Detection of binary phases in CuInSe$_2$ films formed by laser annealing of stacked elemental layers of In, Cu and Se

D. BHATTACHARYYA*, S. BOCKING, M. J. CARTER
Newcastle Photovoltaics Applications Centre, Department of EEEP, University of Northumbria at Newcastle, Newcastle Upon Tyne, NE1 8ST, UK

Thin layers of In, Cu and Se were deposited at ambient temperature by thermal evaporation onto freshly cleaned glass substrates. The films were annealed in an inert atmosphere by an Argon-ion laser operating on all green lines with the power varied from 200 mW to 1 W. The films were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and X-ray diffractometry (XRD). The temperature-increment of the different layers under the incident laser powers were calculated theoretically. These results were used to suggest a mechanism for the formation of the CuInSe$_2$ compound upon annealing the stack of elemental layers. It has been found that for the present form of the stack, the formation of the ternary chalcopyrite phase of CuInSe$_2$ takes place through the appearance of the binary phase and subsequent reaction amongst them.

1. Introduction

The CuInSe$_2$/CdS structure has proved to be an efficient polycrystalline solar cell device. CuInSe$_2$ films deposited by different methods have been shown to produce above 10% efficiency solar cell devices [1–5] and the highest total area efficiency reported so far is 16.4% [2]. Most of the CuInSe$_2$ films for devices with high efficiency have been fabricated by the three-source evaporation technique [4]. Despite the demonstration of cells manufactured by this technique and the excellent efficiency results in research devices, there is still doubt regarding its acceptance as a large scale production technique due to the inherent cost and area uniformity problems. Other techniques which have been extensively tried in order to deposit good quality CuInSe$_2$ films include electrodeposition [6], screen printing [7], the stacked elemental layer (SEL) method [8, 9] involving thermal annealing, sputtering [10] and the laser annealing of a stack of elemental layers [11, 12].

A potential low-cost fabrication technique is the laser processing of stacked elemental layers. The deposition of a stack of elemental layers of Cu, In and Se with subsequent annealing procedure to synthesize the chalcopyrite ternary compound of CuInSe$_2$ is viable for large area and low-cost production became the stoichiometry and hence the electro-optical properties of the films depend only on the initial thickness of the elemental layers, so that no sophisticated control of the deposition rate is required [8, 9]. This is in contrast with the case for the co-evaporation of the elements. The use of well established vacuum tech-

nologies for the deposition of the elemental layers makes it easier to obtain reproducibility.

Laser annealing is a possible method by which large area stacked elemental layers can be treated to synthesize the compound with desired stoichiometry and electro-optical properties. Lasers have already been proved to be useful in material processing and have been used extensively in areas like the recrystallization of ion-implanted regions of silicon single crystals [14], crystallization of amorphous semiconductor films [15] and the synthesis of semiconducting III–V and II–VI compounds such as AlAs, AlSb, CdTe and CdSe starting from the elemental constituents multilayered films [16–18]. As has been found by other workers, the reaction of transformation of materials by laser irradiation takes place in a very short time (over ~100 nm thickness in µs) and is thus suggestive of liquid rather than solid diffusion kinetics. However, estimates of the temperature-rise deny the possibility of fusion of the elements. It has been suggested that the reaction of transformation proceeds via the liberation of the heat of formation of the compound itself. This local heat liberation, coupled to the already high transverse temperature gradients that result from the focused laser beam, tends to produce rapid outward grain growth from the reaction site and large crystals of pure compounds can be produced by using this method. Thus laser annealing seems to be not just a fast furnace annealing process and this method additionally offers the possibility to control and vary the processing parameters such as the scan speed and the laser output power very accurately.

* Corresponding Author

The formation of good quality $CuInSe_2$ films with no binary phases of $CuSe$ or In_2Se_3 has been observed by Laude et al. [12]. It has been suggested that the $CuInSe_2$ formation takes place via the fast diffusion of In and Se atoms in the semi-molten Cu layer where all the Cu atoms have lost their cohesion upon the abrupt intrusion of the foreign atoms in concentrations far exceeding those of ordinary impurity atoms. This results in a chain structure like Cu–In–Se–In–Cu–Se where Se atoms are alternatively coupled to Cu and In atoms.

Thus laser annealing can be successfully used in annealing the stacked elemental layers of Cu, In and Se to produce stoichiometric device quality $CuInSe_2$ films and thus offers a low-cost large area scaling procedure for production of photovoltaic solar cell devices. Here, we report our studies on the evolution of a $CuInSe_2$ chalcopyrite structure from the stacks of thermally evaporated elemental layers of Cu, In and Se on irradiation by a laser. Systematic analysis has been done on the effect of the laser power on the structure of the compound formed and on the presence of other phases.

