Supplementary Material (ESI) for Chemical Science

The Chemical Vapor Deposition of Cu_2ZnSnS_4 Thin Films

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Supporting Information

Experimental

All preparations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All reagents were purchased from Sigma-Aldrich chemical company and used as received. Solvents were distilled prior to use. Elemental analysis was performed by the University of Manchester micro-analytical laboratory. TGA measurements were carried out by a Seiko SSC/S200 model under a heating rate of 10 ^{o}C min^{-1} under nitrogen. Melting point was recorded on a Stuart melting point apparatus and uncorrected.

Deposition of films by AACVD

In a typical deposition, various stoichimetries of the precursors were dissolved in 10 mL of toluene in a two-necked 100 ml round-bottom flask with a gas inlet that allowed the carrier gas (argon) to pass into the solution to aid the transport of the aerosol. This flask was connected to the reactor tube by a piece of reinforced tubing. The argon flow rate was controlled by a Platon flow gauge. Seven glass substrates (approx. 2 x 2 cm) were placed inside the reactor tube, which is placed in a CARBOLITE furnace. The precursor solution in a round-bottom flask was kept in a water bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (Model No. 1077). The aerosol droplets of the precursor thus generated were transferred into the hot wall zone of the reactor by carrier gas. Both the solvent and the precursor were evaporated and the precursor vapor reached the heated substrate surface where thermally induced reactions and film deposition took place.

Characterization of thin films

UV/Vis spectra were measured using a Helios-Beta Thermospectronic spectrophotometer. Measurements were made with a plain quartz substrate in the reference beam. Standardization was done by first replacing the coated substrate with a plain substrate in

the sample position. X-ray diffraction studies were performed on a Philips X'PERT diffractometer using Cu-Kα radiation. The samples were mounted flat and scanned between 10 to 80° in a step size of 0.05 with a count rate of 9 sec. Films were carbon coated using Edward's E306A coating system before carrying out SEM and EDAX analyses. SEM analysis was performed using a Philips XL 30FEG and EDAX was carried out using a DX4 instrument. TEM was carried out on Tecnai.

Synthesis of $[Cu(S_2CNEt_2)_2]$ (1)

Sodium salt of diethyldithiocarbamate (3 g, 1.3 mmol) was dissoloved in 50 mL of methanol in double neck 250 mL RB. Slow addition of methanolic solution of $Cu(NO_3)_2$ (1.24 g, 0.65 mmol) gave black precipitate. Precipitate formed was isolated by filtration. Recrystallisation was performed using chloroform. Yield: 4.78g (73%), Mpt: 201 °C, IR (ν_{max}/cm^{-1}): 2979(w), 2868(w), 1501(s), 1434(m), 1270(s), 1205(m) and 1144(m), Elemental analysis: Calc. for $C_{10}H_{20}N_2S_4Cu$: C, 33.4; H, 5.5; N, 7.7; S, 35.6; Cu, 17.6 %. Found: C, 33.2; H, 5.3; N, 7.3; S, 35.2; Cu, 17.2 %.

Synthesis of $[Zn(S_2CNEt_2)_2]$ (2)

Complex (**2**) was synthesised by method described for complex (**1**) using zinc acetate (1.46 g, 0.65 mmol), The crude product was obtained as white powder. Recrystallisation from chloroform and yielded colourless crystals. yield 4.81 g (79%), Mpt: 181 °C, IR (ν_{max}/cm^{-1}): 2967(w), 2938(w), 1499(s), 1427(m), 1352(w), 1296(w), 1296(m), 1270(s), 1200(s) and 1143(s), Elemental analysis: Calc. for $C_{10}H_{20}N_2S_4Zn$: C, 33.1; H, 5.5; N, 7.7; S, 35.4; Zn, 18.1 %. Found: C, 32.7; H, 5.3; N, 7.4; S, 35.0; Zn, 18.0 %.

Synthesis of $[Sn(C_4H_9)_2(S_2N(C_2H_5)_2)_2]$ (3)

Complex (**3**) was synthesised by method described for complex (**1**) using di-*n*-butyltin dichloride (2.02 g. 0.65 mmol). The methanol was removed by vacuum distillation. Recrystallisation using ethanol-chloroform yielded colourless plates of crystals. White solid, yield 5.5 g, (67%), Mpt: 57 °C, IR (ν_{max}/cm^{-1}): 2953(w), 2924(w), 1483(s), 1456(m), 1417(s), 1353(m), 1298(m) 1253(s), 1205(s) and 1138(s), Elemental analysis: Calc. for $C_{18}H_{38}N_2S_4Sn$: C, 40.8; H, 7.2; N, 5.3; S, 24.2; Sn, 22.4 %. Found: C, 39.9; H, 7.5; N, 5.1; S, 22.8; Sn, 21.4 %.

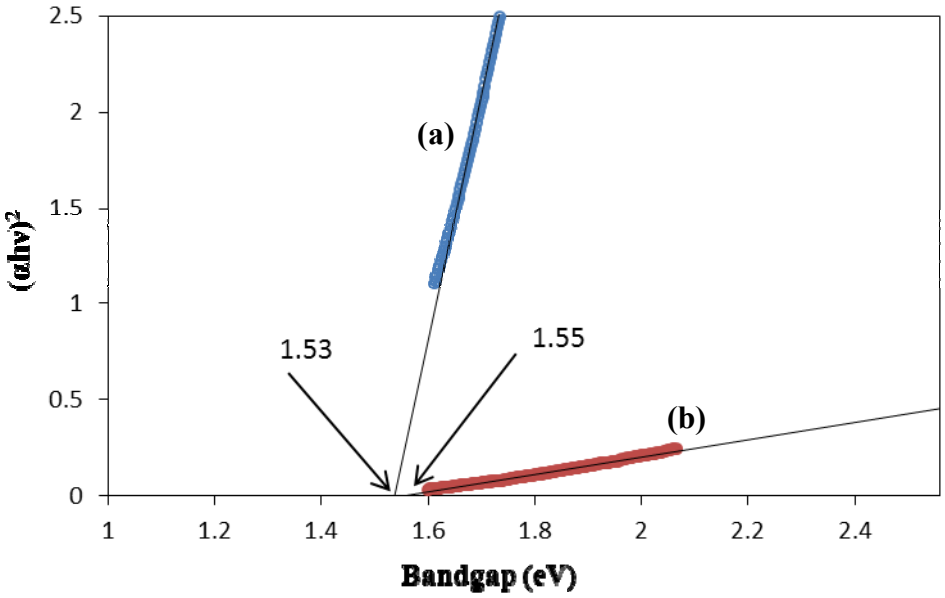

Figure S1. Optical spectra of Cu_2ZnSnS_4 films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1 at a) 400 ºC, b) 440 ºC.

