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Structural and Morphological Analysis of $CuInSe_2$ Thin Films Prepared by Vacuum Free CSVT for Photovoltaic Cells

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Abstract: The aim of the present research is to determine the optimal deposition conditions of copper indium diselenide ($CuInSe_2$ or CIS) thin films for photovoltaic cells. The films were produced by vacuum free Close-Spaced Vapour Transport (CSVT) process. They were deposited on glass substrate from a source heated at temperatures of 400, 450, 500, 550 and 600°C. The deposition time was about 3 h. Characterizations were carried out by means of compositional, structural and morphological analysis. The composition of the CIS films was determined by Energy Dispersive Spectrometry (EDS) coupled to a scanning electron microscope. The results showed a quasi-stoichiometric composition in the range of source temperatures starting from 400 to 600°C. The best stoichiometry was obtained at a source temperature of 500°C. Structural characterization of the CIS films was made by X-ray diffraction (XRD). The spectra revealed that all the films were polycrystalline in nature with chalcopyrite structure. The preferred orientation along (112) direction suitable for photovoltaic device was obtained at a source temperature of 500°C with a maximum intensity. When the source temperature was higher than 500°C, secondary phases appeared and the intensity of the peak (112) decreased. Scanning Electron Microscope (SEM) micrographs showed that the films deposited at source temperature of 500°C had the best morphology to be used as solar cells. As a result of the characteristics of CIS films obtained by EDS, XRD and SEM studies, the source temperature 500°C is the most apt to produce photovoltaic cells with high efficiency.

Key words: Vacuum free CSVT, $CuInSe_2$, thin films, photovoltaic cells

INTRODUCTION

Copper indium diselenide ($CuInSe_2$ or CIS) thin films have been widely studied because of their use in photovoltaic cells permit to reach high solar efficiencies of 18-19% (Delahoy *et al*., 2004; Diehl *et al*., 2005). $CuInSe_2$ thin films offer direct band gap of about 1.04 eV at room temperature and a large absorption coefficient in the range of 10^4-10^5 cm^{-1} (Moudakir *et al*., 2004; Siebentritt, 2002).

According to previous studies (Cabalero *et al*., 2004; Orsal *et al*., 2000), the structural and morphological properties of $CuInSe_2$ thin films are very sensitive to the technique of preparation and the growth conditions. Several $CuInSe_2$ thin films processing techniques have been investigated, such as chemical bath deposition (Dhanam *et al*., 2002), RF sputtering (Yamaguchi *et al*., 1992), metalorganic chemical vapour deposition (MOCVD) (Artaud *et al*., 1998), three sources co-evaporation (Hama *et al*., 1991), electron beam evaporation (Castañeda *et al*., 2000), close spaced selenization (Adurodija *et al*., 1998) and close-spaced vapour transport (CSVT) under vacuum (Massé *et al*., 2004, 2002, 1997; Kannan *et al*., 2004; El Hadj Moussa *et al*., 2002).

In the present research we prepared $CuInSe_2$ thin films by the vacuum free CSVT technique which we have previously used (Konan *et al*., 2006). Then, we studied the compositional, the structural and morphological characteristics of the films as a function of source temperature in the range of 400 to 600°C and we determined the optimal deposition conditions for photovoltaic production.

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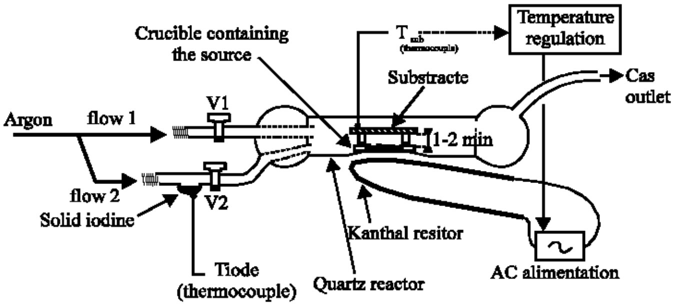

Fig. 1: Diagram of horizontal CSVT open reactor system

MATERIALS AND METHODS

The diagram of vacuum free CSVT apparatus we used to prepare $CuInSe_2$ thin films is shown in Fig. 1 (Konan *et al*., 2006). The evaporation system is an open quartz tube set horizontally without vacuum. The quartz tube has an inner diameter of 35 mm and a length of 400 mm. The source is a powder of $CuInSe_2$ put in a quartz crucible and hand pressed. The starting powder with the ratio (Cu/In) = 0.99 was obtained from bulk $CuInSe_2$, synthesized with elements of high purity (6N) Cu, In, Se. The substrate is a pyrex glass placed above the source and separated from it by a glass spacer of 2 mm thick. The substrate and the crucible containing the source were heated by a U-form Kanthal resistor.

