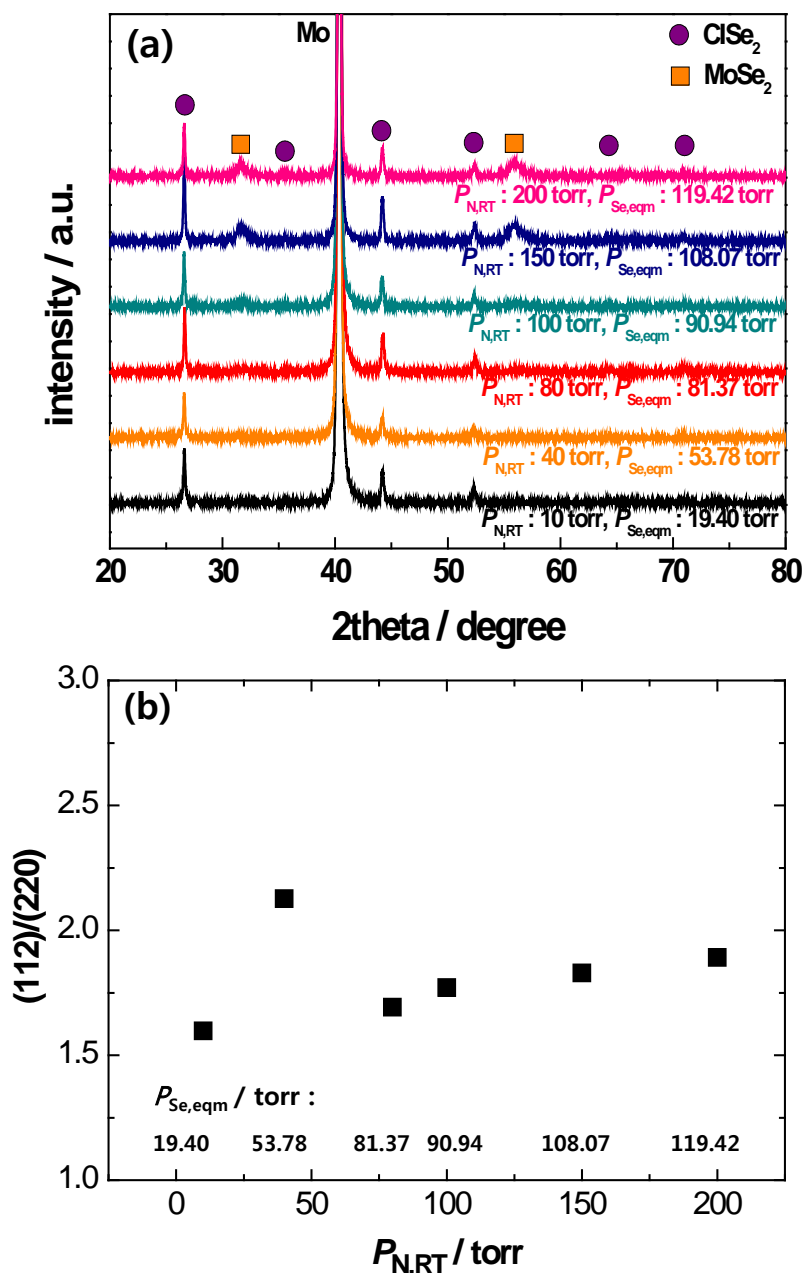


Fig. S8. (a) XRD patterns of the films selenized under different $P_{\text{N,RT}}$, and (b) the intensity ratio of the (112) and (220) peaks. Initial Se amount of 0.2 g for all cases.

S9. Diode parameters and parasitic resistances vs. background pressure

Table S9. Detailed diode parameters and parasitic resistances extracted from devices built with CISE thin films selenized under different background pressures. Initial Se amount of 0.2 g for all cases.

	Background pressure at room temp. ($P_{N,RT}$) / torr					
	10	40	80	100	150	200
j_0 / mA cm ⁻²	0.098	0.048	0.065	0.061	0.096	0.094
R_{SH} / Ω cm ²	101.6	188.7	251.0	261.0	162.3	161.2
R_S / Ω cm ²	0.721	0.553	0.794	0.962	0.963	1.12
K / mA cm ⁻² V ^{-m}	13.37	5.26	4.82	5.61	11.2	7.98
m	2.79	3.12	3.09	3.13	2.97	3.19
A	1.93	1.93	1.97	1.89	1.91	2.05

S10. Dependence of the shunt current density and $1/FF$ on the Se partial pressure

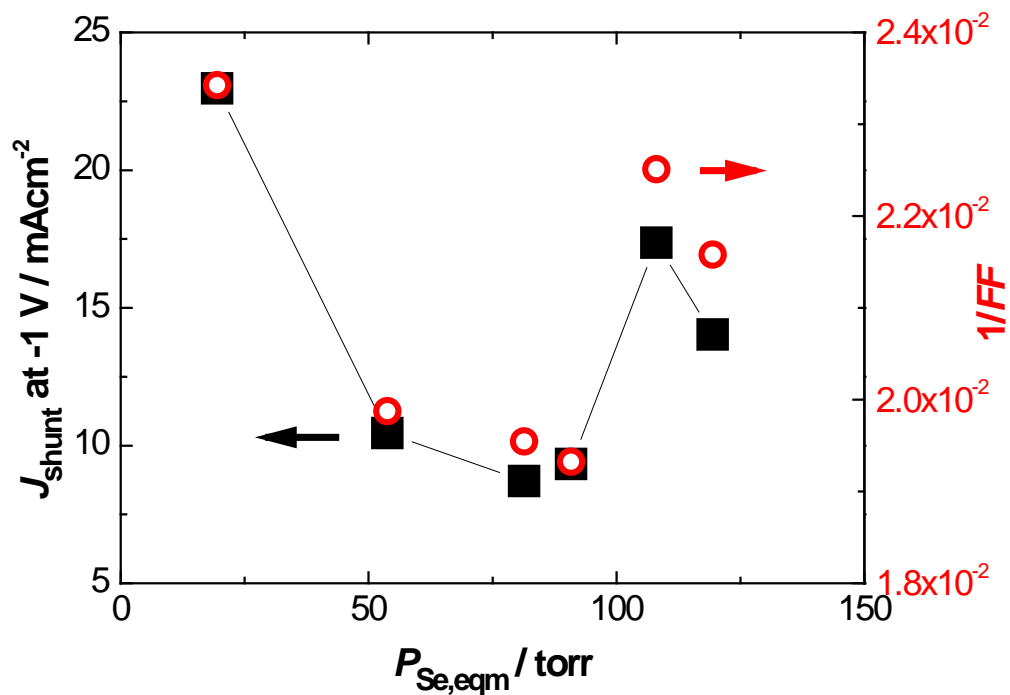


Fig. S10. Variation of the shunt current density and $1/FF$ as a function of the Se partial pressure. Shunt current densities were measured at -1 V in dark I-V curves.

References

1. J.J. Scragg, Studies of $\text{Cu}_2\text{ZnSnS}_4$ films prepared by sulfurisation of electrodeposited precursors, Ph.D. thesis, University of Bath, Department of Chemistry, Bath, 2010.