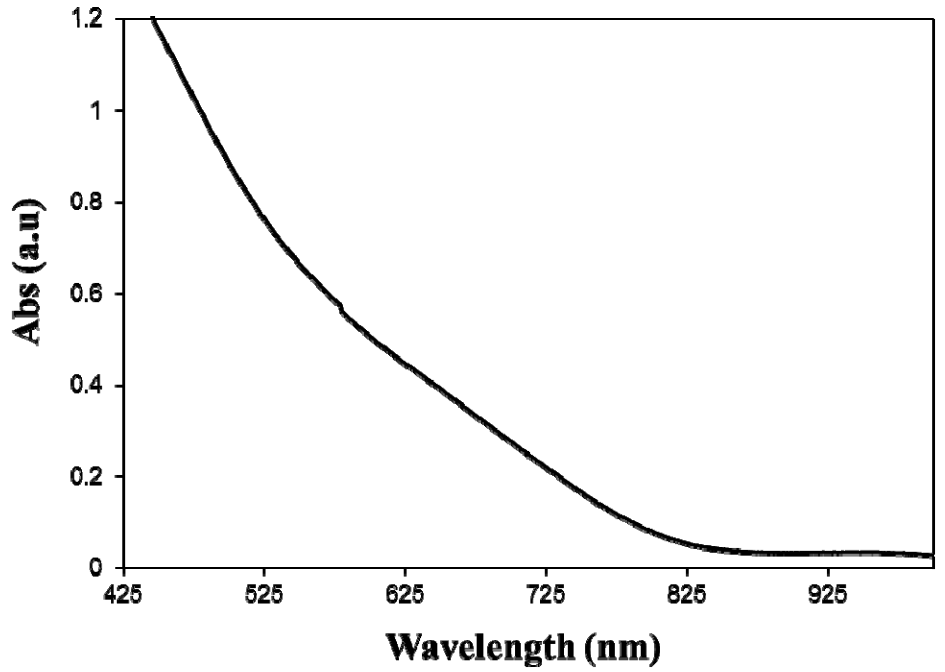

Figure S2.Typical raw UV-Vis spectra of Cu_2ZnSnS_4 films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1 at 400 ºC

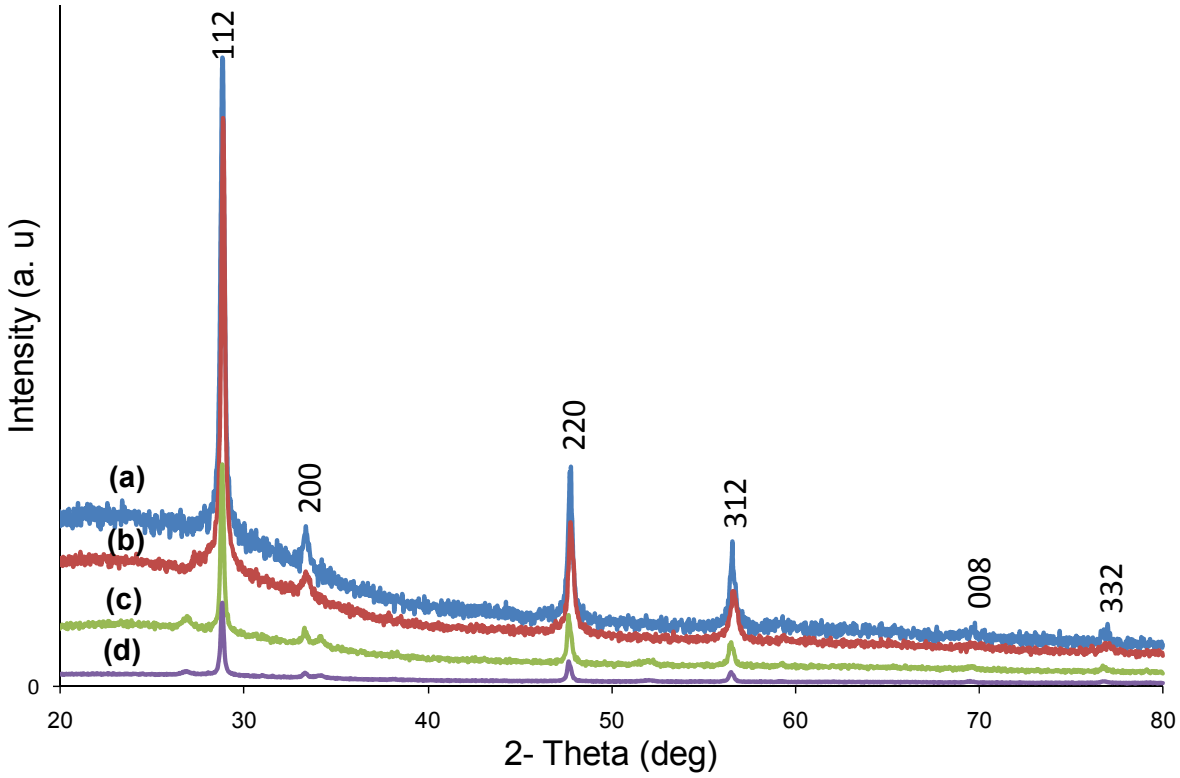

Figure S3. PXRD pattern of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1; a) 360 b) 400 c) 440 d) 480 ºC