The source temperature was indicated by a regulator and the temperature of the upper face of the substrate was directly measured using a chromel-alumel thermocouples. As the substrate was 1 mm thick, the temperature above and below the substrate was practically the same during the experiments. Solid iodine used as a transport agent was outside the reactor and isolated by a valve V2. Before deposition of $CuInSe_2$ thin films, valve V1 was opened and V2 closed. Therefore, no iodine vapour was present in the reactor. Argon-flow 1 removed the air from the reactor, while the source was heated until the desired temperature in the range of 400 to 600°C for the deposition. After the source temperature has been stabilized, V1 was closed and V2 opened. The reaction began when argon-flow 2 transported iodine vapour into the reactor and then invaded it. Solid iodine was heated by an electrical filament to the temperature of 30°C, measured by chromel-alumel thermocouples. The iodine vapour decomposed the surface of the source and transported the elements to the bottom of the substrate which was colder than the source of about 100-170°C. These elements settled and reconstituted the material. After the deposition time of about 3 h, V2 was closed during cooling period. Therefore, no more iodine vapour was transported into the reactor.

$CuInSe_2$ films of different thickness in the range of 0.1-1.3 μm were deposited at source temperatures of 400, 450, 500, 550 and 600°C. The thickness of the films was measured by a surface profilometer (DEKTAK 3).

The chemical composition of $CuInSe_2$ films was determined by Energy Dispersive Spectrometry (EDS) coupled to a scanning electron microscope (Cambridge S 360). Structural analysis of all the samples was made by X-Ray Diffraction (XRD) using a powder diffractometer (Philips PW 1130/90) with CuK_α radiation ($\lambda = 1.54051$ Å). A scanning electron microscope (JEOL JSM-6300 F) was used for films morphology study.

RESULTS

Compositional analysis: The samples of films obtained at source temperatures of 400, 450, 500, 550 and 600°C were respectively noted S-1, S-2, S-3, S-4 and S-5.

Table 1 gives typical compositions of the films prepared at various source temperatures, starting at 400°C. The results showed a quasi-stoechiometric composition of the films with $0.97 \leq Cu/In \leq 1.04$ and $0.93 \leq Se/(Cu+In) \leq 1.10$. Similar results have been reported by Artaud *et al.* (1998). At temperatures below 500°C, the films S-1 and S-2 are slightly rich in copper, whereas at temperatures above 500°C, the films S-4 and S-5 are slightly rich in indium. Such observations have been made by Zouaoui *et al.* (1999). However, we noted a general rising of the amount of Cu and In when the source temperature increased but the amount of Se decreased. These results are in agreement with those previously reported (Konan *et al*., 2006). In Table 1, we noted also the presence of iodine in the films. Its amount is low at 400°C and it disappeared as the source temperature became higher. Similar observations have been made by several researchers (Massé *et al*., 1997; Zaouaoui *et al*., 1999) following the study of some chalcopyrite compounds made also by CSVT, but using different relevant growth conditions. It can be noted that the

Table 1: EDS compositions (atomic %) of the deposited $CuInSe_2$ films at different source temperatures

Samples	Source temp.°C	Substrate temp.°C	Cu	In	Se	I	Cu/In	Se/(Cu+In)
S-1	400	228	24.11	23.12	52.00	0.38	1.04	1.10
S-2	450	274	24.70	23.55	51.26	0.21	1.05	1.06
S-3	500	318	24.80	24.96	49.87	0.00	0.99	1.00
S-4	550	371	25.12	25.93	48.70	0.00	0.97	0.95
S-5	600	422	25.44	26.18	48.16	0.00	0.97	0.93

