



HAL
open science

Detrimental copper-selenide bulk precipitation in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin-film solar cells. A possible reason for the limited performance at large x ?

Polyxeni Tsoulka, Nicolas Barreau, Isabelle Braems, Ludovic Arzel, Sylvie Harel

► To cite this version:

Polyxeni Tsoulka, Nicolas Barreau, Isabelle Braems, Ludovic Arzel, Sylvie Harel. Detrimental copper-selenide bulk precipitation in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin-film solar cells. A possible reason for the limited performance at large x ?. *Thin Solid Films*, 2020, 712, pp.138297. 10.1016/j.tsf.2020.138297. hal-02945507

HAL Id: hal-02945507

<https://hal.science/hal-02945507>

Submitted on 25 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Detrimental copper-selenide bulk precipitation in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin-film**
2 **solar cells. A possible reason for the limited performance at large x?**

3
4 Polyxeni Tsoulka, Nicolas Barreau, Isabelle Braems, Ludovic Arzel, Sylvie Harel

5
6 *Institut des Materiaux Jean Rouxel (IMN), UMR 6502 CNRS, Université de Nantes 2 rue de la*
7 *Houssiniere BP 32229, 44322 Nantes cedex 3, France.*

8
9 **Abstract**

10 In this paper, we propose a possible explanation of the limited $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGSe) performance at
11 high Ga contents, related to the properties of detrimental copper selenide (Cu_5Se) secondary phases. We
12 study CIGSe layers at different x, by means of X-ray diffraction analyses, Raman and energy dispersive
13 X-ray spectroscopy. Our results reveal that for high Ga contents, Cu_5Se secondary phases either
14 precipitate at the interfaces between grains or remain within the layer as intra- or inter-grain clusters,
15 deteriorating the electronic properties of the absorber layer. On the contrary, for low Ga contents, the
16 copper selenide segregates at the surface of the CIGSe and hence it can be easily removed by KCN
17 surface etching. To understand the Cu_5Se precipitation within the bulk of the film for a high Ga ratio, we
18 also investigate In-free CGSe samples at low and high Cu content. Our observations demonstrate that i)
19 Cu_5Se has a preferential grain orientation to segregate and ii) the Cu-enriched regions within the bulk of
20 the high Ga content films are more a kinetic than a thermodynamic issue.

21
22 **Keywords:** Copper indium gallium di-selenide; Thin films; Surface segregation; Bulk precipitation;
23 Copper-selenium; Gallium ratio; Physical vapor deposition

24

1 **1. Introduction**

2 Polycrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGSe) absorber layers count among the most promising materials in the
3 field of thin-film solar cells. The CIGSe alloy can be described as a mixture of two ternary I-III-VI₂
4 semiconductors, CuInSe_2 (CISe) and CuGaSe_2 (CGSe), where the group III lattice sites are randomly
5 occupied by In or Ga [1-3] and x corresponds to the Ga content:

$$6 \quad x = \frac{[\text{Ga}]}{[\text{Ga}] + [\text{In}]}$$

7 The optical band gap energy (E_g) of the absorber layer can be tuned by substituting Ga to In, from
8 $E_g=1.04\text{eV}$ for Ga-free CISe absorber layer ($x=0$) to 1.68 eV for In-free CGSe ($x=1$) [3,4].

9 In recent years, there has been considerable interest in the wide band gap materials like CGSe, since
10 these absorber layers can be used *i*) to reach higher output voltage [4] and *ii*) as the top cell of a tandem
11 stacked-type solar cell [5]. So far, the best lab-scale energy conversion efficiencies of CIG(S)Se-based
12 solar cells are achieved for narrow band gap (23.35% for CIG(S)Se record efficiency [6]). Theoretically,
13 the optimum Ga ratio to achieve the maximum conversion efficiency is around $x\sim 0.7$ [7,8]. However,
14 experimentally the efficiency of the CIGSe-based solar cells strongly decreases when x exceeds the
15 threshold value of 0.4 [4-6,8].

16 The limited performance of Ga-rich ($x>0.4$) solar cells is under question for more than 25 years. The
17 experimental and theoretical explanations behind the decreased photovoltaic performance at large x can
18 be divided into two categories *i*) the detrimental recombination effects at CIGSe interfaces *i.e.* the
19 CIGSe surface [9] and grain boundaries (GB) [10-12] and *ii*) the increased concentration of defects
20 within the bulk of the film [4,13-15] that act as recombination centers.