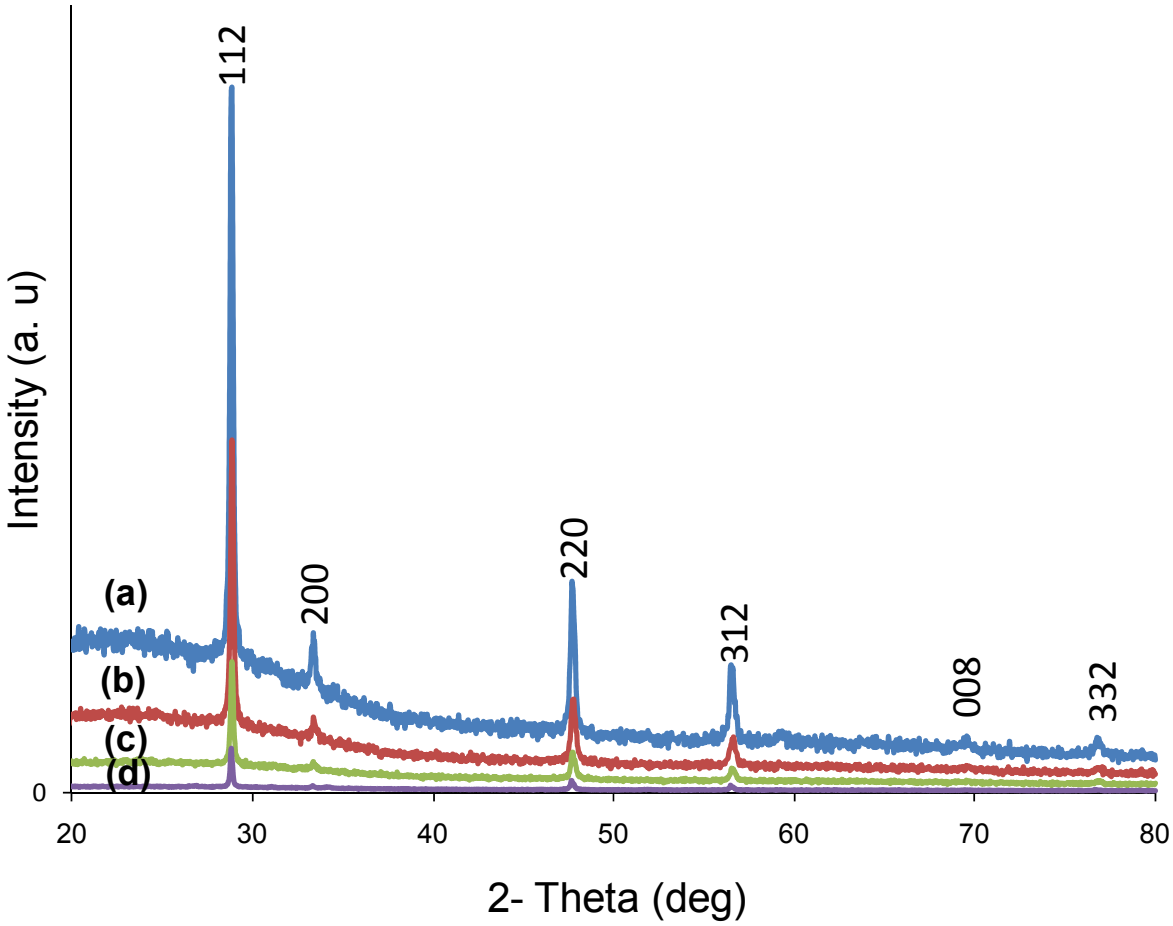

Figure S4. PXRD pattern of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 100 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1; a) 360 b) 400 c) 440 d) 480 ºC

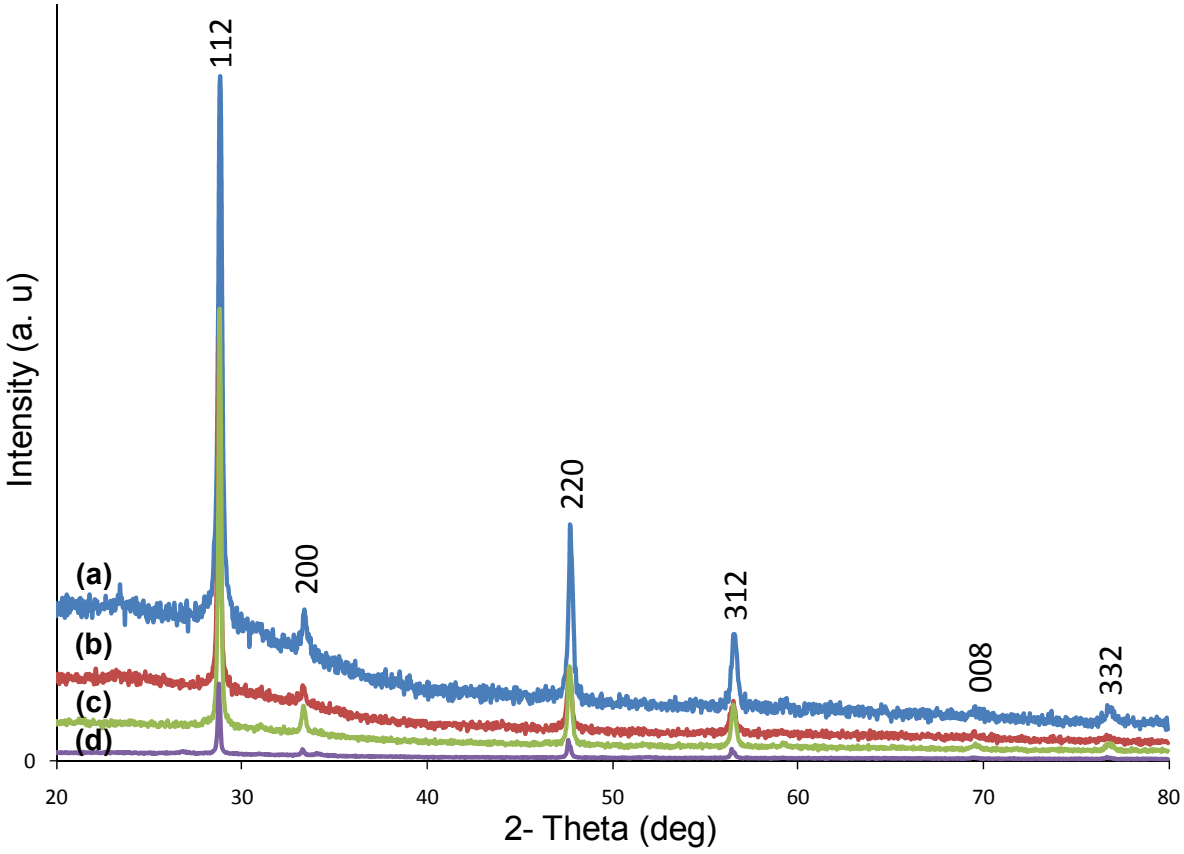

Figure S5. PXRD pattern of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 1.75:1:1; a) 360 b) 400 c) 440 d) 480 ºC