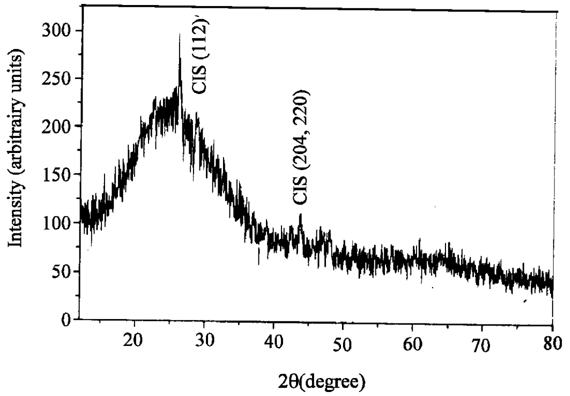

Fig. 2: XRD spectrum of sample S-1

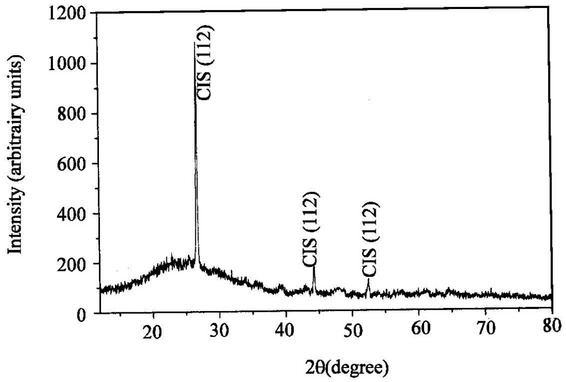

Fig. 4: XRD spectrum of sample S-3

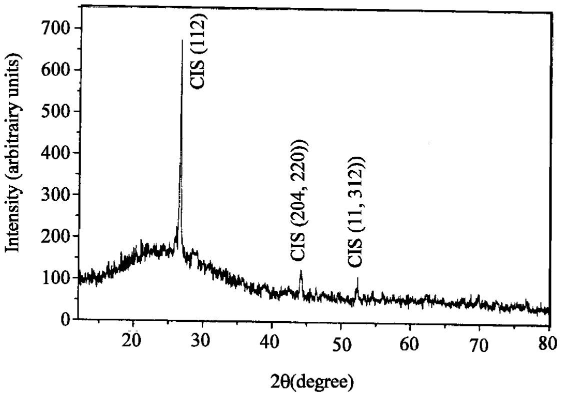

Fig. 3: XRD spectrum of sample S-2

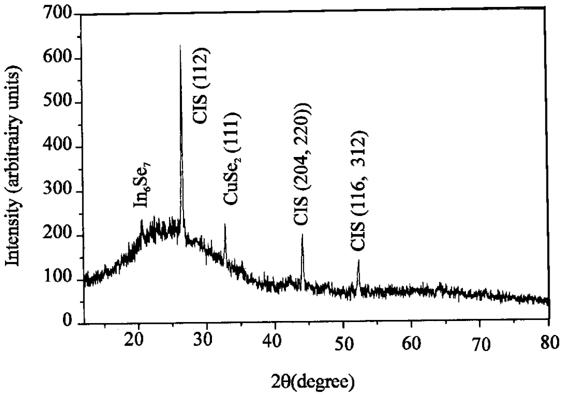

Fig. 5: XRD spectrum of sample S-4

disappearance of iodine in the films was due to the deposition time which was longer than the deposition time in previous experiment (Konan *et al.*, 2006). At source temperature of about 500°C, the ratio (Cu/In) was found to be 0.99. This value is typical as it is the same as the characteristic value of the starting $CuInSe_2$ powder. To our knowledge, no previous work has reported this observation.

Structural analysis: Structural analysis was made by X-Ray Diffraction (XRD) using a powder diffractometer (θ, 2θ geometry) with CuK_α radiation (λ = 1.54051 Å). The spectra are shown in Fig. 2-6.

