Northumbria Research Link

Study of the Al-grading effect in the crystallisation of chalcopyrite $CuIn_{1-x}Al_xSe_2$ thin films.

S. Martín [a,*], G. Zoppi [b], R. Aninat [b+], I. Forbes [b] and C. Guillén [a]

[a] CIEMAT, Departamento de Energía, Avda. Complutense, 40. E-28040 Madrid, Spain.

[b] Northumbria Photovoltaics Applications Centre, Northumbria University, Ellison Building, Newcastle upon Tyne, NE1 8ST, UK

* Corresponding author. Avda. Complutense, 40 Madrid, 28040 Spain.Tel.:+34 913466679; fax: +34 913466037. Avda. Complutense, 40 Madrid, 28040 Spain. E-mail address: sofia.martin@ciemat.es (S. Martín).

[+] Now at Now at: Département Sciences et Analyse des Matériaux, Centre de Recherche Public - Gabriel Lippmann, 41, rue du Brill, L-4422 Belvaux, Luxembourg

Abstract

Chalcopyrite $CuIn_{1-x}Al_xSe_2$ (CIAS) thin films with an atomic ratio of Al/(In+Al)=0.4 were grown by a two-stage process onto soda-lime glass substrates. The selenisation was carried out at different temperatures, ranging from 400ºC to 550ºC, for metallic precursors layers evaporated with two different sequences. The first sequence, C1, was evaporated with the Al as the last layer, while in the second one, C2, the In was the last evaporated element. The optical, structural and morphological characterisations led to the conclusion that the precursors sequence determines the crystallisation pathway, resulting in C1 the best option due to the homogeneity of the depth distribution of the elements. The influence of the selenisation temperature was also studied, finding 540ºC as the optimum one, since it allows to achieve the highest band gap value for the C1 sequence and for the given composition.

Keywords:

Chalcogenides; thin films; crystal growth; evaporation.

1. Introduction

$CuIn_{1-x}Ga_xSe_2$ (CIGS) is currently receiving the most attention as a thin film photovoltaic absorber since it yields the most efficient solar cell devices both on small [1] and large [2] area devices. However there are other options available in the $CuInSe_2$ (CIS) chalcopyrite material family [2], less studied until now, which appear as a good alternative to this compound. Among them, the partial substitution of indium by aluminium presents great advantages: in one hand, the aluminium is more abundant and therefore less expensive than gallium or indeed indium. On the other hand, for equivalent substitution, aluminium produces a larger band gap change in CIS than Ga due to the smaller size of the Al atom [3]. Thus, the $CuIn_{1-x}Al_xSe_2$ (CIAS) compound allows the adjustment of the energy band gap from Eg=1.0 eV ($CuInSe_2$) to Eg= 2.7 eV ($CuAlSe_2$) [4], allowing its use in single and multi-junction solar cells [5]. The optimum band gap for terrestrial applications, i.e. 1.4 eV [6], can be achieved with less Al substitution than Ga, causing less variation in the lattice spacing of CIS structure [7]. Furthermore, in spite of the disorder of the lattice induced by Al incorporation in the CIS matrix, the defects introduced are not as deep as the ones reported in CIGS, which are known to limit the solar cell efficiency in high-Ga content CIGS devices [3]. For all these reasons $CuIn_{1-x}Al_xSe_2$ has been considered as promising alternative. An interesting manufacturing process to obtain CIAS thin films is the two stage process consisting on the selenisation of evaporated stacked metallic precursors [8]. This method allows the control of the individual thicknesses in the metallic precursor layers, as well as their evaporation order. In this work the influence of the precursor stack sequence and the selenisation temperature on the optical, structural and morphological properties are studied for CIAS thin films deposited on soda lime glass (SLG) by a two stage process. Noticeable differences in the depth profile of the metallic ratios have been observed between the two precursors sequences used.

