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$CuInSe_2$ thin films formed by selenization of Cu–In precursors

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$CuInSe_2$ (CIS) thin films were grown by selenization of electro-deposited or electroless-deposited Cu–In precursors. Cu–In precursors were formed by layer-by-layer electro-deposition of Cu and In as well as by electroless co-deposition of Cu and In. The major phases in the precursors were found to be $Cu_{11}In_9$ and elemental In. It was found that the stoichiometric CIS phase ($CuInSe_2$) may be formed by selenization of the precursors at temperatures higher than 500 °C. The Cu–In precursors as well as CIS films were characterized by X-ray diffraction and scanning electron microscopy. The cubic CIS phase was formed when electroless-deposited Cu–In precursor was selenized, whereas the chalcopyrite CIS or the In-rich phase ($CuIn_2Se_{3.5}$) was formed when the layered precursors were selenized at a high temperature.

1. Introduction

Interest in $CuInSe_2$ (CIS) dates back to the work of Wagner *et al.* [1], who demonstrated a 12% conversion efficiency using single crystals. The extraordinarily high absorption coefficient of this material makes thin-film solar cells practical, even though the rather low optical band gap of 1.05 eV is low for optimum conversion efficiency. Interest in CIS for thin-film solar cells increased considerably with the report of 10.6% efficient cells in 1982 [2] by a three-source evaporation method. Key elements to achieve the high conversion efficiency are (i) the use of a $Zn_xCd_{1-x}S$ n-type heterojunction partner for the normally p-type compound and (ii) the growth of an early Cu-rich layer during the deposition process.

CIS film formation can be divided mainly into two major categories: (i) those processes where the metals are delivered separately from Se and (ii) those where Se is incorporated with the metals during material delivery. Both these processes will require thermal activation in Se. Examples of case (ii) include co-evaporation of the three elements in vacuum [3], thermal evaporation in vacuum [4], electro-deposition [5], chemical dipping [6] and chemical vapour deposition [7]. Thermal mixing of stacked binary or elemental layers [8], and selenization of Cu–In precursor using H_2Se [9] or selenium vapour [10, 11] are examples of case (i). The selenization of Cu–In precursor or stacked metal layers has attracted researchers' attention recently [11–13] owing to the prospect of developing low-cost solar cell structures based on CIS, but the conventionally used selenization technique employing H_2Se gas is not a safe method. In the present paper, we report results on the formation of Cu–In precursors by co-deposition and annealing of stacked layers employing electro-deposition or electroless deposition and the formation of CIS films by selenization by a new technique called chemical vapour transport by gas (CVTG). The precursors as well as the CIS films were characterized by X-ray diffraction (XRD), X-ray fluorescence (XF), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

2. Experimental techniques

2.1. Preparation of Cu/In and In/Cu Precursors by using electro-deposition

Glass/Mo, Glass/SnO_2 and Cu foils were used as substrates for electro-deposition of Cu/In and In/Cu precursors. The electro-deposition was carried out by employing the galvanostatic mode, where a graphite electrode was used as the counter-electrode and the working electrode is one of the substrates used for film deposition.

The electrochemical bath for Cu deposition contained 0.3 M copper sulphate pentahydrate, 3.2 M NaOH and 2.3 M citric acid. The chemical bath was aged for several hours before use. The temperature of the deposition bath was maintained at 60 °C during film deposition. On the other hand, the In deposition bath consisted of 0.025 M $InCl_3$ and 0.1 M citric acid. Cu and In layers were deposited one over the other by changing the chemical bath.

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2.2. Preparation of Cu–In alloy by employing the electroless technique

Electroless deposition involves immersing a conducting glass substrate or a noble metal connected with an easily oxidizable redox component such as Al or Cd in a deposition bath containing the required ions and complexing agents. It forms a short-circuited local cell following the dissolution reaction