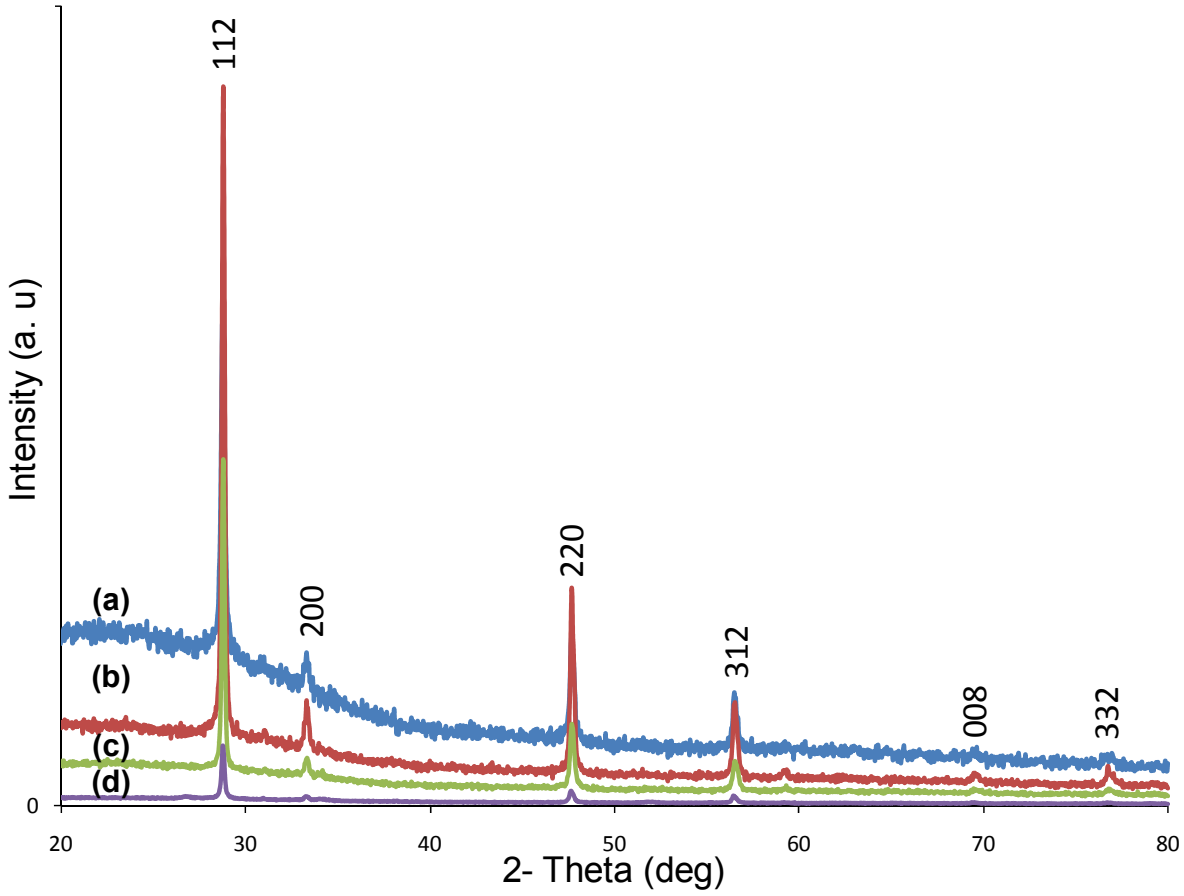

Figure S6. PXRD pattern of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 1.5:1:1; a) 360 b) 400 c) 440 d) 480 ºC

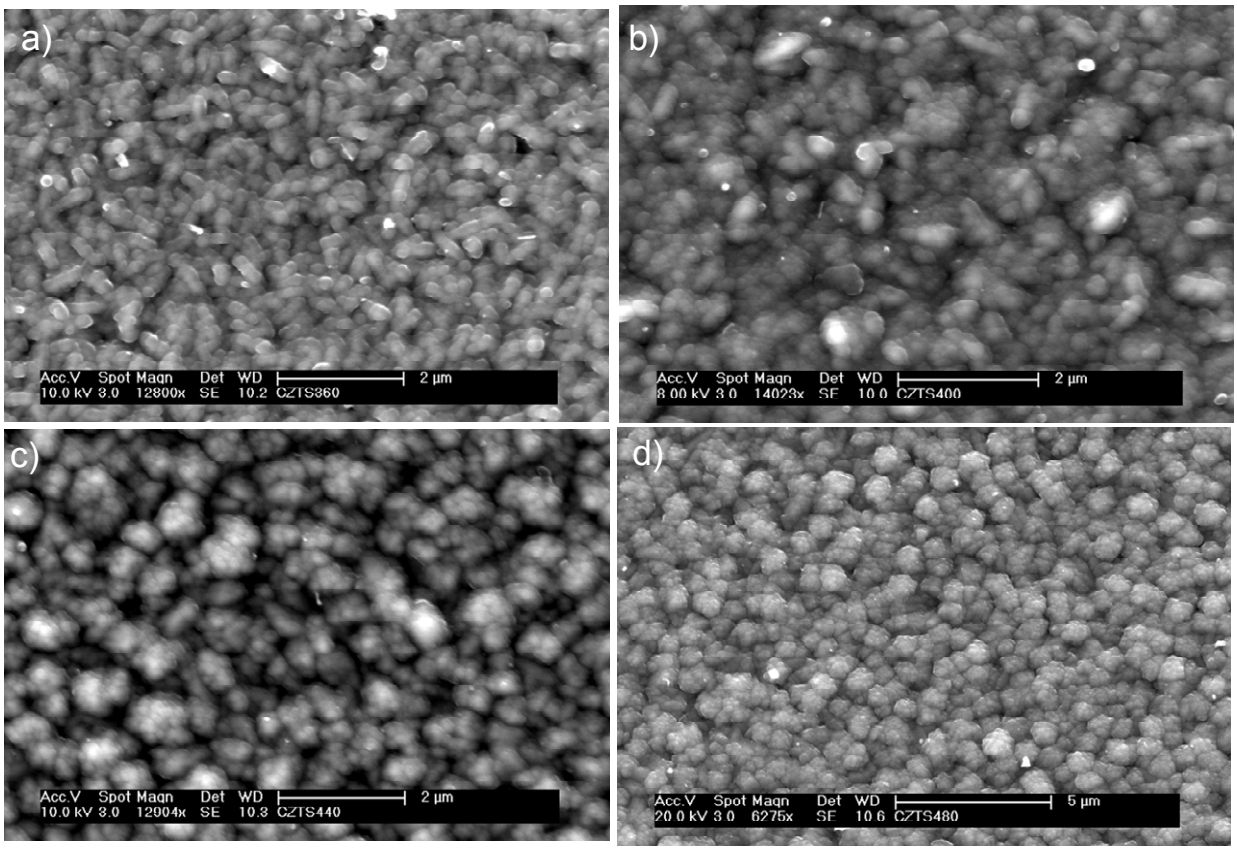

Figure S7. SEM images of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1; a) 360 b) 400 c) 440 d) 480 ºC