2. Experimental details

CuIn$_{1-x}$Al$_x$Se$_2$ absorber layers were produced by selenization of evaporated metallic precursors onto glass substrates. Two different precursor sequences were used in order to investigate their influence in the CIAS formation. The first one, C1, was evaporated in the sequence SLG/In/Cu/In/Al and the second one, C2, followed the sequence SLG/In/Cu/Al/In. Evaporations were carried out in a single deposition system by e-beam evaporation of Cu and In and thermal evaporation of Al. The base pressure in the vacuum chamber was less than 10^{-4} Pa. The substrates were rotated during evaporation to promote good uniformity of the deposited layers. The individual layer thicknesses were controlled by quartz crystal microbalance monitoring and adjusted to obtain the desired metallic proportions. The total thickness of the metallic precursor for both sequences was ~4000Å. The thickness of the individual layer was chosen to yield atomic ratios of Al/(In+Al)=0.4 and Cu/(In+Al)=0.8. The precursor layers and elemental selenium were put together within a partially closed graphite box which was loaded in a quartz tube furnace for selenisation at different temperatures. Selenisation took place at 1,013·10^5 Pa under an Ar flux that remains constant throughout the process. The selenisation process was carried out in three steps as described in previous works [9, 10]. In order to study the influence of the last temperature step in the CIAS formation and crystallization, the samples are analysed over the temperature range 400ºC-550ºC. A distinction is made between the lower range 400ºC to 500ºC and the higher range 520ºC to 550ºC. 400ºC is chosen as the minimum temperature required to form CIS[10, 11]; while temperatures greater than 520ºC are necessary to crystallise CIAS [10, 12]. Absorber thin films of 1.2 ± 0.1 µm average thickness were obtained after the selenisation processes.

The optical transmittance (T) and total reflectance (R) of the samples were measured with a Perkin–Elmer LAMBDA 9 double beam spectrophotometer with integrating sphere in the 300-1800 nm wavelength range at room temperature, taking the air as reference. The optical absorption coefficient was calculated as a function of the photon energy from T, R and the film thickness (DEKTAK 3030 profilometer) values, and allowed to determine the corresponding absorber band gap energy. The chemical composition was determined by energy dispersive analysis of X-ray (EDX) with an Oxford Instruments X-Max detector with a resolution of 124 eV. The surface

morphology was examined by a Hitachi SU-6600 Scanning Electron Microscope (SEM) and the structural characterization was carried out by means of X-ray Diffraction (XRD) using a PHILIPS X'PERT diffractometer with CuK_α (λ= 1.54056 Å) radiation. Peak diffraction angles in the XRD patterns were converted to interplanar d-spacings and thus, phase identification has been carried out by comparison of the observed d-spacing with the Joint Committee on Powder Diffraction Standards (JCPDS). Depth profiling of the elements was performed by secondary ion mass spectroscopy (SIMS) using a VG Scienta and Hiden Analytical combined setup. A primary beam of oxygen or argon with an impact energy of 3.5 keV and beam current of 400 nA was used to sputter over a 500x500 μm rastered area. The data was collected over a 10% gating area in order to eliminate any effect from the side walls of the crater.

3. Results and discussion

3.1 EDX analysis

The EDX analyses carried out for the as-grown precursor layers and for the samples selenised at high temperatures are included in Table I by means of the atomic ratios. The results show the good agreement of the obtained values for the selenised samples with the data of the metallic precursor layers. This indicates that the differences observed in the subsequent properties analysed are not induced by changes in the overall metallic or selenium proportions.

3.2 Structural properties

The crystalline structure of the selenised films was characterised by XRD. The objective of this work is to optimize the formation of crystalline $CuIn_{1-x}Al_xSe_2$ with x=Al/(In+Al) close to 0.4 in order to match optimum absorption of the solar spectrum [13]. Since no JCPDS standard files are available for CIAS, $CuInSe_2$ [14] and $CuAlSe_2$ [15] standards were used to identify the formation of $CuIn_{1-x}Al_xSe_2$ according to Vegard's law, with a linear increase in lattice spacing as a function of x.