The diffraction peaks observed for $CuInSe_2$ films deposited at source temperatures of 400, 450, 500, 550 and 600°C revealed that the films were polycrystalline in nature of chalcopyrite structure. The main diffraction peaks are indicated in Table 2. The peak (112) suitable for photovoltaic cells (Kannan *et al.*, 2004; Artaud *et al.*, 1998) were observed in all the films. However, in Fig. 2-4, corresponding to source temperatures of 400-500°C, the intensity of this peak increased and there were no secondary phases. When the source temperatures became higher than 500°C (Fig. 5 and 6) the peak (112) decreased. This decrease can be explained by the perturbation due to the presence of secondary phases In_6Se_7 and $CuSe_2$ in the films. Following the compositional analysis, these secondary phases were observed for (Cu/In) < 0.99. Several researchers (Artaud *et al.*, 1998; Massé *et al.*, 2002, 1997; Kannan *et al.*, 2004; El Hadj Moussa *et al.*, 2002) have observed the presence of secondary phase CuI in $CuInSe_2$ thin films. This phase has not been identified in the films obtained in our experiments. The preferred orientation along (112) direction with a maximum intensity was observed at source temperature of 500°C (Fig. 7). At this temperature, there was no iodine in the films and no secondary phases were observed, corresponding to the ratio (Cu/In) = 0.99.

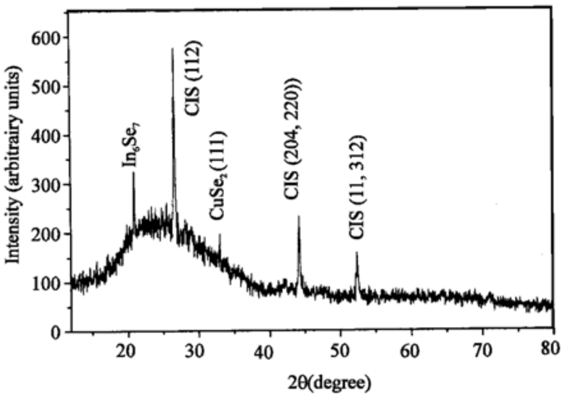

Fig. 6: XRD spectrum of sample S-5

Table 2: Main diffraction peaks observed for $CuInSe_2$ phases

Sample	Observed peaks
S-1	(112) (204, 220)
S-2	(112) (204, 220) (116, 312)
S-3	(112) (204, 220) (116, 312)
S-4	(112) (204, 220) (116, 312)
S-5	(112) (204, 220) (116, 312