21 Many experimental studies have shown that crystal defects [11,15,16], secondary phases and local
22 inhomogeneities [17-20] can be created during the CIGSe deposition process at the inter- or intra-grain
23 regions, *i.e.* segregation or precipitation phenomena at the grain boundaries or within the bulk. Cu-
24 enriched regions or copper-selenide phases can be formed at the surface or/and within the bulk of the

1 CIGSe film at the inter- or intra-grain regions [11, 21-26]. The copper-selenide secondary phase
2 possesses a semi-metallic character that enhance the charge transfer and acts as electron-hole
3 recombination center. The excess of Cu at these regions increases the conductivity and creates an
4 electric shunt. Hence, the electrical and optical properties of the absorber layer are negatively impacted
5 [26-28], leading to the deterioration of the solar cell.

6 Copper-selenide secondary phases at the surface and at the inter-grain regions of the absorber layer have
7 been observed in slightly Cu-rich CGSe layers by Kelvin probe force microscopy in [26] and by
8 transmission electron microscopy (TEM) coupled with energy dispersive X-ray dispersion spectroscopy
9 (EDS) in [27,29]. Additionally, studies of high-resolution scanning transmission electron microscopy
10 (HR-STEM) on CIGSe layers [25] have shown the existence of copper-selenide inter- or intra-grain
11 clusters. Further, a model based on Cu-poor and Cu-rich nanodomains creating a network has been
12 proposed in [19,20].

13 In this paper, we focus on the formation of the detrimental Cu-enriched regions in the wide band gap
14 CIGSe and CGSe compounds. We correlate the formation of the copper-selenide detrimental phase with
15 the Ga ratio and we propose an approach that explains the degradation of the photovoltaic performance
16 at large x .

17 The remainder of the paper is organized as follows:

18 Section 2 describes the co-evaporation process that we followed to synthesized the CIGSe and CGSe
19 layers, the post-deposition treatments and the instruments that we used for our experimental analyses.

20 Section 3.1 examines two CIGSe films of intermediate x and correlates the surface segregation and bulk
21 precipitation phenomena of the copper-selenide with the Ga ratio. In Section 3.2, we study the copper
22 selenide surface segregation mechanism and bulk precipitation in the case of In-free CGSe films at low
23 and high Cu contents. Section 4 explains the observed copper selenide precipitation phenomena in the
24 CIGSe layer from a kinetic point of view and proposes some directions for further research in order to

1 ameliorate the solar cell efficiency of the wide band gap CIGSe. Finally, the main conclusions of this
2 study are drawn in Section 5.

3

4 **2. Experimental**

5 In our work, to investigate whether the Cu-enriched regions are related to the Ga content of the layer or
6 not, we study the homogeneity of the absorber layer and the presence of the detrimental copper selenide
7 phases in CIGSe layers of intermediate ($x=0.3$ and 0.6) and In-free ($x=1$) layers.

8 **2.1 CIGSe co-evaporation process**

9 In the present work, the absorber layers are synthesized by physical vapor deposition (PVD) process
10 under vacuum ($\sim 10^{-4}$ Pa). During the CIGSe deposition process the flux (atoms per time unit) and the
11 arrival rate per unit area of each element is controlled in order to obtain the desirable *i*) CIGSe thickness
12 ($1.5\text{-}2.0\ \mu\text{m}$), *ii*) Ga to In ratio (x) and *iii*) Cu to group-III atoms ratio (y):

$$13 \quad y = \frac{[\text{Cu}]}{[\text{Ga}]+[\text{In}]}$$

14 IR lamps were used as substrate heaters and the temperature was measured by a thermocouple in contact
15 with the back of the substrate. To avoid a possible Ga gradient within the layer and focus only on the Cu
16 diffusion, the Cu-RO process was chosen to synthesize the CIGSe films. The Cu-RO technique is a two-
17 stage isothermal ($T=560^\circ\text{C}$) process which starts with a Cu-Rich step (Stage I, $y>1$) and continues with a
18 Cu-poor step (Stage II, $y<1$). The phase diagram of the ternary CIGSe compound [30, 31] shows that the
19 chalcopyrite α -phase is stable from $y=0.91$ to 1 and that the homogeneous α -phase broadens with Na-
20 doping and/or Ga to In substitution [32]. As regards the CGSe phase diagram [33, 34], the chalcopyrite
21 phase is stable for y between 0.73 and 1 . However, in both cases, the ternary phase diagrams reveal that
22 for $y>1$ the chalcopyrite phase co-exists with the copper-selenide compounds (CuSe_2 , CuSe , Cu_8Se).
23 Hence, to keep the semiconductor character and avoid the presence of semi-metallic copper-selenide