2. Experimental
2.1. Deposition
The stacked sandwich structures of total thickness ~ 1.5 μm were obtained by subsequent deposition of the elemental layers on freshly cleaned Corning 7059 glass substrates maintained at room temperature. The whole structure (Fig. 1) consists of one stack in which the elemental layers were deposited in the order of glass/In/Cu/Se by thermal evaporation under a vacuum of 10^{-4} Pa. The In, Se and Cu layers were deposited in a thickness ratio of 2.2:4.6:1.00 which is supposed to give rise to a nearly stoichiometric film. Cu and In were evaporated from molybdenum boats whilst Se was evaporated from a graphite effusion source with a greater thickness than that required for stoichiometry in order to compensate for Se loss during the annealing step. The in-situ thicknesses were controlled by quartz crystal monitors.

2.2. Laser annealing
The sandwich structures of about $1.5\ cm^2$ area were scanned with a focused cw Ar^+ ion laser beam oper-

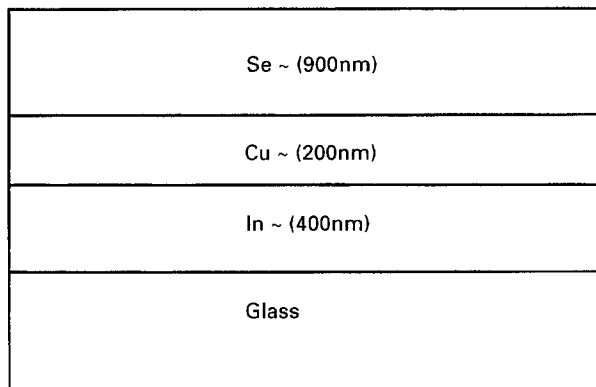| Se ~ (900nm) |
| Cu ~ (200nm) |
| In ~ (400nm) |
| Glass |

Figure 1 Schematic diagram of the stack of elemental layers.

ating on all green lines (457.9–514.5 nm). The actual maximum power output of the laser is 4.4 W. However the power was varied only between 0.4 to 1 W in this case after which ablation of the films was found to take place. The spatial profile of the beam is Gaussian with a diameter of $(1/e^2)$ on the sample of 1.25 mm at 514.5 nm. The samples were mounted on the outer edge of a rotatable disc. The disc could also be stepped laterally by small increments. The whole mounting assembly was computer controlled with the scanning speed and incremental displacements being pre-set. A typical scan speed of $2\ mm\ s^{-1}$ and a step increment of $80\ \mu m\ s^{-1}$ was used. The width of the processed track varied according to the power density and thus the lateral increments were adjusted to ensure that processed areas were adjacent and that there was no overlapping during successive scans. The processing was carried out in an inert atmosphere in order to avoid oxidation. The samples, thus annealed, were characterized by energy dispersive X-ray analysis (EDAX), scanning electron microscopy (SEM) and X-ray diffractometry (XRD).

3. Results and discussions
3.1. Scanning electron microscopy
The scanning electron micrographs of the films taken at low magnifications are shown in Fig. 2a–c, for films annealed at laser powers varying between 0.2 W and 1.0 W. The dark regions represent the areas scanned by the laser beam while the bright regions are the unannealed portions of the films. It has been clearly revealed from the micrographs that with an increase in laser power intensity an increasing amount of Se from the evaporated layer reacts with the Cu/In layer underneath. The dark areas in the micrographs are regions where $CuInSe_2$ grains are found to be formed. The SEM micrographs of those regions at higher magnifications are shown in Fig. 3a–c. There is no indication of grain growth in samples annealed at laser powers upto 0.4 W. Significant grain growth started to take place only at a laser power of 0.6 W. The grain sizes varied from 0.5 to 1.0 μm.