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^- \qquad E_0 = -1.67\,\mathrm{V} \qquad (1)$$

where E_0 is the standard potential measured with respect to standard hydrogen electrode. The idea behind connecting a noble metal or a conducting glass with an easily oxidizable metal is to create an electrochemical potential difference between the two electrodes without applying an external voltage. The solution used for the electroless deposition of Cu–In alloy consisted of $\mathrm{CuCl_2}$ (0.025 M), $\mathrm{InCl_3}$ (0.025 M), triethanolamine (1% v/v) and $\mathrm{NH_4OH}$ (0.75% v/v). The pH of the solution was adjusted to 1.5 with HCl. The bath temperature was kept at 40 °C. Cu and In ions from the solution are reduced at the noble metal or conducting glass following the electrochemical reactions

$$\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Cu} \quad E_0 = 0.337\,\mathrm{V} \qquad (2)$$

$$\mathrm{In}^{3+} + 3\mathrm{e}^- \rightarrow \mathrm{In} \quad E_0 = -0.342\,\mathrm{V} \qquad (3)$$

Because of the large difference between the standard potentials for the reduction of Cu^{2+} and In^{3+}, electroless deposition of Cu–In alloy requires complexing of the ions.

2.3. Selenization of Cu–In alloy and stacked Cu–In layers by chemical vapour transport by gas

CVTG is a new method, developed in the Laboratorio de Energia Solar, Temixco, to grow semiconductor thin films. This technique may be classified as follows.

(i) *Condensation chemical vapour transport by gas* (*CCVTG*). This is related to chemical vapour transport, where the sublimed chemical vapour is transported by employing a carrier gas and allowed to condense on a cooler substrate [14]. Thin films of the materials can be deposited directly by this process.

(ii) *Reactive chemical vapour transport by gas* (*RCVTG*) . This is similar to chemical vapour deposition in the sense that a chemical reaction is brought about between the transported chemical vapour and the substrate, leading to the formation of a semiconductor film.

In the present case, RCVTG was used for selenization of Cu–In alloy and stacked layers. Fig. 1 shows the sketch of the CVTG reactor used for selenization. It consists of a tubular furnace with facilities for temperature control along the length of the tube. A quartz tube 60 cm in length and 5.4 cm in diameter is kept inside the furnace. The controlled gas flow mechanism is at the inlet port and the pumping system is connected at the exit port. There is a temperature gradient along the length of the tube with the maximum temperature at the centre of the tube and minimum temperatures at the two ends. The temperature at the exit port is also influenced by the air-cooling mechanism at the exit port. The reactor is evacuated first to a pressure of the order of 1×10^{-3} mbar. Later the reactor was fluxed with pure argon gas. During vapour transport the gas pressure was kept constant at 3×10^{-1} mbar at a constant flow rate of 100 sccm. As-prepared precursors were kept along the length of the tube at different temperatures and Se powder kept at the inlet port was allowed to sublime at 200 °C.