Fig. 1 and 2 show the XRD patterns for the two sequences, C1 and C2, selenised at low temperatures, 400ºC, 450ºC and 500ºC. In both sequences it is observed the presence of the main peaks (1 1 2), (2 0 4)/(2 2 0), (3 1 2)/(1 1 6) and (4 0 0) together with the smaller ones (1 0 1), (1 0 3), (2 1 1) and (1 0 5) which indicates the chalcopyrite structure of all these thin films. CuSe phases [16] are also detected together with the main structure.

For the samples selenised at 400ºC the two sequences show the same angular position for the main peak (1 1 2) corresponding to an interplanar spacing of d=3.35 Å, indicating the formation of CIS chalcopyrite [14]. Other peaks more difficult to see, marked in the graphs by red asterisks, are also identified to the right of the most intense peaks. This seems to indicate the presence of a CIAS phase, with low crystallinity. A similar behaviour is observed for the C2 samples selenised at these low temperatures. A noticeable difference is observed in C1_500 spectrum, which shows an elevated content in CuSe together with a broadening of the main diffraction peaks.

The XRD patterns for the C1 and C2 sequences heated at high temperatures (520ºC, 540ºC and 550ºC) also show the main chalcopyrite structure together with secondary CuSe phases (not shown). A more detailed analysis of these spectra is given in Fig. 3 and 4 where detail of the main (112) peak of these samples is presented. It is noticed in Fig. 3 that C1 samples selenised at 520ºC and 540ºC have the (112) peak located in the same position. At the highest temperature this position shifts to lower values closer to that expected of lower Al containing CIAS. However, at this temperature of 550ºC, the main peak also exhibits a shoulder, indicating phase separation with several Al content ranging from x=0.1 to x=0.5. The region around the (112) peak of C2 samples selenised at high temperature are plotted in Fig. 4. The samples selenised at 520ºC and 550ºC present both the same localization for the main peak (26.70°), and also show other shoulder peaks at higher angles. The maximum shift of the main peak to higher angles is achieved at 540ºC (26.84°). This peak also exhibits a splitting of phases indicated by the non-symmetry of the peak.

Fig. 5 displays the dependence between the (1 1 2) interplanar spacing, d(112), and the temperature for C1 and C2 samples. The graph is bounded between the standard values for CIS (d=3.35) and the calculated value

according to the Vegard's law for the Al ratio x=0.4 (d=3.29). Both sequences show similar trends; the increase in selenisation temperature promotes the decrease of the interplanar distance until the lowest value is achieved for 540⁰C. The C1 samples show a larger displacement in d(112) compared to CIS, indicating a higher Al incorporation in the lattice. In both situations the increment of the temperature to 550⁰C entails an increase in d(112) indicating a lower Al incorporation. In all cases the value of d(112) is greater than expected for x=0.4 indicating incomplete Al incorporation.

In order to measure the effect of the precursor sequence and selenisation temperature on the texture and preferential orientation of the samples, the texture coefficients C_{hkl} were studied for the reflections exhibited in the XRD spectra, excluding (103) due to the overlapping with the CAS phase detected. These coefficients were calculated by means of the following equation [17, 18]:

$$C_{hkl} = \frac{I(hkl)}{I_0(hkl)} \Big/ \frac{1}{n} \sum_{hkl} \frac{I(hkl)}{I_0(hkl)} \tag{1}$$

where *I(hkl)* is the measured intensity of the peak *(hkl)* for the film, $I_o(hkl)$ the relative powder intensity, and *n* is the number of diffraction peaks considered, 7 in this case. Since no patterns are available for CIAS, CIS is used as the reference standard. Due to the difficulty of distinguishing the two peaks existing in (204)/(220) and (312)/(116), only one peak has been considered, using the highest intensity registered in the measurement and the powder intensity of the $I_0(220)$ and $I_0(312)$ peaks, respectively. $C_{hkl} = 1$ indicates random orientation for all peaks *hkl,* whereas the highest possible value, $C_{hkl} = 7$, will be obtained only for one reflection, for films totally textured in that particular direction.. C_{112} is shown (Table II) to be invariant along the temperature range investigated and this is also valid for the other C_{hkl}, C_{112} being of the highest value indicating only a slight texturing in the (112) direction. C1 samples appeared slightly more textured than C2 in the low temperature range, but are indistinguishable for higher temperatures.