3.2. Compositional analysis
The EDAX analysis was done on both the annealed and unannealed portions of the films as found from the SEM observations. The EDAX analysis of the unannealed portions of the films show mainly Se which comes from the evaporated Se layer at the top. Fig. 4 shows the phase representation of the ternary compositional triangle for $CuInSe_2$ in terms of the binary compositions and the compositions of the samples annealed at different laser powers are shown on it. It has been found that for samples annealed at laser powers ~ 0.2–0.4 W, the composition of the annealed and the unannealed portions as measured by the EDAX are almost the same due to the presence of excess amount unreacted Se. However, for samples annealed at powers higher than 0.6 W, the compositions of the films get closer to that of the stoichiometry of $CuInSe_2$.
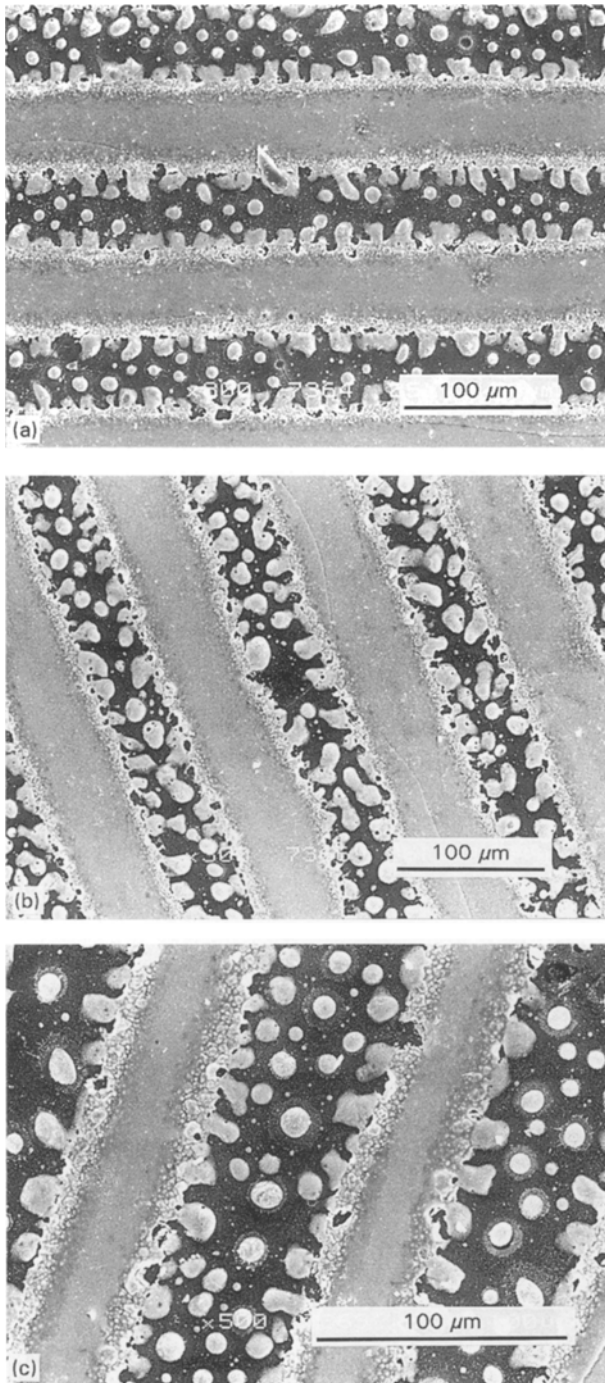
Figure 2. SEM micrographs at low magnification of the samples annealed at different laser powers: (a) 200 mW, (b) 600 mW and (c) 1 W.
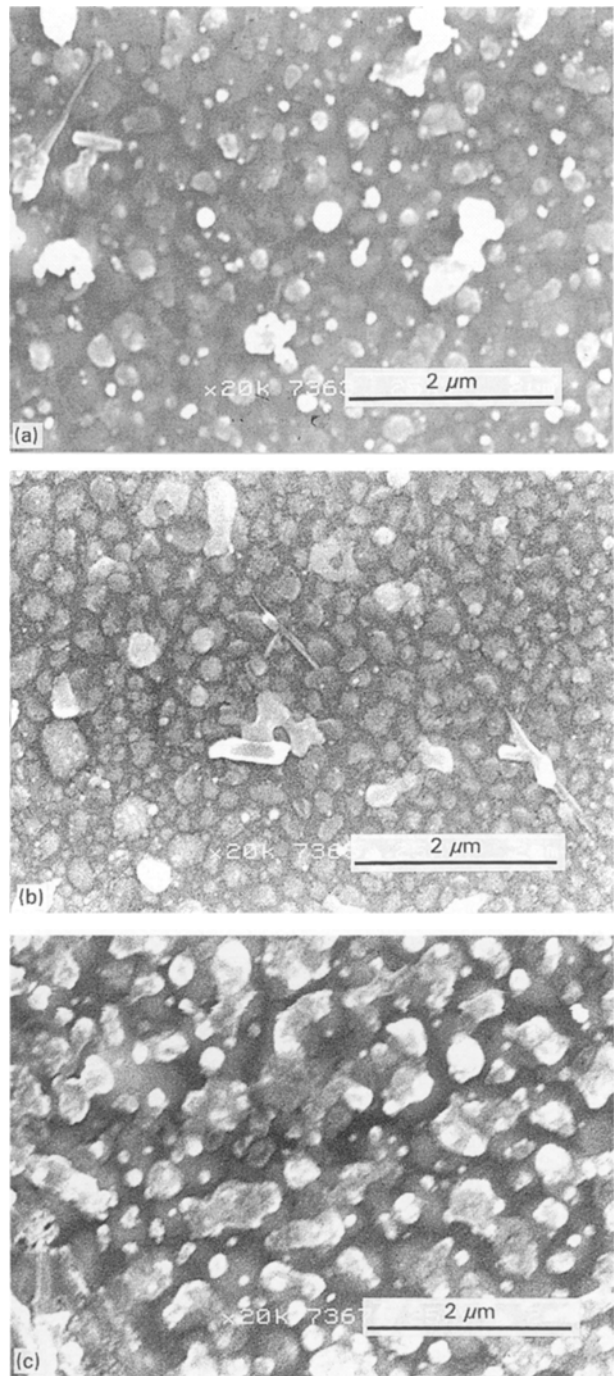

Figure 3 SEM micrographs at high magnification of the samples annealed at different laser powers: (a) 200 mW, (b) 600 mW and (c) 1 W.