1 secondary phases the final composition of the absorber layer is slightly Cu-poor ($y < 1$). However, it
2 should be noted that the thermodynamic equilibrium may not be reached during the CIGSe deposition
3 process and hence the presence of secondary phases, such as the detrimental copper-selenides. During
4 the whole co-evaporation process the Se flux is in excess and the overall deposition rate is 30 nm/min.
5 More details about the Cu-RO co-evaporation technique can be found in [35]. A single-stage co-
6 evaporation process at 560°C substrate temperature was also carried out to study separately the case of a
7 Cu-rich CGSe layer.

8 The CIGSe layers of intermediate x were deposited on soda-lime glass (SLG)/Si_xN/Mo substrate at
9 560°C. The Si_xN layer serves as an alkali diffusion barrier. Studies have shown that Na diffusion within
10 the CIGSe layer, hinders the In-Ga interdiffusion [36, 37, 38]. Hence, to avoid any possible Ga grading
11 within the CIGSe layers of intermediate x , the absorbers were co-evaporated on soda-lime glass
12 (SLG)/Na-barrier(Si_xN)/Mo substrate. The In-free CGSe layers were deposited on standard SLG/Mo
13 substrates.

14 **2.2 Post-deposition treatments**

15 After the end of the co-evaporation process, we applied a wet-chemical etching of the CIGSe surface
16 using a potassium cyanide (KCN) solution [39] in order to remove any possible surface segregated Cu-
17 rich secondary phases. Here, we should notice that the KCN etching removes only the copper selenides
18 from the surface, without acting on any possible Cu-rich compound in the bulk or the inter-grain regions
19 of the CIGSe film [26-28]. Finally, after the KCN etching some of the samples were annealed under
20 vacuum at 350°C for 24h or 30 days in order to reach the thermodynamic equilibrium and avoid the
21 presence of secondary phases. Table I summarizes the samples that we used in our study.

22 **2.3 Characterization**

1 The composition of the CIGSe layer was measured by EDS coupled with a SEM (scanning electron
2 microscope) using a JEOL JSM 5800LV at 5 kV (surface analysis) and 20 kV (bulk analysis)
3 acceleration voltage. In-line cross-section elemental profile was also performed on one of our samples
4 (#04) using SEM-EDS at 10 kV acceleration voltage. The cross-section analyzed area was mechanically
5 polished using the ultramicrotome Leica UC7 equipped with a diamond knife. For the high resolution
6 SEM images a JEOL JSM 7600F microscope was used.

7 Raman spectroscopy was applied for the chemical analysis of the near surface region of the CIGSe
8 layers (surface analysis). The system used is a Renishaw InVia Reflex and the wavelength of the
9 excitation beam was set to 488 nm using an Ar⁺ laser source. The interaction depth at 488 nm excitation
10 wavelength corresponds to less than 150 nm.

11 The structural observation of the CIGSe films was based on an XRD (X-ray diffraction) study, with a
12 Siemens D8 integrated with a Cu-Ka source radiation ($\lambda=1.54056 \text{ \AA}$).

13

14 **3. Results**

15 **3.1 Copper selenide precipitation phenomena in CIGSe layers of intermediate x**

16 In the present section, we study the samples of intermediate Ga content (sample #01 with $x=0.30$ and
17 #02 with $x=0.60$) and the creation of Cu-enriched local inhomogeneities within the bulk of the CIGSe
18 layers.

19 The CIGSe layers were deposited on SLG/Si_xN/Mo using the Cu-RO process. After the end of the co-
20 evaporation process, the samples were KCN-etched, sealed under vacuum in a quartz tube and annealed
21 at 350°C for 30 days.