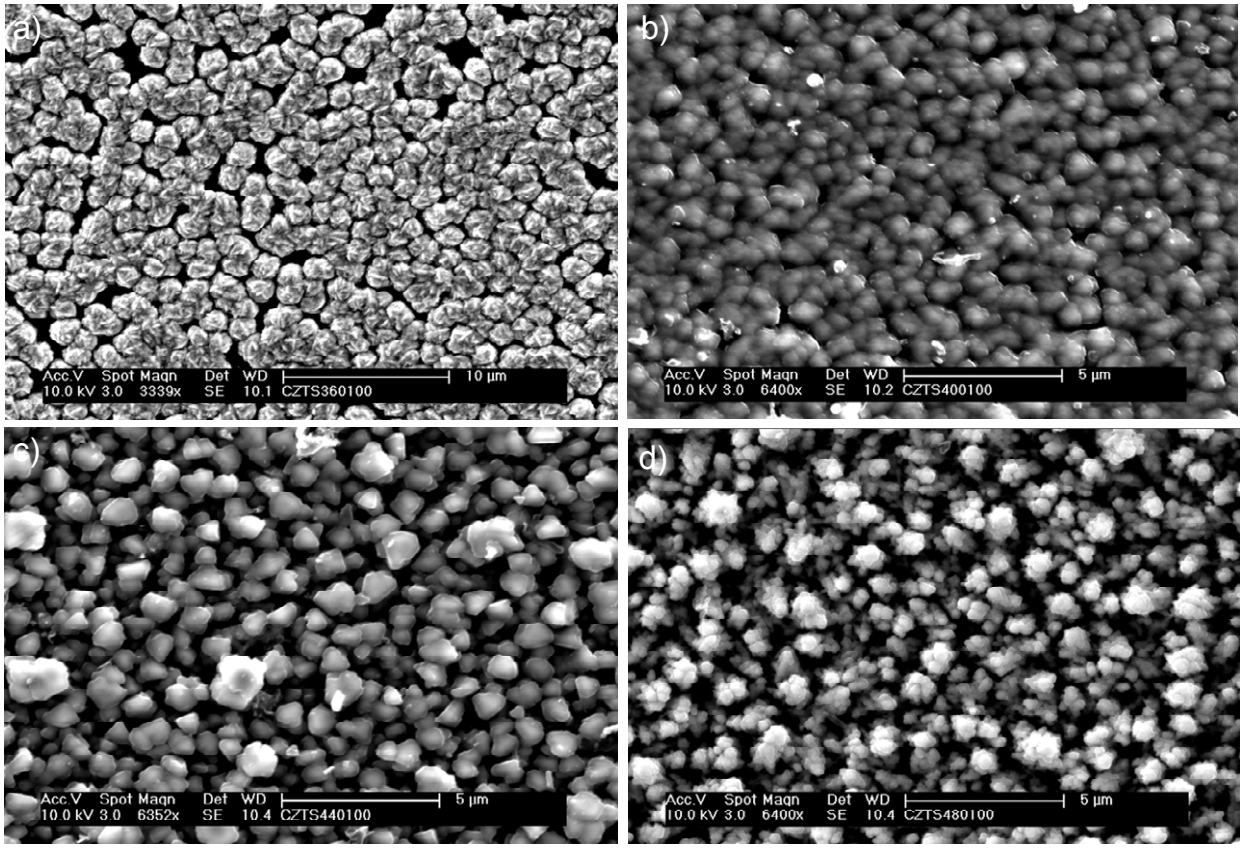

Figure S8. SEM images of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 100 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1; a) 360 b) 400 c) 440 d) 480 ºC

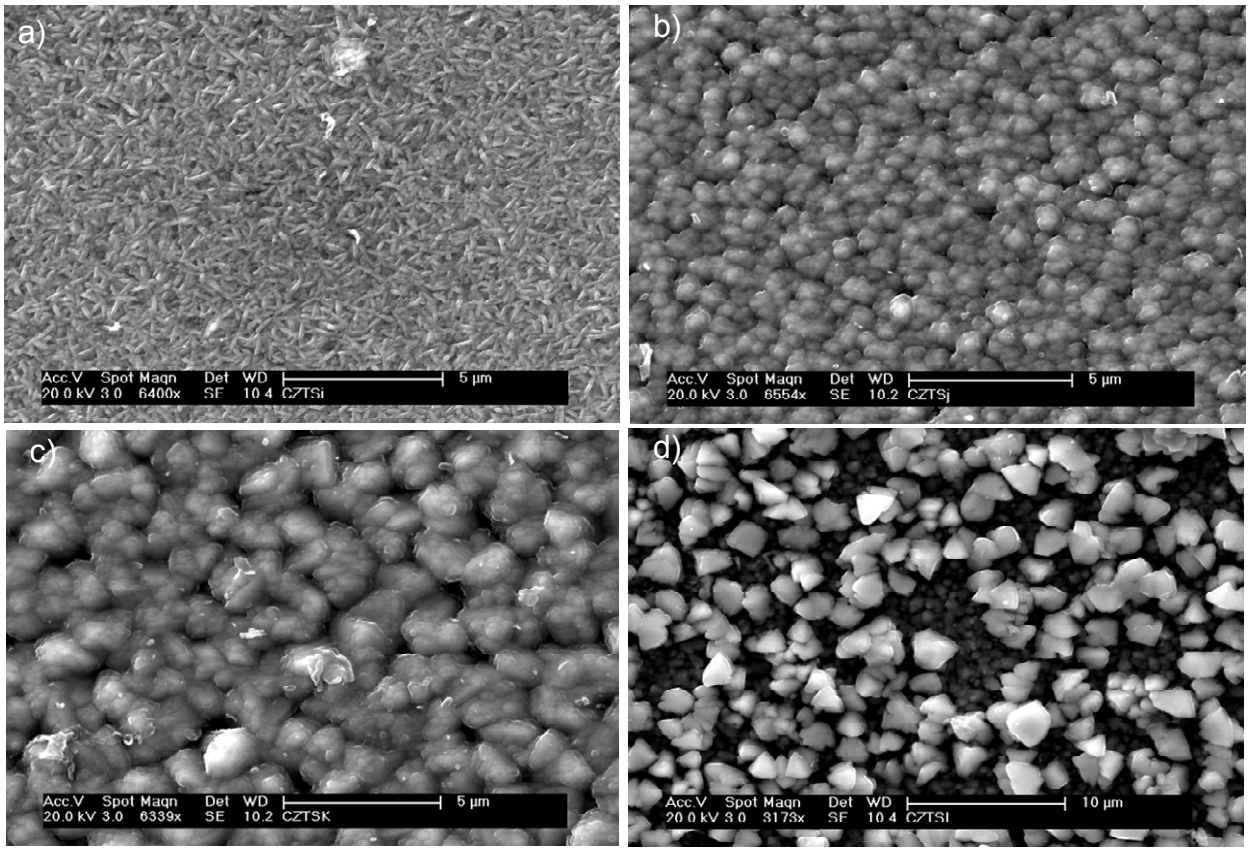

Figure S9. SEM images of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 1.75:1:1; a) 360 b) 400 c) 440 d) 480 ºC