The degree of preferential orientation, σ, calculated as

$$\sigma = \sqrt{\sum \frac{1}{n} \left(C_{hkl} - 1\right)^2} \tag{2}$$

allows the comparison of different samples as a whole. The preferred orientation, shown in Table II for the different samples and sequences, exhibits values far from the maximum expected for totally oriented layers, σ=2.5, confirming the randomness of the samples. Those results are typical for chalcopyrite films deposited by a 2-stage process [19, 20].

The average crystallite size in the (1 1 2) plane direction was estimated according to the Scherrer's formula:

$$S_{112} = \frac{0.9\lambda}{B\cos\theta} \tag{3}$$

where S_{112} is the crystallite mean size in nm, λ the X-ray wavelength in nm, θ the diffraction angle and B is the value of the full width at half maximum (FWHM). The results as function of the selenisation temperature are plotted in the insert of Fig. 5. The obtained data show that the crystallite sizes derived from the most intense peak of C1 samples decrease sharply in the low temperatures from 69 nm to 26 nm, whereas for C2 samples the crystallite size remains constant at 52 nm. At high temperatures C1 shows small sizes S_{112}=23-30 nm for T=520ºC-540ºC, which correspond to the lowest d(112) values, and also C2 shows a minimum of S_{112}=30 nm at T=540ºC. By increasing to T=550ºC, C1 size increases to 35 nm, whereas in the case of C2 sample S increased to 52 nm.

3.3 Optical properties

The transmission, T, and reflection, R, spectra of all the samples analysed in this work are shown in Fig. 6-9. Fig. 6 shows the T and R variations of C1 samples for 400ºC ≤ T ≤ 500ºC. It is noticed that the transmission increases with temperature, achieving the highest value at 500ºC. In the reflectance spectra it is observed a high similarity between the samples heating at 400ºC and 450ºC, with the same position and width of the edge appreciated.

However, C1_500 sample exhibits a widening of this edge, indicating the appearance of additional phases which absorb at higher energies. For C2 samples (Fig. 7) the change between the different temperatures is harder to see. In this case, C2_400 transmission registers the highest values. C2_450 and C2_500 exhibit the same transmission and reflectance curves, although the edge observed in the R curves of C2_500 is softer than C2_450, indicating again the existence of extra phase(s).

For C1 samples selenised at high temperatures (Fig. 8), the highest transmission value achieved is 15%, at 540ºC, whereas 550ºC and 520ºC provide values around those obtained at 500ºC. In the reflection spectra C1_540 also exhibits the maximum displacement of the edge toward low wavelengths. For C2 layers (Fig. 9) the edge observed in the reflectance curve appears exactly in the same position, 1200 nm, however, this edge is also wider than that exhibited at lower temperatures.

The absorption coefficient α was calculated from the transmission T and reflection R data and the film thickness, t, for the different samples by using the following equation [9]:

$$\alpha = -\left(\frac{1}{t}\right) \ln \left(\frac{\left[(1-R)^4 + 4T^2 R^2 \right]^{1/2} - (1-R)^2}{2TR^2} \right) \qquad (4)$$

Since these chalcogenide compounds are direct gap semiconductors [21], in order to estimate the optical energy band gap (E_g) the next equation is used [22]:

$$\alpha = \frac{A_a}{h\nu} \left(h\nu - E_g \right)^{1/2} \qquad (5)$$

where A_a is a constant which depends on the transition nature, the effective mass and the refractive index and $h\nu$ is the incident photon energy. The energy band gap E_g is estimated from the extrapolation of the linear portion of the curve $(\alpha h\nu)^2$ vs $h\nu$ from Eq. 5. This is shown in Fig. 10 and 11 for the samples selenised at high temperatures for C1 and C2 samples, respectively. The

values obtained for all the samples are included in Table II. As it was already deduced from the T and R spectra, the C1 sequence allows for a greater widening of the band gap compared to C2.