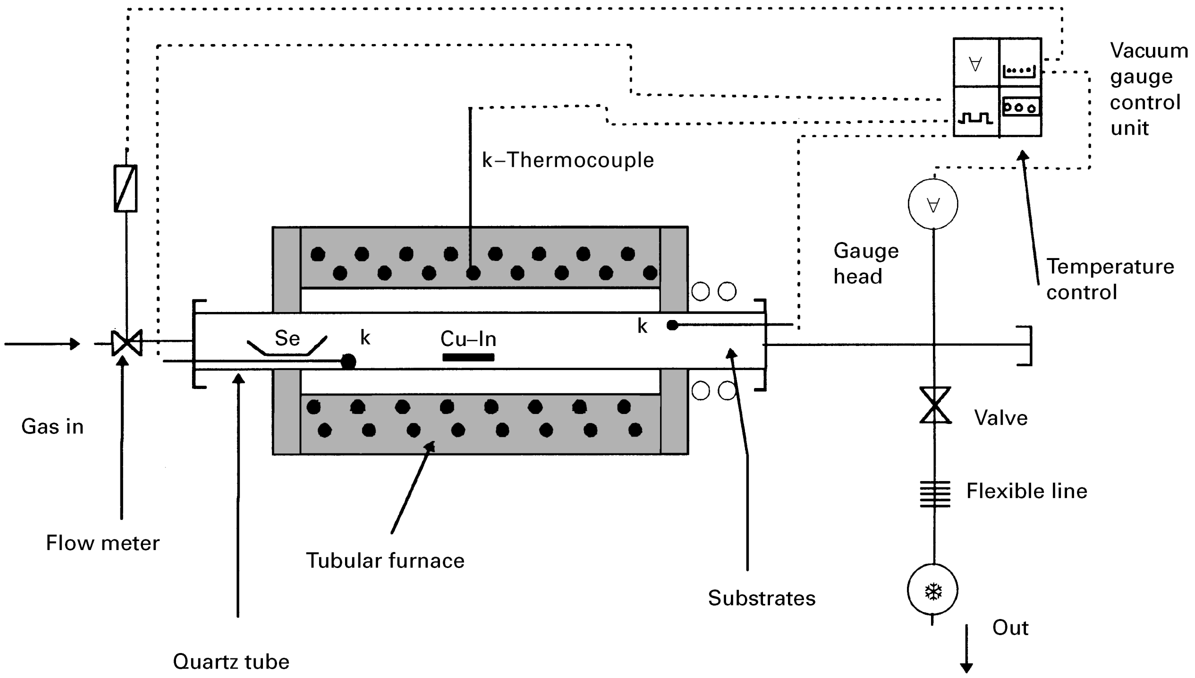


Figure 1 A two-dimensional sketch of the CVTG system for selenization of Cu–In precursors.

3. Results and discussion

The Cu–In alloy and stacked layers were generally adherent to the substrates. As-deposited films were characterized with respect to their structural, morphological and compositional nature. Fig. 2a shows the XRD patterns for electroless deposited Cu–In and Fig. 2b displays those for Cu/In and In/Cu precursors. These figures consist of XRD reflections corresponding mainly to $Cu_{11}In_9$ (Card 41-0883 of [15]) alloy phase. There are also a few additional peaks corresponding to elemental In phase. These observations are in agreement with those of Yamanaka *et al.* [11] and Tuttle *et al.* [16] that the Cu/In metal stack is known to alloy spontaneously at room temperature to form a $Cu_{11}In_9$ and an In-rich phase. This is consistent with the binary phase diagram [17] where the Cu–In composition is not indicated.

The Cu–In precursors were subjected to selenization at different temperatures from 300 to 550 °C by employing the RCVTG technique. The results of structural characterization of the precursors after selenization at various temperatures are given in Figs 3–5. The *d* values calculated from XRD results corresponding to the three cases, together with the standard