3.3. X-ray diffraction

Fig. 5a–d shows the X-ray diffraction spectra of the laser annealed samples for different laser powers, which are characterized by the presence of peaks from the binary phases of CuIn, In_2Se_3, CuSe, $CuSe_2$ and Cu_2Se along with the peaks from the ternary chalcopyrite $CuInSe_2$. There is no sharp lower limit in the laser power intensity for the formation of only the ternary phase, although films annealed at laser powers equal to or higher than 1 W show mainly the characteristic chalcopyrite peaks of $CuInSe_2$. Fig. 6a shows the variation of the CuIn phase with the increase in the annealing power. It is found that the height of the CuIn peak decreases considerably for a laser power of
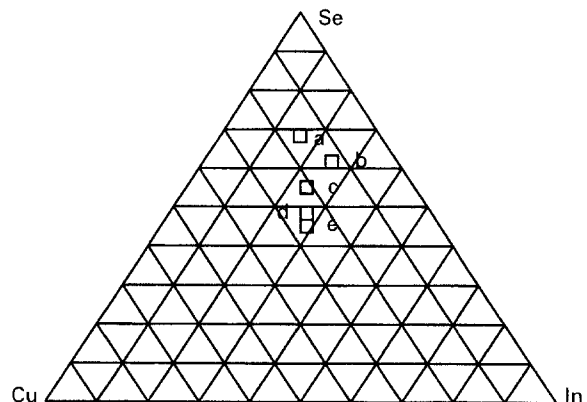

Figure 4 Representations of the compositions of the samples annealed at different laser powers in the ternary phase diagram: (a) 200 mW, (b) 400 mW, (c) 600 mW, (d) 800 mW and (e) 1 W.
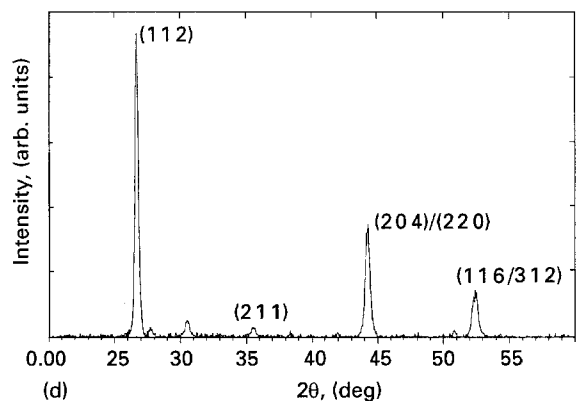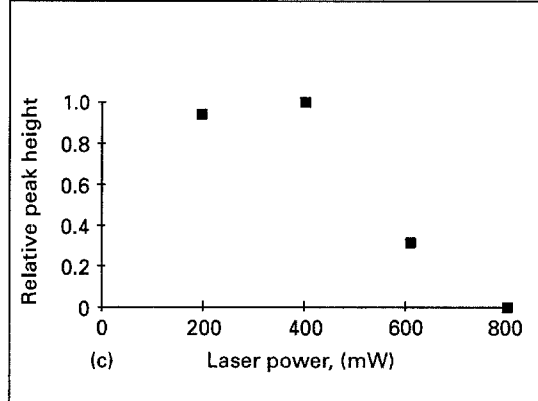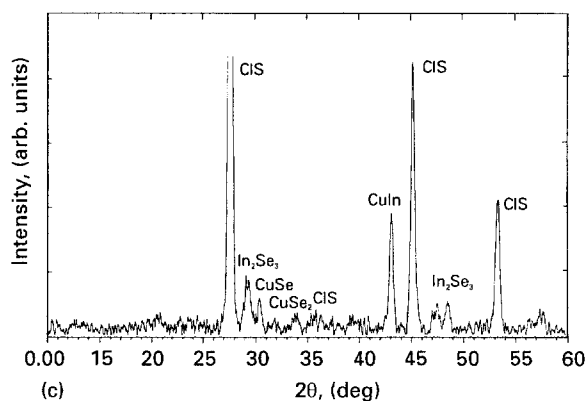
5453