22 **- Surface morphology**

23 The CIGSe surface morphology of the samples without any post deposition treatment is shown in Figure

24 1. The Sample #02 ($x=0.60$) presents a rough surface and an important amount of grains with a

1 triangular morphology. According to [40,41] the faceted grains are {112}-oriented and the ledges of the
2 triangles correspond to {220}/{204} planes. The $x=0.30$ samples present a smoother surface than the
3 $x=0.60$ ones. Figure 2 gives a high-magnification SEM image of the surface after the KCN treatment and
4 the annealing.

5 On the $x=0.30$ annealed sample, we observe the existence of voids at the surface which are created by
6 the removal of the copper-selenide phases after the KCN surface etching. This observation is in line with
7 the EDS analysis (see table I), which shows that after the KCN treatment and annealing, the overall Cu
8 content is decreased from $y=0.98$ to 0.92 , due to the copper-selenide removal after the KCN etching. In
9 contrast, on the CIGSe $x=0.60$ annealed sample the Cu content did not significantly change (from
10 $y=0.87$ to 0.86) after the KCN treatment and the annealing. Moreover, in Figure 2 we can see small
11 clusters aligned along precise orientations of grains having the ledge-patterned morphology.

12 - **Copper selenide surface segregation in CIGSe of intermediate x**

13 To identify the probable existence of different phases at the surface of the CIGSe film and investigate
14 the chemical composition of the ledge-patterned grains containing the clusters, we performed a Raman
15 analysis (see Fig. 3) at the upper CIGSe layers. The Raman peak at 175 cm^{-1} for the $x=0.30$ CIGSe film
16 and at 179 cm^{-1} for 0.60 is related to the main A_1 CIGSe vibration mode [42, 43] of the Se anions. The
17 two spectra also depict the weak B_2/E stretching In/Ga-Se mode [42, 43] around 216 cm^{-1} and 239 cm^{-1}
18 for $x=0.30$ and around 226 cm^{-1} and 242 cm^{-1} for $x=0.60$. The shift of chalcopyrite peaks at larger
19 wavenumber, observed for $x=0.60$, is due to the decrease of the lattice parameters [44] of the high Ga
20 content crystals. The additional peak at 259 cm^{-1} corresponds to the A_1 vibration mode of a copper-
21 selenide compound as the CuSe , Cu_2Se or $\text{Cu}_{2-\delta}\text{Se}$, according to [42, 43, 45]. Moreover, our results show
22 that after the end of the co-evaporation process both samples exhibit a copper-selenide phase at the
23 surface, while after the KCN chemical etching and the annealing only the Ga-rich ($x=0.60$) sample

1 presents a copper-selenide phase at the surface. In the In-rich sample there is no Cu-Se Raman peak after
2 the post-deposition KCN treatment and the annealing.

3 Comparing the black lines in Figures 3a and 3b, we notice that prior to the KCN etching and the
4 annealing, the intensity of the Cu_5Se peak is more pronounced for the sample with $x=0.60$ than for the
5 one with $x=0.30$, indicating a larger Cu content. This observation could be related with the smoother
6 surface observed for $x=0.30$ (see Fig. 1).

7 The red lines correspond to the Raman spectra after the KCN treatment and the annealing. Within the
8 $x=0.30$ all the Cu_5Se was removed from the CIGSe surface after the KCN etching and no further Cu_5Se
9 accumulation was observed at the CIGSe upper layers after the annealing. In contrast, the $x=0.60$ KCN
10 treated and annealed sample presents a Cu_5Se compound at the surface after the annealing, which could
11 be related with the aligned clusters observed at the CIGSe surface after the annealing (Fig. 2) as
12 mentioned above.

13 Thus, comparing the $x=0.60$ (Ga-rich CIGSe) Raman spectra before and after the post deposition
14 treatment, it can be assumed that there are Cu_5Se precipitates in the bulk of the Ga-rich ($x=0.60$) layer
15 after the end of the CIGSe co-evaporation process and the KCN etching. Hence, after the annealing
16 where the thermodynamic equilibrium has been reached, the bulk-precipitated Cu_5Se segregates at the
17 surface. Thus, the copper selenide peak in Raman spectra after the post deposition treatment corresponds
18 to the Cu_5Se phase that has segregated at the surface after the annealing. In contrast this is not the case
19 for $x=0.30$ (In-rich CIGSe), since there is no Cu_5Se peak in the Raman spectra after the KCN treatment
20 and the annealing, indicating that all the Cu_5Se was segregated at the surface after the end of the co-
21 evaporation process, and removed afterwards by the KCN treatment. Hence, no Cu_5Se remained trapped
22 in the bulk of the film after the CIGSe deposition process.