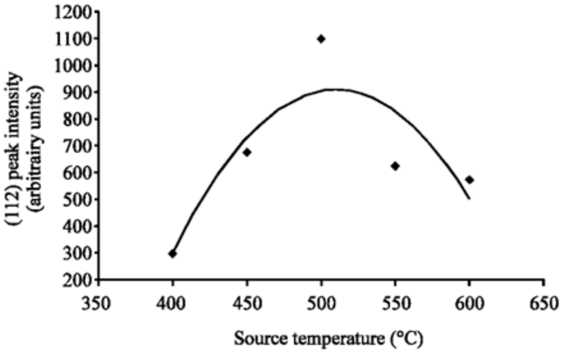

Fig. 7: (112) peak intensity as a function of source temperatures

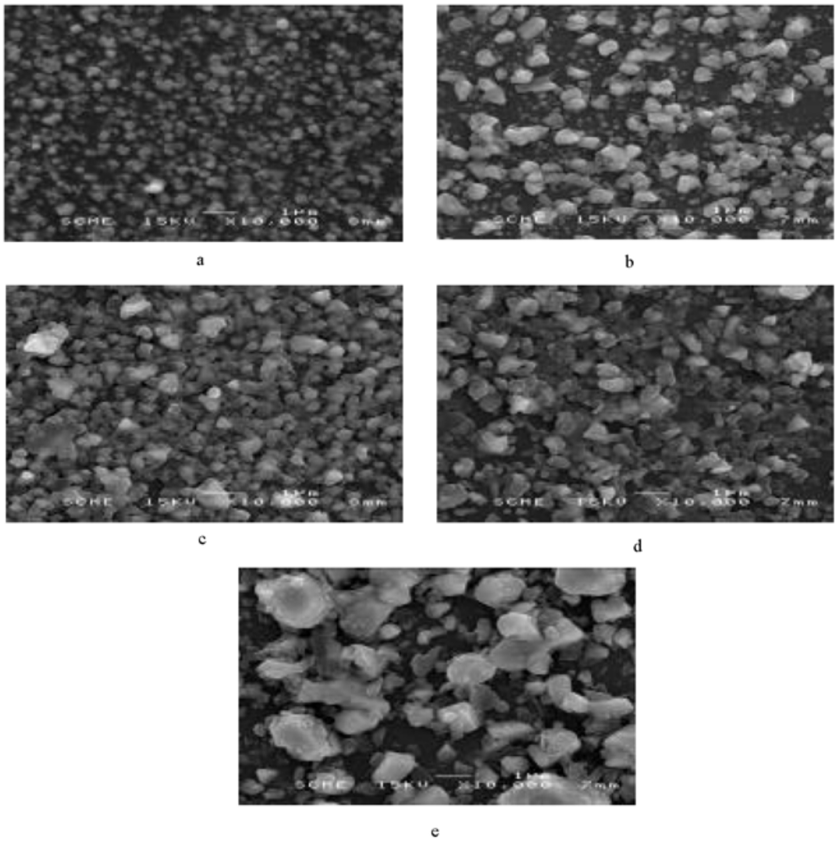

Fig. 8: SEM micrographs of CIS films: (a) Tsource = 400°C, (b) Tsource = 450°C, C Tsource = 500°C, (d) Tsource = 550°C and (e) Tsource = 600°C

Morphological study: Figure 8 shows SEM micrographs of CIS films. The morphology was strongly dependent on the growth temperature. The average size of the crystallites increased with the source temperature. Indeed, at 400°C (Fig. 8a), the crystallites are small and exhibit a polyhedral form. At 450°C (Fig. 8b), two typical polyhedral crystallites were observed. During the early stage of growth, the crystallites were very small. The structure changes with the increasing time of deposition to finally produce polyhedral crystallites of bigger size of about 1 µm. In both cases of these source temperatures (400 and 450°C), the crystallites were less densely packed. At 500°C (Fig. 8c), the layer was composed of melt of triangular and polyhedral grains. Such observations have been reported by Orsal *et al.* (2000). At this temperature, the average size of the grains is also about 1 µm and the layer was very densely packed. At 550°C (Fig. 8d), the morphology of the layer was similar to that of 500°C, but the density of the grains decreased. At 600°C (Fig. 8e), we observed as in the case of 450°C, two typical polyhedral crystallites with different sizes. The bigger size is about 2.5 µm. According to Caballero and Guillén (2004), chalcopyrite structure with bigger grain growth was more appropriate to produce photovoltaic cells with high efficiency. Our SEM study showed that CIS films obtained at source temperature of 500°C were more suitable for photovoltaic cells since the crystallites were denser. Indeed, at this temperature the XRD analysis exhibit the maximum of the (112) peak intensity (Fig. 7). On the contrary, at the two latest source temperatures (550 and 600°C) the presence of secondary phases in the films perturb the (112) peak as already noted.

CONCLUSIONS

Polycrystalline CIS films were prepared onto pyrex glass substrates by the vacuum free CSVT technique. The films obtained were characterized by EDS, XRD and SEM studies. These characterization methods allowed us to determine the optimal deposition conditions of suitable films for photovoltaic production.

EDS study showed a quasi-stoichiometric composition of the films in the range of source temperatures from 400 to 600°C. The best result of stoichiometry was obtained at 500°C since the ratio (Cu/In) found to be 0.99 was the same as the characteristic value of the starting $CuInSe_2$ powder.

The polycrystallinity of the films was in nature of chalcopyrite structure as revealed by XRD study. No secondary phases were observed in the range of source temperatures 400- 500°C. Above 500°C, secondary phases as In_6Se_7 and $CuSe_2$ appeared and the intensity of the peak (112) decreased. The maximum intensity of this peak was obtained at 500°C.

SEM micrographs of the films showed the best morphology at 500°C. At this source temperature, the layer has a homogeneous surface. The crystallites are well compacted with an average size about of 1 µm. These results corroborated those obtained by EDS and XRD studies.

In view of these different characterization methods, the source temperature of 500°C was more suitable to produce CIS films for photovoltaic cells with high efficiency. However, further experiments should be carried out, such as optical absorption measurements for more accurate determination of the optimal deposition conditions.

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REFERENCES

Adurodija, F.O., S.K. Kim, S.D. Kim, J.S. Song, K.H. Yoon and B.T. Ahn, 1998. Characterization of co-sputtered Cu-In alloy precursors for $CuInSe_2$ thin films fabrication by close-spaced selenization. Solar Energy Materials Solar Cells, 55: 225-236.