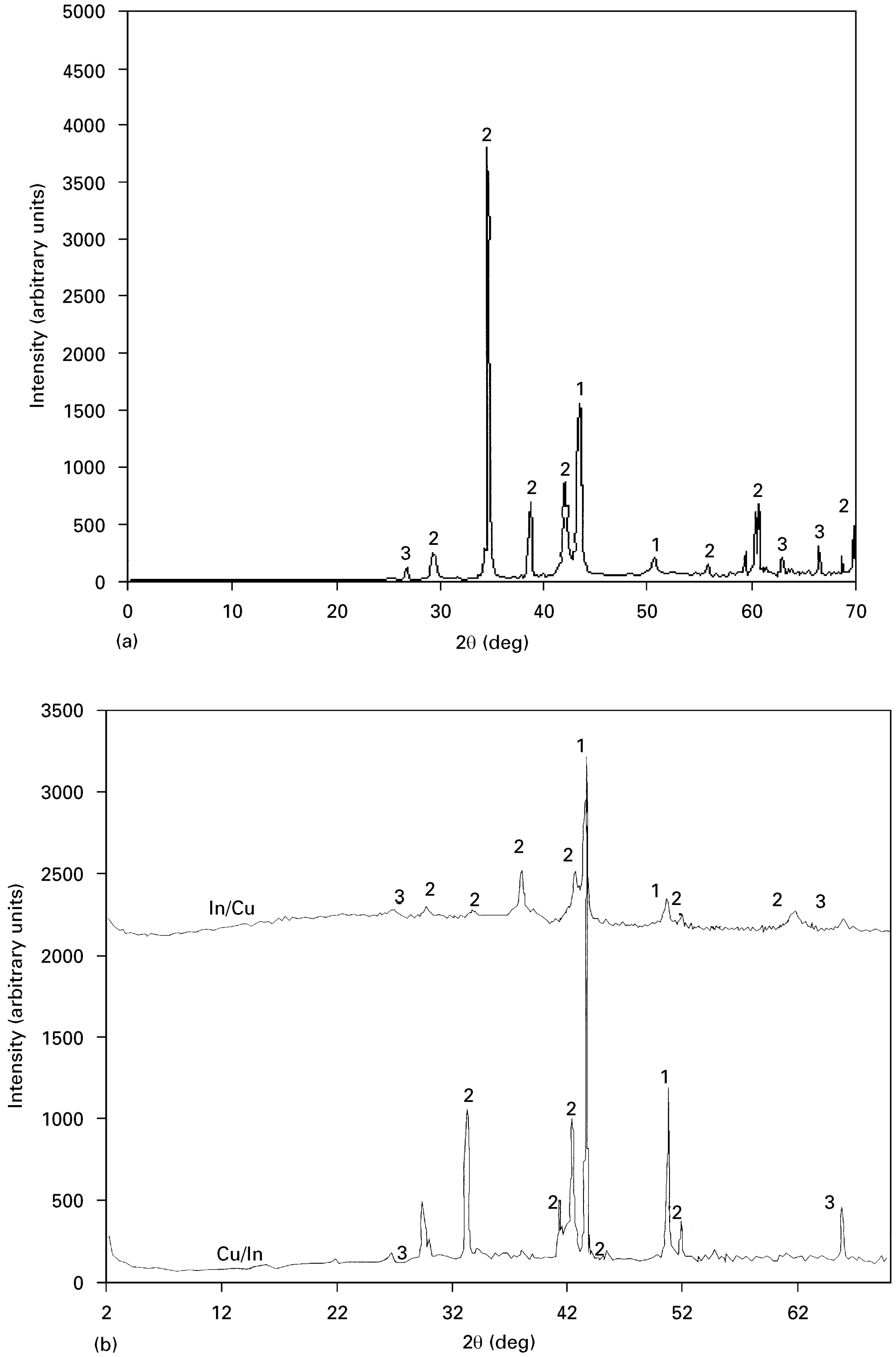


Figure 2 The XRD patterns for (a) the electroless-deposited Cu–In precursor and (b) the Cu/In and In/Cu precursors. Peaks 1, Cu; peaks 2, $Cu_{11}In_9$; peaks 3, In.

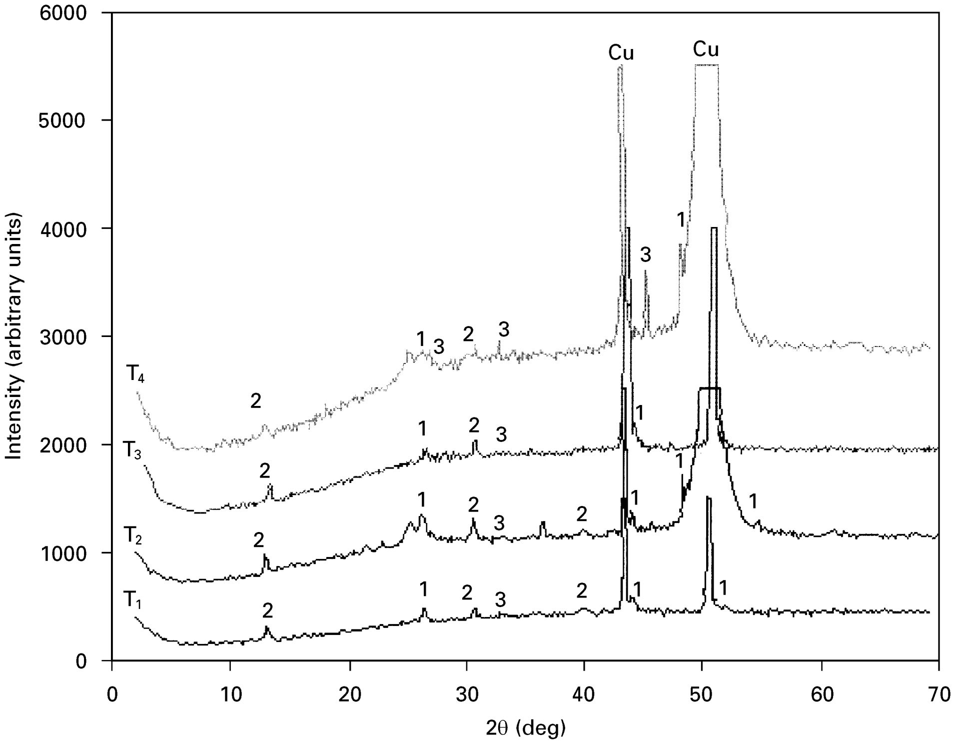


Figure 3 The XRD pictures for the Cu–In precursor after selenization at different temperatures.