Figure 6 Variation of the XRD peak intensities of the different binary phases with laser powers: (a) CuIn, (b) In$_2$Se$_3$ and (c) CuSe.
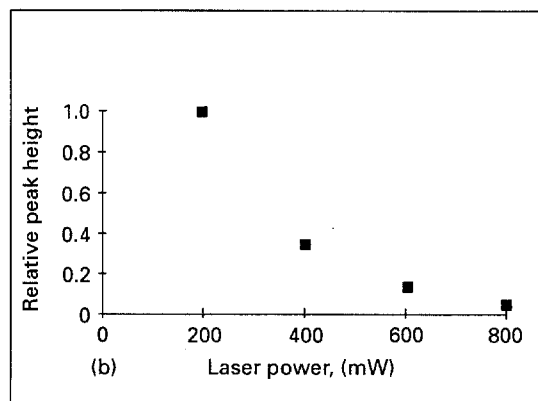
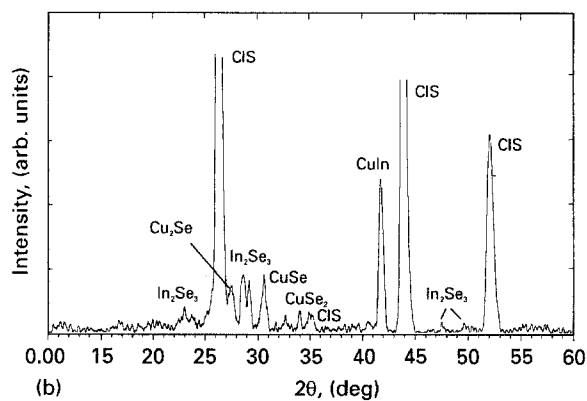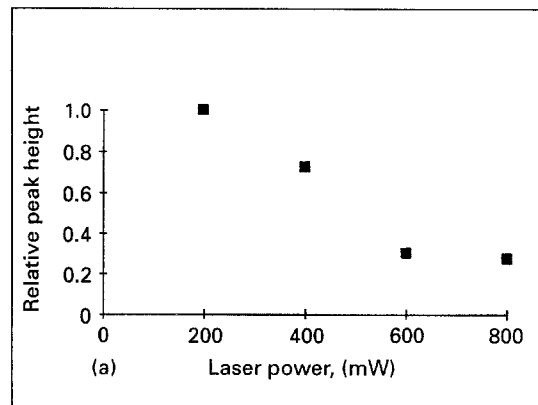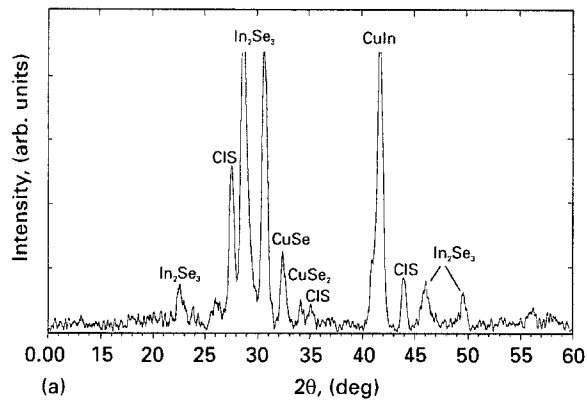Figure 5 XRD spectra of the samples annealed at different laser powers: (a) 200 mW, (b) 400 mW, (c) 600 mW and (d) 1 W.

phase is also found to decrease considerably above a laser power of 800 mW. The XRD spectrum of the samples annealed at 400 mW laser power (Fig. 5b) shows also the presence of the Cu$_2$Se peak which confirms the appearance of this binary phase in the process of formation of CuInSe$_2$. The above results suggest that the formation of CuInSe$_2$ from the elemental stacks considered here (Fig. 1), takes place through reaction amongst the binary phases.

Laude *et al.* [12] have suggested that the formation of CuInSe$_2$ by laser annealing does not involve the formation of the intermediate binary selenide phases. According to them, In and Se diffuse heavily into the Cu layer resulting in homogeneous and complete mixing of the three elements which couple together forming the strongest possible bond of ternary CuInSe$_2$. However, in the present stack of the three elemental layers as shown in Fig. 1, it has been found that the probability of complete mixing of the three elemental atoms is very small since the temperature rise of the In layer by the incident laser beam is too

600 mW above which most of the Cu–In is assumed to be reacted with Se to form CuInSe$_2$. Fig. 6b shows the variation of the In$_2$Se$_3$ peak (which arises at 2θ values of 27–28°) with laser annealing. It has been found that the In$_2$Se$_3$ peak exists also for samples annealed at higher laser power (1 W). Fig. 6c shows the variation of the CuSe peak with annealing power. The CuSe

little to allow sufficient diffusion of the In atoms into the Cu layer.