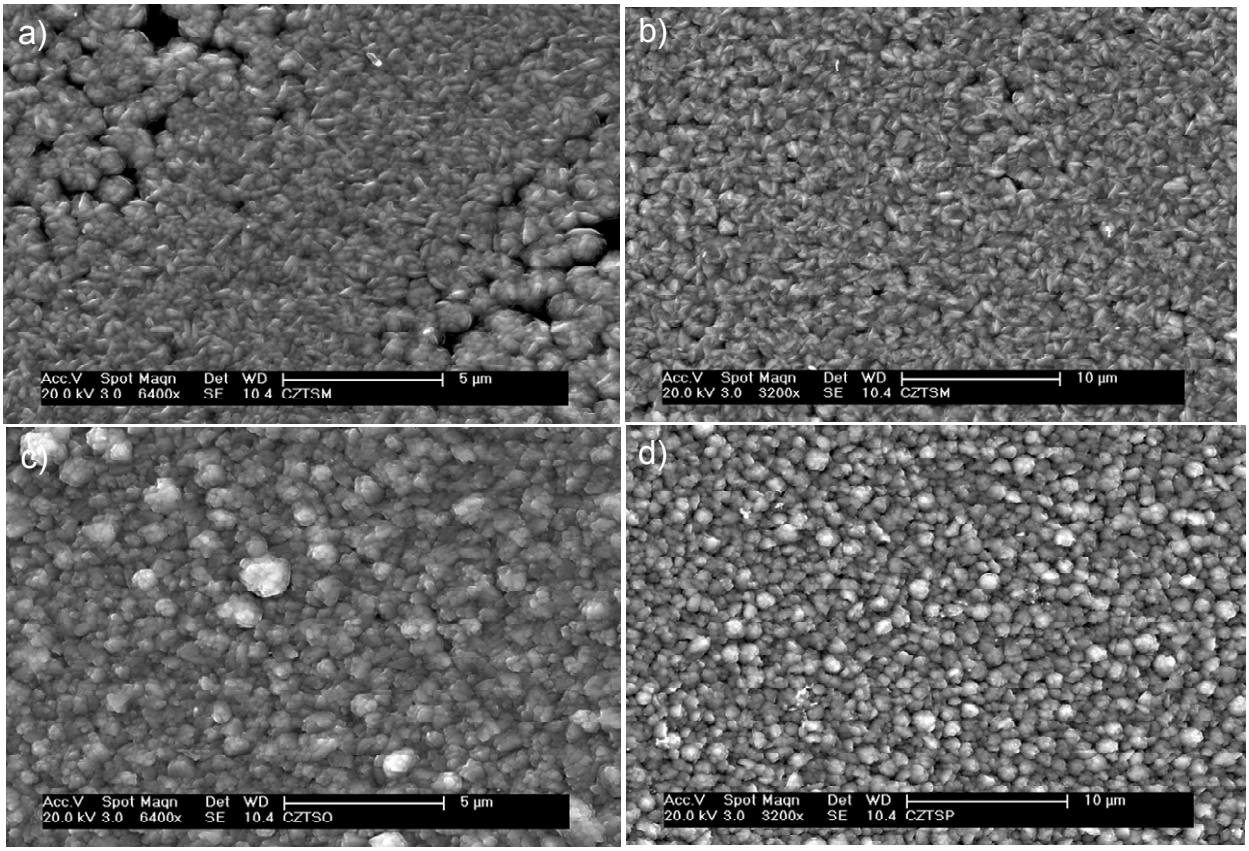

Figure S10. SEM images of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 1.5:1:1; a) 360 b) 400 c) 440 d) 480 ºC

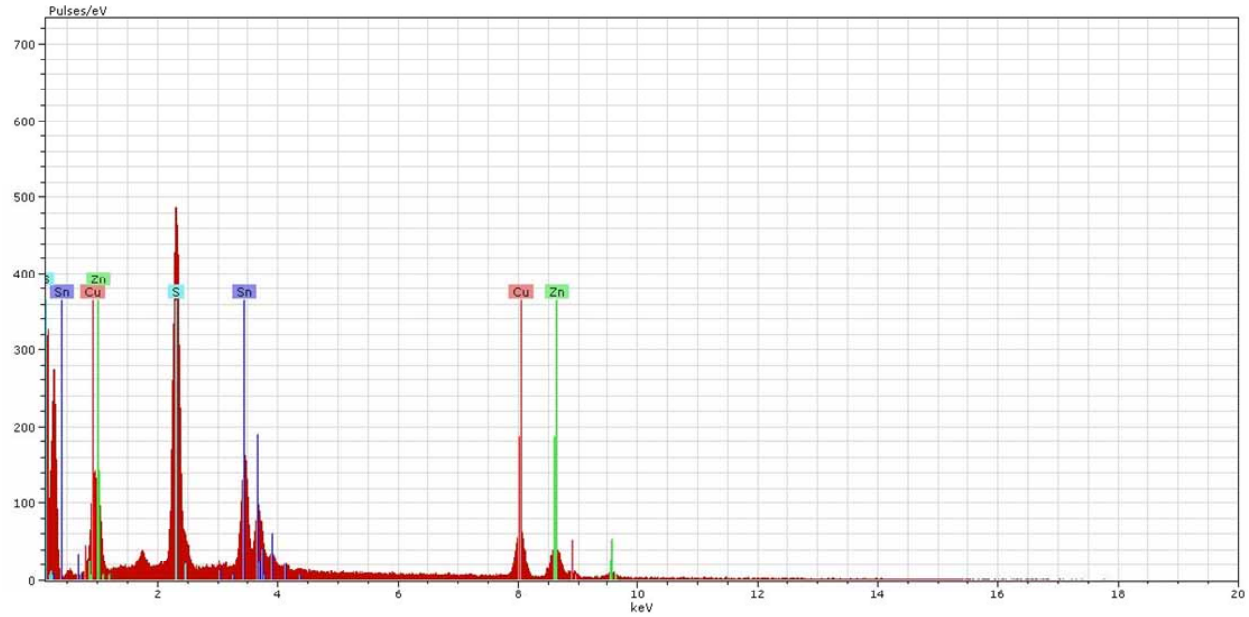

Figure S11. EDX spectra of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1.