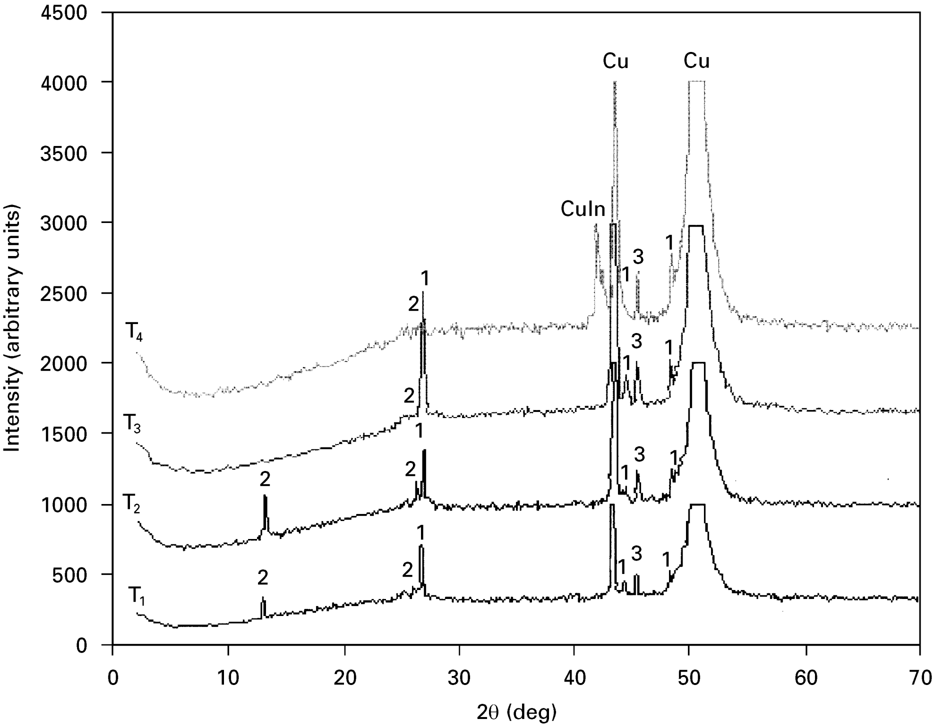


Figure 4 The XRD pictures for the Cu/In precursor after selenization at different temperatures.

d values for the cubic CIS [15], the chalcopyrite CIS [15] and the In-rich phase ($CuIn_2Se_{3.5}$) are given in Table I. Fig. 3 displays the XRD pattern for RCVTG-deposited CIS film corresponding to electroless-deposited Cu–In alloy on Cu substrate. In this case the CIS forms in the cubic form (Card 23-207 of [15]) with the maximum XRD reflection intensity originating from (2 2 0) planes. The *d* values of the CIS phase agree well with those of the standard cubic phase. Cu_2Se (Card 27-1131 of [15]) and In_2Se_3 appear to be the secondary phases at lower selenization temperatures.

The XRD pictures for the selenized stacked Cu/In and In/Cu precursors are shown in Figs 4 and 5, respectively. In both cases, the XRD reflections corresponded predominantly to the CIS chalcopyrite phase [15], but a few lines corresponded to the In-rich $CuIn_2Se_{3.5}$ phase [15]. In other words, it is correct to say that the film has a mixed phase. The formation of