23 - **CIGSe texture**

1 The XRD diffractograms (Fig. 4) do not show any copper selenide peak and the only identified phase is
2 the chalcopyrite. This raises questions about the Cu_8Se form within the bulk, since it could be present as
3 an amorphous phase at the inter- or intra-grain region or as small crystallites that cannot be detected with
4 the XRD analysis.

5 The diffractograms show that the CIGSe layers are mainly (112)-oriented (peak at 26.9° for $x=0.30$ and
6 at 27.2° for $x=0.60$) and none of the samples presents a peak related to a copper-selenide phase. The shift
7 of the (112) peak to higher angles for $x=0.60$ indicates that the lattice parameters are decreased
8 compared to $x=0.30$. In our case the resulting (112) preferential orientation strongly depends on the high
9 isothermal deposition temperature and the texture of the Cu-rich precursor layer, where the cubic Cu_2Se
10 and tetragonal non-stoichiometric Cu_8Se phases are (111)-oriented.

11 Examining the samples before and after annealing reveals that the full width at half maximum (FWHM)
12 of the (112) orientation is decreasing after the annealing ($\text{FWHM}(112)_{\text{before}} - \text{FWHM}(112)_{\text{after}} = 0.01^\circ$)
13 which indicates a grain size enlargement.

14 **Proposed scenario: Detrimental copper-selenide bulk precipitation at large x**

15 The comparison between the $x=0.30$ and $x=0.60$ XRD and Raman data leads us to conclude that the Cu-
16 Se segregation phenomena differ for low and high Ga ratios: in the Ga-rich sample there are Cu_8Se
17 precipitates within the bulk after the end of the co-evaporation process, contrary to the In-rich sample
18 where the whole Cu_8Se has segregated at the surface. A longer annealing is then required for $x=0.60$ to
19 make the entire Cu_8Se segregate at the surface. In addition the fact that no $(\text{In,Ga})_2\text{Se}_3$ or other Cu-poor
20 phases (i.e. $\text{Cu}(\text{In,Ga})_3\text{Se}_5$) were observed after the annealing, reveals that copper selenide compounds
21 observed at the surface after the annealing came from the bulk and no $(\text{In,Ga})_2\text{Se}_3$ - Cu_2Se phase
22 separation occurred during the annealing. Figure 5 presents a schematic model of Cu_8Se behavior in the
23 case of low ($x=0.30$) and high ($x=0.60$) Ga content, before and after the post-deposition treatment.

24 **3.2 Bulk precipitation and surface segregation phenomena in CuGaSe_2**

1 To further understand the cause of the copper-selenide bulk precipitation observed in CIGSe layers with
2 large Ga ratios, we focus on In-free CGSe layers with high and low Cu content and we investigate the
3 Cu_6Se segregation mechanism and the crystallinity of the copper-selenide compounds at the surface and
4 within the layer.

5 - **Cu_6Se surface segregation via a precise grain orientation**

6 To study the Cu_6Se surface segregation in the case of high Ga contents, we perform a surface SEM-EDS
7 cartography on a Cu-rich ($\gamma > 1$) CGSe sample (#03) before and after annealing. The layer was deposited
8 using a single-stage process, resulting in a final CGSe layer with $\gamma = 1.50$. After the end of the deposition
9 process the sample was annealed for 24h at 350°C under vacuum.

10 Figure 6 shows SEM images of the Cu-rich surface before and after the annealing. As shown in Figure
11 6a, the surface of the sample before annealing presents two main types of grains: *i*) smooth single
12 faceted grains and *ii*) rough grains where periodic steps create a ledged patterned surface. In the surface
13 of the annealed sample (Fig. 6b and 6c) small clusters accumulate at the ledges of the rough grains.
14 Recall that the same phenomenon was observed for the Ga-rich sample (see Fig. 2 in Section 3.1).

15 Further an EDS cartography was carried out at 5 kV acceleration voltage, in order to decrease the
16 interaction depth of the electron beam and be able to analyze only the upper layers of the surface. Using
17 the Casino software [46], we carried out a Monte Carlo simulation (not shown here) of the interaction
18 volume of our SEM-EDS analysis at 5 kV beam energy and we found that the interaction depth is
19 around 150 nm. The EDS cartography (see Fig. 7) revealed that the upper layers of the grains containing
20 the clusters on their surface are Cu-rich. Thus, we conclude that the Cu_6Se has a preferential grain
21 orientation to segregate, since after the annealing, it accumulates only at the ledges of the $\{112\}$ -oriented
22 grains with the precise step-patterned surface.