The temperature of the individual layers were calculated according to the model of Garrido et al. [19], which suggests that at a particular point (i, j) of a film (assuming that the thermal conductivities of the film and the substrates are independent of temperature):

$$T(i,j) = \frac{\Delta z^2}{2A} [T(i+1,j) + T(i-1,j)]$$
$$+ \frac{r^2 \Delta z^2}{4rA} [T(i+1,j) - T(i-1,j)]$$
$$+ \frac{\Delta r^2}{2A} [T(i,j+1) + T(i,j-1)] + \frac{\Delta r^2 \Delta z^2}{2KA} Q$$

(1)

where, K is the thermal conductivity ($K = K_D$ in the film and $K = K_S$ in the substrate), Δr is an element in the radial direction and Δz is an increment in vertical direction ($\Delta z = \Delta z_1$ in the film and $\Delta z = \Delta z_2$ in the substrate), $A = \Delta r^2 + \Delta z^2$ and Q gives the energy generated in a cylindrical volume ΔV of thickness Δz and radius R_0 placed inside a depth d from the surface, as:

$$Q = -(1-R)P \left[1 - \exp\left(-\frac{2R_0^2}{w^2}\right) \right]$$
$$\times \exp(-\alpha d) \frac{1 - \exp(-\alpha \Delta z)}{\Delta V}$$

(2)

where R is the reflection coefficient of the surface of the film, P is the laser power, α is the absorption coefficient and w is the radius of the laser beam at its focal point $(1/e^2)$. With the boundary conditions included, the Eqn. 1 at the boundary points give:

$$T(i,m) = B \left[\frac{T(i+1,m) + T(i-1,m)}{2\Delta r^2} (K_D \Delta z_1 - K_S \Delta z_2) \right.$$
$$+ \frac{T(i+1,m) - T(i-1,m)}{4r\Delta r} (K_D \Delta z_1 + K_S \Delta z_2)$$
$$\left. + T(i,m-1)\frac{K_D}{\Delta z_1} + T(i,m+1)\frac{K_S}{\Delta z_2} + Q \right]$$

(3)

where,

$$B = \frac{\Delta r^2 \Delta z_1 \Delta z_2}{\Delta z_2 K_D (\Delta z_1^2 + \Delta r^2) + \Delta z_1 K_S (\Delta z_2^2 + \Delta r^2)}$$ (4)

Considering the temperature to be almost constant at a depth far below the surface of the film where the laser beam is incident, i.e., $T(i, m+1) = T(i, m)$ for large values of m, we have:

$$T(i,m)\left(1 - \frac{BK_S}{\Delta z_2}\right) = B\left[\frac{T(i+1,m) + T(i-1,m)}{2\Delta r^2} \right.$$
$$\times (K_D \Delta z_1 - K_S \Delta z_2)$$
$$+ \frac{T(i+1,m) - T(i-1,m)}{4r\Delta r}$$
$$\times (K_D \Delta z_1 + K_S \Delta z_2)$$
$$\left. + T(i,m-1)\frac{K_D}{\Delta z_1} + Q \right]$$

(5)

and if we concentrate only at the centre of the layers, i.e., $i = 0$, we get:

$$T(0,m)\left(1 - \frac{BK_S}{\Delta z_2}\right) = B\left[\frac{T(0,m)}{\Delta r^2}(K_D \Delta z_1 - K_S \Delta z_2) \right.$$
$$\left. + T(0,m-1)\frac{K_D}{\Delta z_1} + Q \right]$$ (6)

which gives,

$$T(0,m-1) = T(0,m)\left\{ \left[\left(1 - \frac{BK_S}{\Delta z_2}\right) - \frac{B}{\Delta r^2} \right. \right.$$
$$\left. \left. \times (K_D \Delta z_1 - K_S \Delta z_2) \right] \middle/ \left(\frac{BK_D}{\Delta z_1}\right) \right\} - \frac{Q\Delta z_1}{K_D}$$

(7)

so that the temperature at the boundary points can be obtained by considering that the substrate is kept at an infinite sink of ambient temperature and the temperatures of the subsequent upper layers can be obtained from Eqn. 1.