3.4 SIMS analysis

Since 540ºC seems to be the best option for both sequences, the samples selenised at this temperature were analysed by SIMS. The results obtained are depicted in Fig. 12. It is observed that the In and Se profiles for both C1 and C2 are similar slightly decreasing as a function of depth. However the Al and Cu profiles exhibit noticeable differences. For C1 sample the distributions of Al and Cu remain constant with depth, but in C2 sample both profiles increase towards the glass substrate. The uniform distribution of metals throughout C1 film suggests a good homogeneity of the phases formed, whereas the C2 profiles indicates phase separation with the formation of Al-rich phases near the glass interface, and In-rich near the surface of the film. The comparison of the depth profiles indicates that the x values remains fairly constant with depth for C1 but increases significantly for C2 towards the glass substrate. This is consistent with the previous optical data that showed a lower overall gap value for the C2_540 than the C1_540 sample. This can be used as an interesting tool for future studies of the natural Al-grading in CIAS thin film solar cells, as has been previously studied in CIGS, where Ga grading increases the carrier collection and improves back contact passivation [23, 24].

The utilization of Al as the top layer of the precursor preparation would generally be avoided due to the strong oxidation rate of Al. As shown in Fig. 13 the aluminium oxides depth profiles were marginally different. Although the samples exhibit completely different Al profile, both are equally oxidised throughout the depth, although near the surface the oxides intensities are higher in C1, possibly due to the higher Al content. Therefore, the presence of Al on the top of the precursors does not seem to produce the Al oxidation before the selenisation, according to previous results [25].

Due to the important differences exhibited in the structural and optical properties between C1_540 and C1_550, the SIMS depth profiles obtained of

these samples are depicted in Fig. 14. The spectra can be divided into two zones, separated by the dotted line. On the left side, Al and In are detected at the same intensity levels, whereas Cu is higher for C1_550. However, when the sample is sputtered further, Cu remains constant for both samples, whereas Al and In intensities are higher for C1_550 sample. Therefore the differences observed previously between C1_540 and C1_550 are not a consequence of a sharp change of the Al/(In+Al) ratio as is the case for the C2 sequence (Fig. 13), since the In and Al profiles change simultaneously.

3.5 Morphological properties

SEM images of the film surface of the samples C1 and C2 selenised at high temperatures are shown in Fig. 15. Both sequences show a homogeneous morphology across the surface, exhibiting a similar evolution from small (520ºC) to higher aggregates (540ºC), with an enhancement of the grain coalescence at the highest temperature (550ºC). At 520ºC, C1 samples show a mix of grains with larger grain surrounded by smaller features related to CuSe phases. The grains become larger as the temperature increases, and the CuSe grains disappear. However, at 550ºC, the presence of small grains under the top conglomerates can be seen. This heterogeneity is best observed in C2 sequence, heated at 520ºC. It is clearly noticed different grain sizes, with the largest ones on top of smaller grains. With the increment of the temperature, the surface morphology shows high interdiffusion among the grains indicating an advanced stage of recrystallisation.

4. Conclusions

Chalcopyrite $CuIn_{1-x}Al_xSe_2$ thin films have been grown onto soda-lime glass substrates by a selenisation process at different temperatures ranging from 400ºC to 550ºC using two different sequences of stacked evaporated metallic precursors (C1 named after Al ending and C2 after In ending). Optical, morphological and structural properties have been studied, concluding that both the temperature and the sequence play an important role in the CIAS formation and crystallisation. At low temperatures (400-500ºC) the evolution for the two

sequences is notably different. Using C1 precursor great changes in the structural and optical properties are detected, suggesting a correct pathway to CIAS crystallisation, C2 samples remains fairly invariant. These results observed at low temperatures affect noticeably the growth at high temperature (520-550ºC). Therefore, the precursor sequence is the determinant parameter in order to get a good CIAS crystallisation. Thereby the Al evaporation as the last layer of the stack stimulates the homogeneity of this element toward the depth profile, promoting a best interdiffusion and CIAS crystallisation. While, due to the Al tendency to go to the bottom, phase separation is produced in the C2 samples. It has been also shown that there is an optimum temperature, 540ºC, which promotes the best Al incorporation for both sequences.