23 - **Crystallinity of the bulk-precipitated Cu_6Se phase**

1 Here, we examine the presence of Cu-rich regions within the layer of slightly Cu-poor CGSe samples
2 and we investigate the Cu_5Se form in the bulk. The CGSe samples were synthesized by a two-stage (Cu-
3 RO) co-evaporation process on Mo (#04, $y=0.95$) the sample was chemically etched with KCN after the
4 end of the deposition process. Figure 8 depicts the XRD diffractogram of the CGSe sample (#04) with
5 $y=0.95$ grown on Mo and no peak of Cu_5Se is apparently observed. However, the in-line cross-section
6 elemental profile, using a SEM-EDS at 10 kV acceleration voltage (Fig. 9), presents a small variation of
7 the Cu content, resulting in a slight Cu-rich region close to the back contact. The fact that the XRD
8 analysis of the sample did not indicate any Cu_5Se peak, while the EDS cross-section profile detects a
9 Cu-rich region, leads us to the conclusion that the Cu_5Se precipitates in the bulk are present in an
10 amorphous form. However, this assumption does not exclude a possible Cu_5Se precipitation at the inter-
11 grain regions or the existence of small not-detectable crystallites within the grains.

12

13 **4. Discussion**

14 In this paper, we examined the copper-selenide precipitation and the presence of Cu-rich secondary
15 phases in regard to the Ga content of the thin films. Our investigations suggest that for large Ga ratios
16 ($x > 0.4$), copper-selenide compounds precipitate within the bulk of the film or/and close to the back
17 contact, whereas for low Ga contents the whole undiluted Cu_5Se segregates at the surface. This is a vital
18 issue for future research in the wide band gap CIGSe absorber layers since the Cu-rich regions within
19 the bulk could be a possible explanation of the observed photovoltaic degradation at large Ga contents
20 (when $x > 0.4$).

21 Our observations are consistent with the findings in [19] where the cubic Cu_2Se phase was observed by
22 TEM-EDS micro-analysis, on the CIGSe surface and the $\text{Cu}_{2-\delta}\text{Se}$ tetragonal phase at the interface
23 between the grains. Additionally, in [11] an atom probe tomography (APT) analysis on CIGSe revealed
24 the presence of Cu-enriched grain boundaries when $x > 0.8$ and In-enriched GBs for $x < 0.4$.

1 Our studies have also shown that the copper selenide is facilitated by a precise orientation of the grains.
2 This observation could be correlated with the findings in [25], where studies of HR-STEM and electron
3 energy-loss spectroscopy revealed the presence of platelets of copper selenides within the grains,
4 parallel to the {112} planes of the CIGSe.

5 An interesting question to address is how is it possible to have Cu-enriched regions in a stoichiometric
6 or slightly Cu-poor ($y < 1$) film of large Ga content, since according to the CIGSe, CGSe and CIGSe [30-
7 34, 47, 48] phase diagrams the copper selenide phase is formed and co-exists with the chalcopyrite phase
8 only when $y > 1$. For $y < 1$ there is only the co-existence of Cu-poor CIGSe compositions with the
9 chalcopyrite phase. Taking into account, that *i*) during the deposition process we are not under
10 thermodynamic equilibrium and *ii*) the CIGSe and CGSe kinetic properties differ [38,49-51], we can
11 assume the creation of local inhomogeneities during the CIGSe formation. Moreover, of particular
12 interest is the fact that only in the case of Ga-rich film a long annealing is needed to make the copper-
13 selenide segregate at the surface.

14 In contrast, for the In-rich CIGSe synthesis, the duration of the deposition process is sufficient to make
15 the excess of copper segregate at the surface, resulting in a homogeneous and close to stoichiometry
16 bulk composition of the film. The same result is also observed in the In-free CGSe layer of $y > 1$ where
17 segregated clusters are observed at the step-patterned grains after an annealing of 24 hours. Hence, the
18 Cu-rich precipitates within the bulk of the Ga-rich films is more a kinetic than a thermodynamic issue.