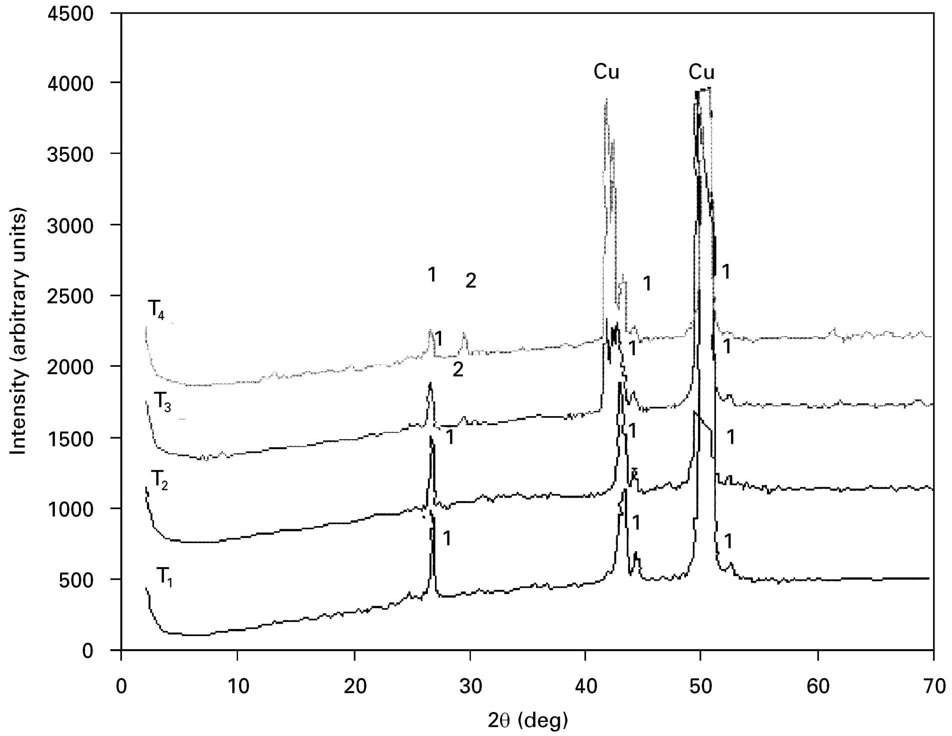


Figure 5 The XRD pictures for the In/Cu precursor after selenization at different temperatures. Peaks 1, CIS; peaks 2, Cu_xSe.

TABLE I The *d*-values for the selenized (550 °C) Cu–In precursors together with those of cubic CIS, chalcopyrite CIS and $CuIn_2Se_{3.5}$

d (nm)					
Cubic CIS	chalcopyrite CIS	$CuIn_2Se_{3.5}$	Cu–In	Cu/In	In/Cu
0.338	0.3351	0.3329	0.3385	0.3346	0.3341
	0.2154	0.2141			0.2152
0.207	0.2046	0.2039	0.2065	0.2057	0.2046
0.176	0.1745	0.174	0.1780	0.1763	0.1747

the In-rich phase together with that of the stoichiometric CIS has been reported earlier [18]. The $CuInSe_2$ and $CuIn_2Se_{3.5}$ phases have very similar XRD line positions and *d* values. The *d* values of the standard phases (CIS and In-rich phase) and that obtained in the present study are given in Table I for a comparison. In addition to the ternary compositions, Cu_2Se and In_2Se_3 phases are present in those films, which correspond to lower selenization temperatures.

The formation and composition of CIS films formed by selenization at different temperatures may be interpreted by the following chemical processes taking place during selenization [19] :

$$2In + Se \rightarrow In_2Se$$

$$In_2Se + Se \rightarrow 2InSe$$

$$2Cu_{11}In_9 + 20Se \rightarrow 11Cu_2Se + 9In_2Se$$

$$Cu_2Se + 2InSe + Se \rightarrow 2CuInSe_2$$

There is also another route [18] by which $CuInSe_2$ and $CuIn_2Se_{3.5}$ phases are formed as the final compositions during selenization. This is represented as a sketch in Fig. 6.

The morphologies of CIS films formed from different precursors are displayed in Fig. 7; Fig. 7a, b and c corresponds to CIS formed from Cu–In, Cu/In and In/Cu precursors, respectively. These SEM pictures exhibit two types of morphology, which are (i) well-defined ball-like crystals and (ii) crystals with a compact structure. It has been reported [20] that the compact structure is related to a more or less stoichiometric film composition with predominantly $CuInSe_2$ phase. The well-defined ball-like structure has been attributed to non-stoichiometric film composition with either Cu or In excess [21, 22], where Cu_2Se- or $CuIn_2Se_{3.5}$-like phases are present.