Acknowledgements

References

[1]   I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, R. Noufi, Prog. Photovol: Res. Appl. 16/3 (2008) 235.

[2]   A. Jager-Waldau, Sol. Energy Mater. Sol. Cells 95/6 1509.

[3]   D. Dwyer, I. Repins, H. Efstathiadis, P. Haldar, Sol. Energy Mater. Sol. Cells 94/3 (2010) 598.

[4]   P.D. Paulson, M.W. Haimbodi, S. Marsillac, R.W. Birkmire, W.N. Shafarman, J. Appl. Phys. 91/12 (2002) 10153.

[5]   Y.B.K. Reddy, V.S. Raja, B. Sreedhar, J. Phys. D: Appl. Phys. 39/24 (2006) 5124.

[6]   M.A. Contreras, K. Ramanathan, J. AbuShama, F. Hasoon, D.L. Young, B. Egaas, R. Noufi, Prog. Photovol: Res. Appl. 13/3 (2005) 209.

[7]   S. Marsillac, P.D. Paulson, M.W. Haimbodi, R.W. Birkmire, W.N. Shafarman, Appl. Phys. Lett. 81/7 (2002) 1350.

[8]   J. López-García, C. Maffiotte, C. Guillén, Sol. Energy Mater. Sol. Cells 94/7 (2010) 1263.

[9]   R. Caballero, C. Guillén, Sol. Energy Mater. Sol. Cells 86/1 (2005) 1.

[10]   S. Martín, C. Guillén, J. Cryst. Growth 336/1 (2011) 82.

[11]   C. Guillén, J. Herrero, Sol. Energy Mater. Sol. Cells 73/2 (2002) 141.

[12]   J. Olejnícek, C.A. Kamler, S.A. Darveau, C.L. Exstrom, L.E. Slaymaker, A.R. Vandeventer, N.J. Ianno, R.J. Soukup, Thin Solid Films 519/16 (2011) 5329.

[13]   V. Avrutin, N. Izyumskaya, H. Morkoç, Superlattices Microstruct. 49/4 337.

[14]   Joint Committee on Powder Diffraction Standards (JCPDS), file number 00-40-1487 for CuInSe2.

[15]   Joint Committee on Powder Diffraction Standards (JCPDS), file number 00-44-1269 for CuAlSe2.

[16]   Joint Committee on Powder Diffraction Standards (JCPDS), file number 00-049-1456 for CuSe.

[17]   H.R. Moutinho, M.M. Al-Jassim, D.H. Levi, P.C. Dippo, L.L. Kazmerski, Papers from the 44th national symposium of the AVS, AVS, San Jose, California (USA), 1998, p. 1251.

[18]   G. Zoppi, K. Durose, S.J.C. Irvine, V. Barrioz, Semicond. Sci. Technol. 21/6 (2006) 763.

[19]   R. Caballero, C. Guillén, Thin Solid Films 431-432 (2003) 200.

[20]   F. Itoh, O. Saitoh, M. Kita, H. Nagamori, H. Oike, Sol. Energy Mater. Sol. Cells 50/1-4 (1998) 119.

[21]   J.E. Jaffe, A. Zunger, Physical Review B 28/10 (1983) 5822.

[22]   W. Hörig, H. Neumann, H. Sobotta, B. Schumann, G. Kühn, Thin Solid Films 48/1 (1978) 67.

[23]   O. Lundberg, M. Edoff, L. Stolt, Thin Solid Films 480-481/0 (2005) 520.

[24]   H. Monig, C.A. Kaufmann, C.H. Fischer, A. Grimm, R. Caballero, B. Johnson, A. Eicke, M.C. Lux-Steiner, I. Lauermann, J. Appl. Phys. 110/9 (2011) 7.

[25]   D. Dwyer, I. Repins, H. Efstathiadis, P. Halder, 2009 34th IEEE Photovoltaic Specialists Conference, Vols 1-3, Ieee, New York, 2009, p. 872.

Tables

Table I. Compositional data obtained by EDAX measurements.