The variation of temperature at different depths of the stack are shown in Fig. 7. It has been found that due to the high absorption coefficient of Cu, almost all of the laser radiation that can transmit through the Se layer, gets absorbed within a few nm layer near the surface of the Cu and consequently the temperature of the layers far below from the surface is not increased to a large extent. The surface temperature of the In layer is around 150 °C, irrespective of the intensity of the laser beam. This suggests that there should not be significant diffusion of the In atoms into the Cu layer to complete a homogeneous mixing. However, some of the CuIn binary phases, which can appear even at room temperature [20], can be present at the Cu–In interface, as has been obtained in the XRD spectra. The temperature of the Se layer is however, quite high since the laser beam is absorbed throughout the volume and also the temperature near the surface of the Cu layer is increased to a large extent before the heat is dissipated to the substrate.
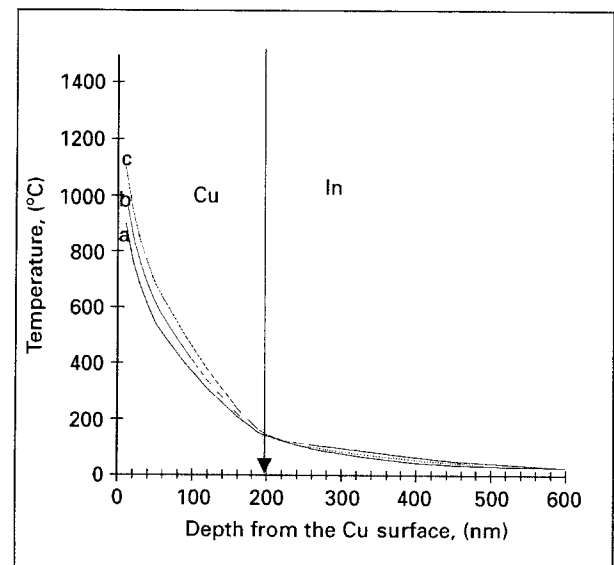

Figure 7 Variation of temperature at the centre of the different layers within the Cu–In stack under the incident laser beams of different powers: (a) 200 mW, (b) 600 mW and (c) 1 W.

This suggests that the formation of $CuInSe_2$ by the laser annealing of the stack of elemental layers involves the formation of the intermediate binary phases. Se atoms being highly energized come out breaking the amorphous-like loose structure of Se, diffuse heavily within the Cu layer and also into the In layer to produce $CuSe$, $CuSe_2$ and In_2Se_3. These binary phases liberate large amount of energies of formation (ΔH for $CuSe$ is $10\,kCal\,mol^{-1}$ and that for In_2Se_3 is $78\,kCal\,mol^{-1}$ (where $4.187\,cal = 1J$) [21]), which is sufficient to raise the temperatures of the Cu and In layers significantly. $CuSe$ and $CuSe_2$ at high temperature break up to form Cu_2Se. In_2Se_3 and Cu_2Se finally react to form the $CuInSe_2$ compound. That there is no sharp experimental lower limit to the laser power for the formation of $CuInSe_2$ can be realized in the light of the fact that the formation of $CuInSe_2$ at high temperature is assisted mainly by the heat generated from the formation of the binary phases.
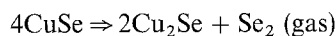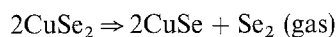
The formation of $CuInSe_2$ by laser-annealing of the stack of elemental layers is thus found to follow a similar reaction mechanism to that obtained in the case of fast furnace annealing of the stack [22, 23]. For an annealing temperature $T < 200\,°C$, Cu and In from the solid CuIn phase or liquid Cu or In phase reacts with Se to form the binary selenides:

$$Cu + Se \Rightarrow CuSe$$

$$Cu + 2Se \Rightarrow CuSe_2$$

and

$$2In + 3Se \Rightarrow In_2Se_3$$
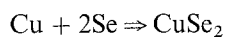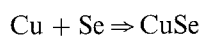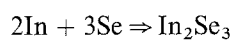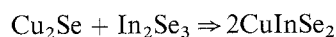
For annealing temperatures between 250–400 °C, the Se-rich copper selenides transform into Cu-rich selenides with the possible following exothermic reactions involving a considerable loss of Se.

$$2CuSe_2 \Rightarrow 2CuSe + Se_2 \text{ (gas)}$$

$$4CuSe \Rightarrow 2Cu_2Se + Se_2 \text{ (gas)}$$

and finally, at 400 °C or above, Cu_2Se reacts with In_2Se_3 to form $CuInSe_2$:

$$Cu_2Se + In_2Se_3 \Rightarrow 2CuInSe_2$$

4. Conclusion

Laser annealing of a thermally evaporated In/Cu/Se stack at different laser powers has been done to investigate the mechanism of formation of the ternary chalcopyrite compound $CuInSe_2$. Calculations show that the temperature-increments at different layers of the stack caused by the incident laser beam are not high enough to allow sufficient diffusion to form a complete and homogeneous mixture of the three elements. Based on the XRD observations, a model has been suggested for the formation of $CuInSe_2$, where Se atoms being highly energized diffuse into the Cu and In layers, forming the binary selenides viz. $CuSe$, $CuSe_2$ and In_2Se_3. It liberates a considerable amount of energy which further increases the temperature of the different layers and finally $CuInSe_2$ is formed by the reaction among the binary selenides.