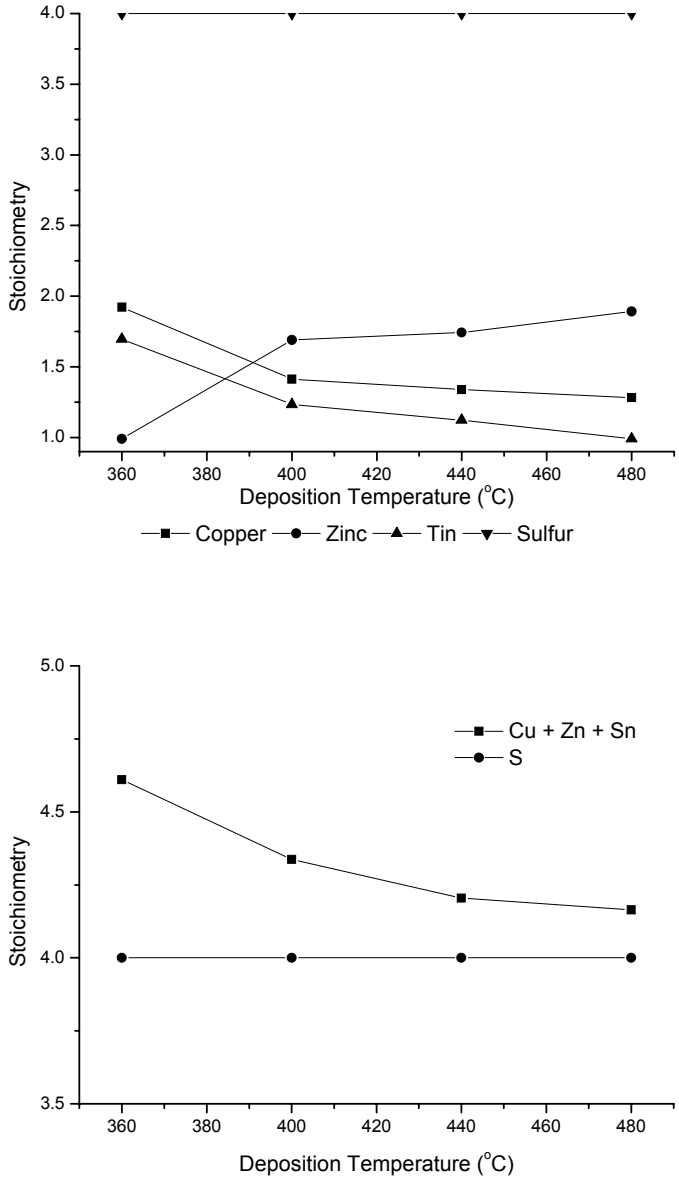

Figure S12. Graph showing elemental composition of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1.

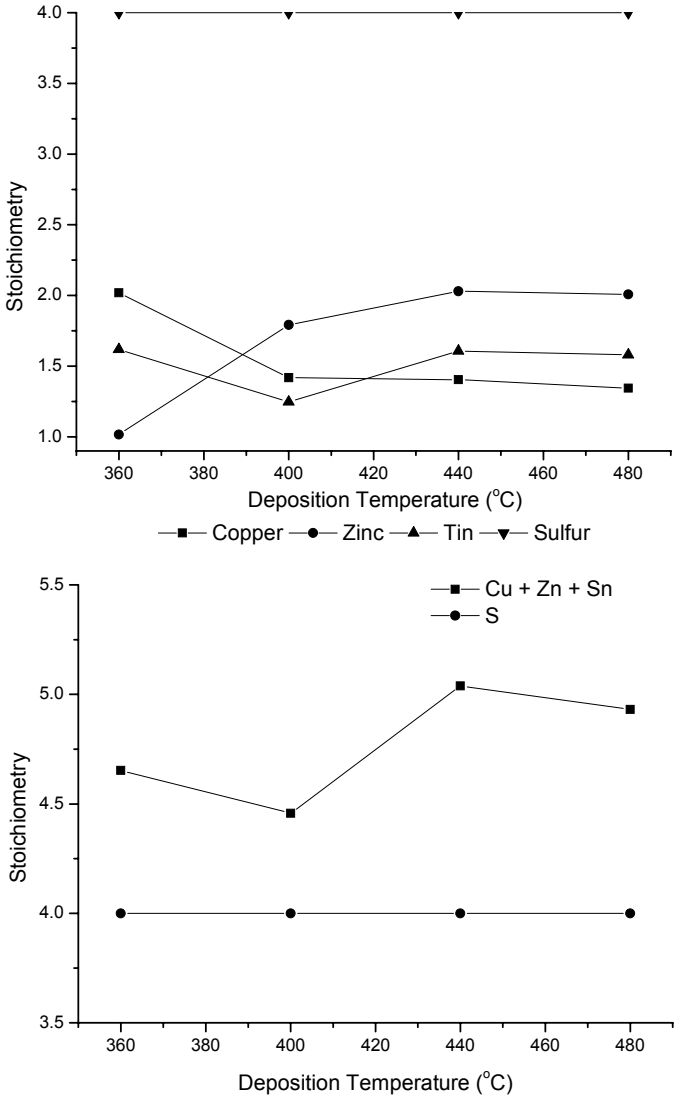

Figure S13. Graph showing elemental composition of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 100 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1.

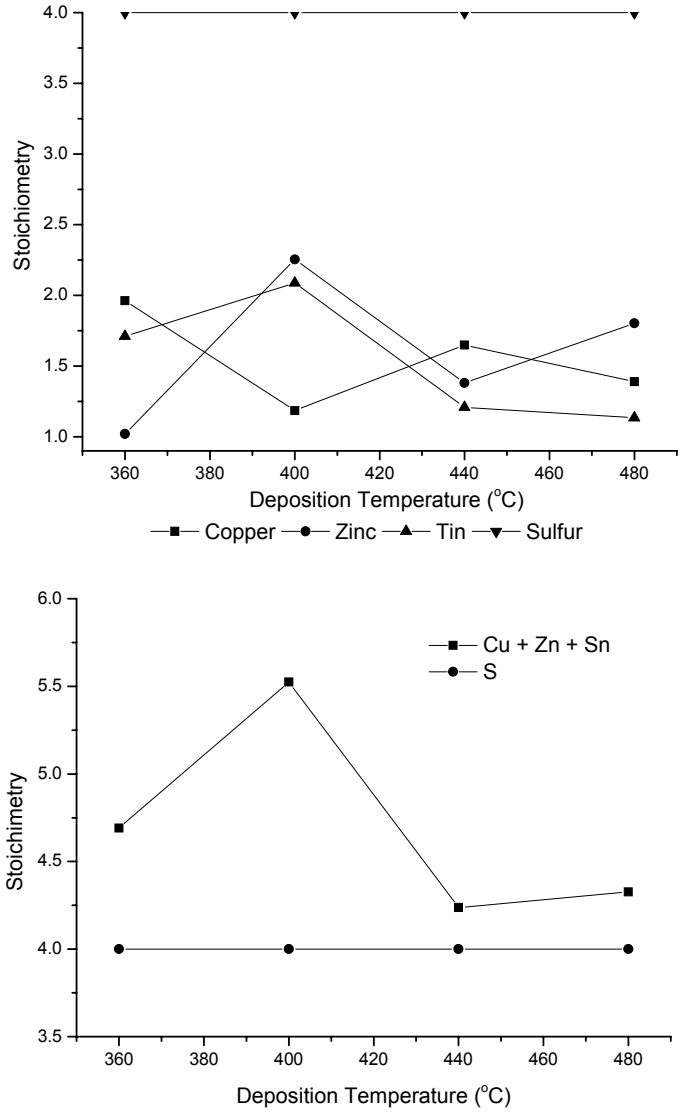

Figure S14. Graph showing elemental composition of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 1.75:1:1.