Sample	Al/(Al+In)	Cu/(Al+In)	Se/(Cu+In+Al)
C1 as-grown	0.4	0.8	--
C1 520ºC	0.4	0.7	1.0
C1 540ºC	0.4	0.8	1.0
C1 550ºC	0.4	0.8	1.0
C2 as-grown	0.4	0.8	--
C2 520ºC	0.4	0.9	0.9
C2 540ºC	0.3	0.8	1.0
C2 550ºC	0.4	0.8	0.9

Table II. Interplanar spacing measured by XRD (d), texture coefficient (C_{112}), degree of preferential orientation (σ), crystallite size (S_{112}) and bandgap energy (E_g) of C1 and C2 samples selenised at different temperatures.

Sample	d (Å)	C_{112}	σ	S_{112} (nm)	E_g (eV)
C1 400	3.35	1.78	0.4	69	1.02
C1 450	3.34	1.67	0.4	52	1.02
C1 500	3.32	1.81	0.6	26	1.08
C1 520	3.31	1.34	0.3	23	1.08
C1 540	3.31	1.50	0.3	30	1.49
C1 550	3.33	1.33	0.3	35	1.35
C2 400	3.35	1.43	0.4	52	1.01
C2 450	3.34	1.36	0.3	52	1.02
C2 500	3.34	1.28	0.4	52	1.02
C2 520	3.34	1.29	0.3	42	1.22
C2 540	3.33	1.27	0.3	30	1.13
C2 550	3.34	1.49	0.3	52	1.16

Figure caption:

Fig. 1. XRD patterns of the samples with precursors sequence C1 (In/Cu/In/Al) selenised at low temperatures, 400ºC, 450ºC and 500ºC. Red asterisk indicates the presence of CAS compound.

Fig. 2. XRD patterns of the samples with precursors sequence C2 (In/Cu/Al/In) selenised at low temperatures, 400ºC, 450ºC and 500ºC. Red asterisk indicates the presence of CAS compound.

Fig. 3. Detail of the normalised XRD (112) reflection of C1 samples selenised at high temperatures, 520ºC, 540ºC and 550ºC.

Fig. 4. Detail of the normalised XRD (112) reflection of C2 samples selenised at high temperatures, 520ºC, 540ºC and 550ºC.

Fig. 5. Variation in the interplanar spacing as a function of selenisation temperature for C1 and C2 samples. The evolution of the average crystallite size with the selenisation temperature is shown in the insert.

Fig. 6. Optical transmission $T(\%)$ and reflection $R(\%)$ curves of C1 samples selenised at low temperatures, 400ºC, 450ºC and 500ºC.

Fig. 7. Optical transmission $T(\%)$ and reflection $R(\%)$ curves of C2 samples selenised at low temperatures, 400ºC, 450ºC and 500ºC.

Fig. 8. Optical transmission $T(\%)$ and reflection $R(\%)$ curves of C1 samples selenised at high temperatures, 520ºC, 540ºC and 550ºC.

Fig. 9. Optical transmission $T(\%)$ and reflection $R(\%)$ curves of C2 samples selenised at high temperatures, 520ºC, 540ºC and 550ºC.

Fig. 10. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for C1 samples selenised at high temperatures. The inset shows their optical absorption spectra.

Fig. 11. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for C2 samples selenised at high temperatures. The inset shows their optical absorption spectra.

Fig. 12. SIMS depth profiles of samples of C1 and C2 selenised at 540ºC. The solid lines represent the elements of C1_540, and the symbol curves the elements of C2_540. The dashed vertical line marks the interface with the glass substrate.

Fig. 13. SIMS depth profile of the Al element and compounds. C1_540 curves are plotted with solid lines. C2_540 profiles are plotted with symbols. The dashed vertical line marks the interface with the SLG.

Fig. 14. SIMS depth profile of C1 samples heated at 540⁰C and 550⁰C. The solid lines represent the elements of C1_540, and the symbol lines the elements of C1_550. The dotted line divides the profile in two distinct composition zones. The dashed vertical line marks the interface with the SLG. Fig. 15 SEM images of (a) C1_520, (b) C1_540, (c) C1_550, (d) C2_520, (e) C2_540 and (f) C2_550 layers.