Artaud, M.C., F. Ouchen, L. Martin and S. Duchemin, 1998. $CuInSe_2$ thin films grown by MOCVD: Characterization, first devices. Thin Solid Films, 324: 115-123.

Caballero, R. and C. Guillen, 2004. Structural and morphological properties of Cu (In,Ga) Se_2 thin films on Mo substrate. Applied Surface Sci., 238: 180-183.

Castañeda, S.I. and F. Rueda, 2000. Differences in copper indium selenide films obtained by electron beam and flash evaporation. Thin Solid Films, 361-362: 145-149.

Delahoy, A.E., L. Chen, M. Akhtar, B. Sang and S. Guo, 2004. New technologies for CIGS photovoltaics. Solar Energy, 77: 785-793.

Dhanam, M., R. Balasundaraprabhu, S. Jayakumar, P. Gopalakrishnan and M.D. Kannan, 2002. Preparation and study of structural and optical properties of chemical bath deposited copper indium diselenide thin films. Physica Status Solidi (a), 191: 149-160.

Diehl, W., V. Sittinger and B. Szyszka, 2005. Thin film solar cell technology in Germany. Surface and Coatings Technol., 193: 329-334.

El Hadj, M., G.W. Ariswan, A. Khoury, F. Guastavino and C. Llinarès, 2002. Fabrication and study of photovoltaic material $CuIn_xGa_{1-x}Se_2$ bulk and thin films obtained by the technique of closed-spaced vapor transport. Solid State Commun., 122 : 195-199.

Hama, T., T. Ihara, H. Sato, H. Fujisawa, M. Ohsawa, Y. Ichikawa and H. Sakai, 1991. Structural properties of $CuInSe_2$ thin films for solar cell applications. Solar Energy Materials, 23: 380-387.

Kannan, M.D., R. Balasundaraprabhu, S. Jayakumar and P. Ramanathaswamy, 2004. Preparation and study of structural and optical properties of CSVT deposited $CuInSe_2$ thin films. Solar Energy Material and Solar Cells, 81: 379-395.

Konan, K., B. Hadjoudja, J.K. Saraka and P. Gbaha, 2006. Development of a vacuum free CSVT low cost technique to deposit $CuInSe_2$ thin films. Global J. Pure Applied Sci., (In Press).

Massé, G., K. Guenoun, K. Djessas and F. Guastavino, 1997. p-and n-type, $CuInSe_2$ thin films grown by close-spaced vapour transport. Thin Solid Films, 293: 45-51.

Massé, G., K. Djessas, C. Monty and F. Sibieude, 2002. Morphology of $Cu(In,Ga)Se_2$ thin films grown by closed-spaced vapor transport from sources with differents grain sizes. Thin Solid Films, 414: 192-198.

Massé, G., T. Moudakir and K. Djessas, 2004. New low cost CSVT method to deposit $Cu(In,Ga)Se_2$ thin films and solar cells. 19th European Photovoltaic Solar Energy Conference (EPVSEC) Paris, France.

Moudakir, T., K. Djessas and G, Massé, 2004. $CuIn_{1-x}Ga_xS_2$ wide gap absorbers grown by close-spaced vapor transport. J. Crystal Growth., 270: 517-526.

Orsal, G., F. Mailly, N. Romain, M.C. Artaud, S. Rushworth and S. Duchemin, 2000. Study of polycrystalline $CuGaSe_2$ thin films deposited by MOCVD onto ZnO substrates. Thin Solid Films, 361-362: 135-139.

Siebentritt, S., 2002. Wide gap chalcopyrites: material properties and solar cells. Thin Solid Films, 403-404: 1-8.

Yamaguchi, T., J. Matsufusa and A. Yoshida, 1992. Thin films of $CuInSe_2$ prepared by RF sputtering from various compositional powder targets. Solar Energy Materials Solar Cells, 27: 25-35.

Zouaoui, A., M. Lachab, M.L. Hidalgo, A. Chaffa, C. Liinarès and N. Kesri, 1999. Structural, compositional and photoluminescence characterisics of $CuInSe_2$ thin films prepared by close-spaced vapour transport. Thin Solid Films, 339: 10-18.