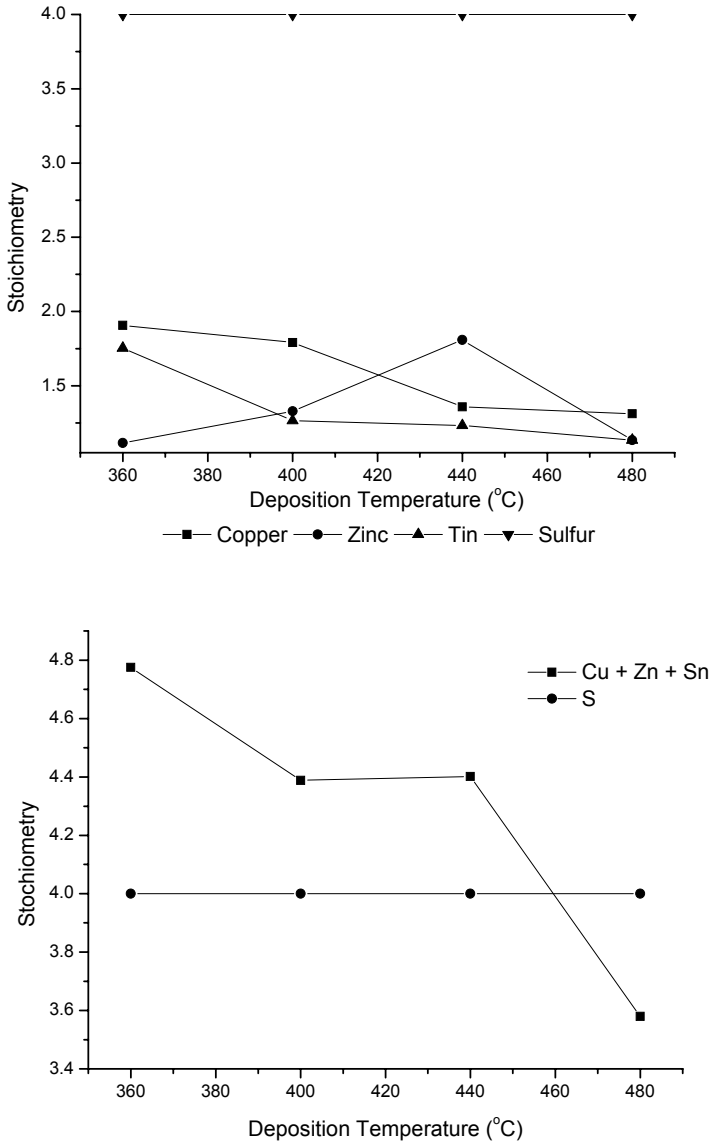

Figure S15. Graph showing elemental composition of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 1.5:1:1.

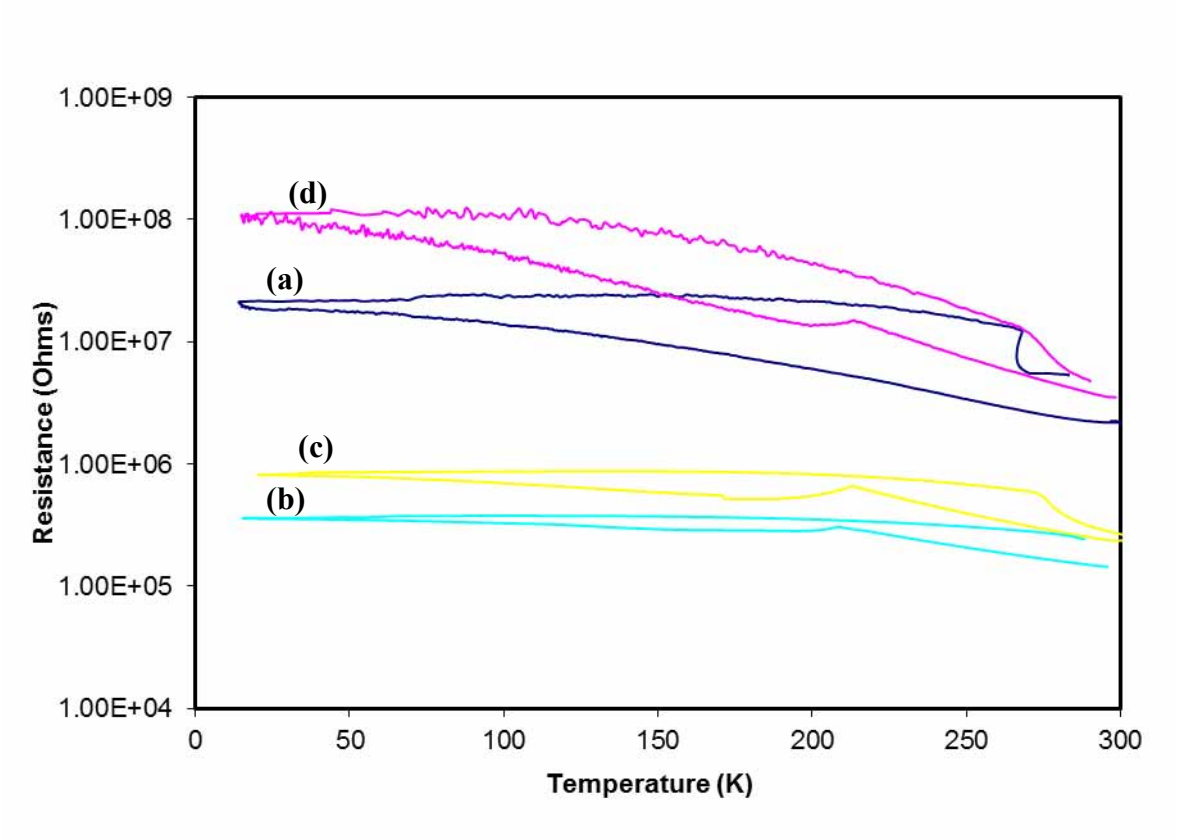

Figure S16. Variable temperature resistance of Cu_2ZnSnS_4 thin films deposited on glass substrate at argon flow rate of 160 sccm, using the molar ratio of $[Cu(S_2CNEt_2)_2]$, $[Zn(S_2CNEt_2)_2]$ and $[Sn(Bu)_2(S_2CNEt_2)_2]$ precursors 2:1:1. a) 360 ºC, b) 400 ºC, c) 440 ºC, d) 480 ºC.