4. Conclusion

Electro-deposited or electroless-deposited Cu–In precursor films were selenized at various temperatures from 300 to 550 °C to form CIS thin films. Cu–In precursors were formed by layer-by-layer electrodeposition of Cu and In, but in electroless deposition the Cu–In precursor was formed by co-deposition. The major phases in the precursors were found to be $Cu_{11}In_9$ and elemental In. At lower selenization temperatures, the film composition consisted of binary phases (Cu_xSe and In_xSe_y), in addition to the ternary phases. It was found that the stoichiometric CIS phase ($CuInSe_2$) may be formed by selenization of the precursors at temperatures higher than 500 °C. The cubic CIS phase was formed when electroless-deposited Cu–In precursor was selenized, whereas the chalcopyrite CIS or the In-rich phase ($CuIn_2Se_{3.5}$) was formed when the layered precursors were selenized at a high temperature. The CVTG selenization has

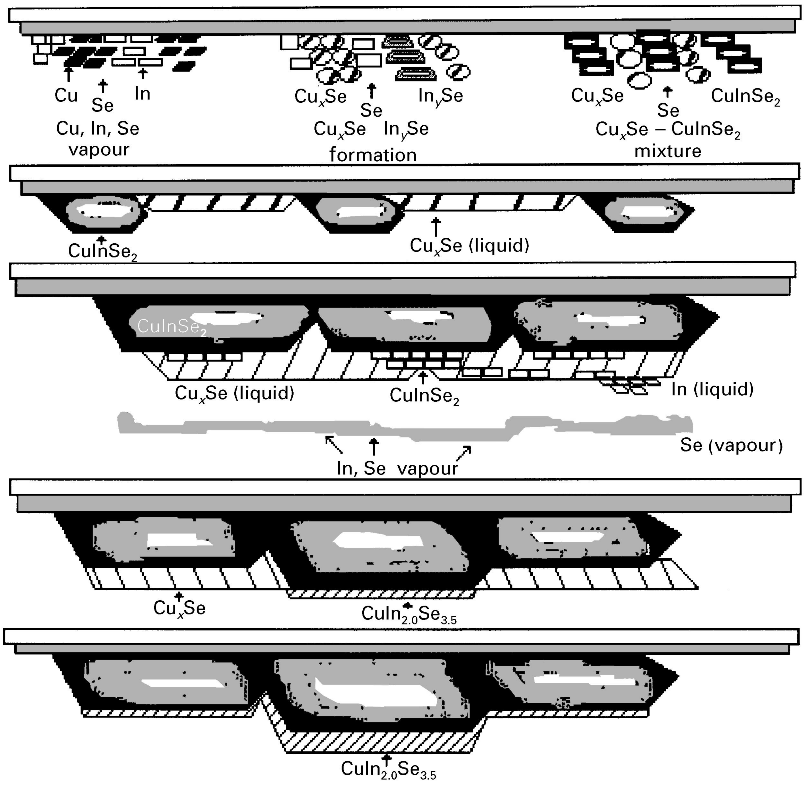
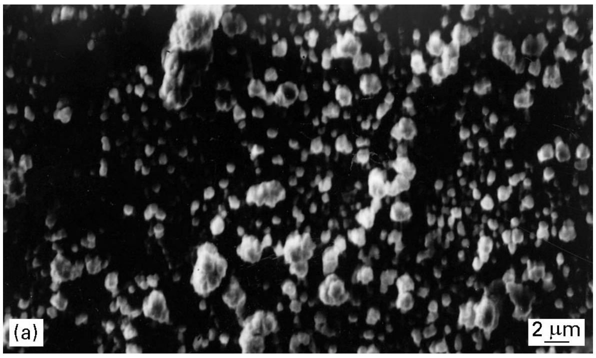


Figure 6 A representative sketch of the growth of $CuInSe_2$ and $CuIn_2Se_{3.5}$ phases from Cu–In precursors by selenization.



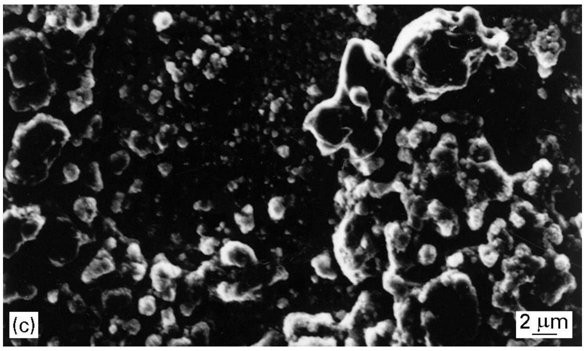


Figure 7 The scanning electron micrographs for CIS formed by selenization of (a) Cu–In, (b) Cu/In and (c) In/Cu precursors, (Magnifications, 1500x.)

turned out to be a viable CIS film-processing technique to develop CIS-based solar cell structures. Further studies are in progress in this direction.

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