19 As highlighted in our previous paper [52] for the CGSe wide band gap solar cells, applying two
20 annealing stages during the 3-stage (Cu Poor-Rich-Off) process results in an improved lateral uniformity
21 of the metal atoms and better solar cell device performance (the current density is increased by 11.2%
22 and the solar cell efficiency by 8% . In [52] the Raman analysis at the front and rear surface of CGSe
23 samples with and without annealing stages show that the absorber synthesized without any annealing
24 step presents a nonuniform Cu/Ga distribution and higher amount of Cu at the rear surface, while the

1 CGSe sample synthesized with two relaxation stages during the growth exhibits homogeneous Cu/Ga
2 distribution. Similarly, another previous study [53] on CGSe samples grown with and without relaxation
3 stages by a Cu-RO process and analyzed by Raman spectroscopy at the front and rear CGSe surface
4 indicate an improved homogeneity and solar cell efficiency when the relaxation stage is applied during
5 the growth.

6 Considering *i)* the different electronegativity between Ga and In, *ii)* the structural CIGSe variation with
7 the Ga content (x) and *iii)* the different reaction pathways and reaction speed of the two pure ternary
8 compounds [38, 50, 51], it can be assumed that different precipitation and segregation phenomena will
9 take place at low and high x . Taking into account previous studies on the thermodynamic and kinetic
10 properties of CIGSe and CGSe, it appears more probable to have local inhomogeneities and secondary
11 Cu-rich phases in the case of high Ga contents, since:

12 i) The reaction rates of CIGSe and CGSe are different, CGSe being formed much slower than CIGSe
13 at a given temperature [49, 54]. In fact, in [49, 54], studies on the formation rates of CIGSe and CGSe by
14 selenization of Cu/In and Cu/Ga precursors, respectively, demonstrated that the time to form CGSe by
15 selenization of a Cu/Ga precursor at 500°C is six times larger than the formation of CIGSe [49] and that at
16 400°C the CIGSe needs 30 min to be formed when CGSe needs 90 min at 450°C [52].

17 ii) Studies of the CGSe and CIGSe reaction kinetics using isothermal soak of glass/GaSe/CuSe and
18 glass/InSe/CuSe precursors, show that the activation energy of the CGSe formation is larger than the
19 activation energy of CIGSe (115 kJ/mol and 66 kJ/mol, respectively) [50, 51].

20 Hence, given that the Cu-enriched regions within the bulk of the Ga-rich layer are a kinetic issue and the
21 copper selenide surface segregation takes place via a precise orientation of the grains, special attention
22 should be taken to the deposition process for Ga-rich CIGSe layers in order to:

23 a) Control the texture of the CIGSe film.

1 Studies on the CIGSe deposition process have shown that the preferential orientation of the CIGSe
2 films depends on: a) the alkali impurities such as K and Na, that diffuse via the SLG substrate [55-59] b)
3 the Se flux during the co-evaporation process [40, 58-60], c) the deposition temperature [56, 57, 59] and
4 d) Cu concentration [56, 57, 61].

5 b) Enhance the interdiffusion of the elements in order to obtain a more homogeneous absorber
6 layer.

7 The presence of a high amount of Ga in the CIGSe lattice seems to weaken the interdiffusion of
8 elements and so it could be responsible for the creation of secondary intra-grain phases as the Cu_3Se . In
9 [8], it was observed that for $0.3 < x < 1$, the CIGSe films presented higher efficiencies for substrate
10 temperatures higher (600°C - 650°C) than the commonly used ones (500°C - 600°C).

11 Additionally, attention should be paid on the fact that the annealing of our samples was performed under
12 vacuum. As a result, the observed grain enlargement and homogenization of the film could be also
13 related with the increased amount of Se vacancies that could act as diffusion pathways [54, 62].

14

15 **5. Conclusions**

16 In this paper, we developed an approach to understand the copper selenide behavior in the CIGSe layer
17 at low and high Ga content. We studied CIGSe samples at intermediate x (0.3 and 0.6) and at low ($y < 1$)
18 and high ($y > 1$) Cu content. Our work revealed that the copper selenide segregation phenomena depend
19 on the Ga ratio. We demonstrated that for large Ga content there are Cu-enriched detrimental precipitates
20 within the bulk of the layer, while for low Ga ratio the whole copper selenide segregates at the surface
21 and then can be easily removed by KCN wet-chemical etching.