References

1. J. KESSLER, S. WIEDEMAN, L. RUSSELL, T. LOMMASSON, S. SKIBO, J. FOGLEBOCH, T. CLOSS and R. R. ARYA, Proceedings 24th Institute of Electrical and Electronic Engineers Photovoltaic Specialists Conference, Hawii 1994 (IEEE, New York, 1994) 206.
2. A. M. GABOR, J. R. TUTTLE, M. CONTRERAS, D. S. ALBIN, A. FRANZ, D. W. NILES and R. NOUFI, Proceedings 12th European Photovoltaic Solar Energy Conference, Amsterdam 1994 edited by R. Hill, W. Palz and P. Helm (H. S. Stephens, Bedford, 1994) 939.
3. B. M. BASOL, V. K. KAPUR, A. HALANI, Proceedings 22nd Institute of Electrical and Electronic Engineers Photovoltaic Specialists Conference, Las Vegas 1991 (IEEE, New York, 1991) 893.
4. K. MITCHELL, C. EBERSPACHER, J. ERMER and D. PIER, Proceedings 20th Institute of Electrical and Electronic Engineers Photovoltaic Specialists Conference, Las Vegas 1988 (IEEE, New York, 1988) 1384.
5. W. E. DAVANEY, R. A. MICKELSEN and W. S. CHEN, Proceedings 18th Institute of Electrical and Electronic Engineers Photovoltaic Specialist Conference, Las Vegas 1985 (IEEE, New York, 1985) 1733.
6. Y. H. KIM, Y. E. LEE, H. J. KIM and J. SONG, Proceedings 24th Institute of Electrical and Electronic Engineers Photovoltaic Specialists Conference, Hawii 1994 (IEEE, New York, 1994) 203.
7. A. VARVAET, M. BURGELMAN, I. CLEMMINCK and J. CAPON, Proceedings 9th European Photovoltaic Solar Energy Conference, Frieberg, 1989 edited by W. Palz, G. T. Wrixon and P. Helm (Kluwer, Dordrecht, 1989) 480.
8. A. KNOWLES, H. OUMOUS, M. J. CARTER and R. HILL, Proceedings 20th Institute of Electrical and Electronic Engineers Photovoltaic Specialists Conference, Las Vegas 1988 (IEEE, New York, 1988) 1482.
9. F. ADURODIJA, M. J. CARTER and R. HILL, Proceedings 24th Institute of Electrical and Electronic Engineers Photovoltaic Specialists Conference, Hawii 1994 (IEEE, New York, 1994) 186.
10. N. ROMEO, V. CANEVERI, G. SBERVEGLIERI, A. BOSIO and L. ZANOTTI, Solar Cells 16 (1986) 155.
11. T. W. WALTER, M. J. CARTER and R. HILL, Proceedings 9th European Photovoltaic Solar Energy Conference, Frieberg, 1989 edited by W. Palz, G. T. Wrixon and P. Helm (Kluwer, Dordrecht, 1989) 115.
12. L. A. LAUDE, M. C. JOLIET and C. ANTONIADIS, Thin Solid Films 16 (1986) 199.
13. A. KNOWLES, H. OUMOUS, M. J. CARTER and R. HILL, Semiconductor Science and Technology 3 (1988) 1143.
14. J. F. GIBBONS, K. A. MITROPOULOS and N. B. MYANT (eds), Laser and Electronbeam Solid Interactions and Materials Processing, Vol. 1, (North-Holland, Amsterdam 1981).
15. G. VITALI and G. CREA, Vacuum 36 (1986) 643.
16. M. NEUMANN-SPALLART, C. LEVY-CLEMENT and G. GRABNER, J. Phys. D. Appl. Phys. 27 (1994) 407.
17. R. ANDREW, M. LEDEZMA, M. LOVATO, M. WAUTELET and L. D. LAUDE, Appl. Phys. Lett. 35 (1979) 418.
18. R. ANDREW, L. BAUFAY, A. PIGEOLET and L. D. LAUDE, J. Appl. Phys. 53 (1982) 4862.
19. C. GARRIDO, J. Appl. Phys. 69 (1991) 1133.
20. H. DITTRICH, U. PRINZ, J. SZOT and H. W. SCHOCK, Proceedings 9th European Photovoltaic Solar Energy Conference, Frieberg, 1989 edited by W. Palz, G. T. Wrixon and P. Helm (Kluwer, Dordrecht, 1989) 163.
21. O. KUBASCHOWSKI and E. L. EVANS, Metallurgical Thermochemistry, (Pergamon, N. Y, 1958) p. 123.
22. F. O. ADURODIJA, Ph.D. Thesis, University of Northumbria at Newcastle, Newcastle Upon Tyne, U.K, 1994.
23. F. O. ADURODIJA, M. J. CARTER and R. HILL, Sol. En. Mater. and Solar Cell 37 (1995) 203.