22 We also investigated pure CGSe layers at low and high Cu contents grown on SLG/Mo. We concluded
23 that the Cu-enriched regions within the bulk of the Ga-rich layer are a kinetic issue and the copper
24 selenide surface segregation mainly occurs via a precise orientation of the grains.

1 Considering that the $\text{Cu}_\delta\text{Se}$ compounds have a metallic character which degrades the electrical
2 properties of the solar cell, our findings could be a possible explanation for the limited photovoltaic
3 performance at high Ga contents. Hence, the copper selenide secondary phases in the CIGSe layer are an
4 important issue for future research.

5 What is known about the $\text{Cu}_\delta\text{Se}$ in the CIGSe field is largely based on narrow band gap CIGSe ($x < 0.4$)
6 and so, further investigation on the $\text{Cu}_\delta\text{Se}$ formation at the Ga-rich CIGSe layers is required. In addition,
7 a re-investigation of the co-evaporation processes should be considered, since for large Ga ratios, the
8 excess of Cu during the Cu-rich stage seems to create Cu-enriched regions within the bulk, which are
9 not diluted or segregated at the surface during the Cu-poor co-evaporation step. Nevertheless, the Cu-
10 rich deposition stage is essential for a high quality CIGSe absorber layer, since during this step the
11 mobility and the interdiffusion of the elements is increased, facilitating the grain growth [61].

12 Taken together, the results of our study suggest that the deposition process should be adapted to the
13 needs of the wide band gap CIGSe and CGSe absorbers. To improve the quality of the wide band gap
14 CIGSe absorbers and obtain high-efficiency solar cells, it is important to: *i*) keep the Cu content as close
15 as possible to stoichiometry ($y=1$), during the Cu-rich co-evaporation step, *ii*) control the texture of the
16 CIGSe layer, *iii*) increase the diffusion pathways by decreasing the Se flux during the process and *iv*)
17 increase the deposition temperature or/and the duration of the process by adding a relaxation stage or by
18 decreasing the deposition rate, in order to enhance the Cu-Ga interdiffusion.

19

20 **Acknowledgments**

21 This work was supported by the Jean Rouxel Institute of materials and the University of Nantes. We
22 gratefully acknowledge Prof. Angus Rockett, who gave us much valuable advice at the beginning of this
23 work. Thanks is due to Nicolas Stephant and Nicolas Gautier for their technical assistance in our
24 experimental work.

25

26

1 **References**

- 2 [1] J.E. Jaffe, A. Zunger, Electronic structure of the ternary chalcopyrite semiconductors CuAlS_2 ,
3 CuGaS_2 , CuInS_2 , CuAlSe_2 , CuGaSe_2 , and CuInSe_2 , *Phys. Rev. B* 28 (1983) 5822-5847
- 4 [2] C. Stephan, Structural trends in off stoichiometric chalcopyrite type compound semiconductors, PhD
5 Thesis, Berlin (2011)
- 6 [3] T. Tinoco, C. Rincón, M. Quintero, G.S. Pérez, Phase diagram and optical energy gaps for $\text{CuIn}_y\text{Ga}_{1-y}\text{Se}_2$
7 alloys, *Phys. Status Solidi (a)* 124 (1991) 427–434
- 8 [4] S.-H. Wei, S.B. Zhang, A. Zunger, Effects of Ga addition to CuInSe_2 on its electronic, structural, and
9 defect properties, *Appl. Phys. Lett.* 72 (1998) 3199-3201
- 10 [5] S. Nishiwaki, S. Siebentritt, P. Walk, M.Ch. Lux-Steiner, A stacked chalcopyrite thin-film tandem
11 solar cell with 1.2V open-circuit voltage, *Prog. Photovoltaics Res. Appl.* 11 (2003) 243-248
- 12 [6] http://www.solar-frontier.com/eng/news/2019/0117_press.html
- 13 [7] W. Shockley, H.J. Queisser, Detailed balance limit of efficiency of p-n junction solar cells, *J. Appl.*
14 *Phys.* 32 (1961) 510-519
- 15 [8] M.A. Contreras, L.M. Mansfield, B. Egaas, J. Li, M. Romero, R. Noufi, E. Rudiger-Voigt, W.
16 Mannstadt, Wide bandgap $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells with improved energy conversion efficiency,
17 *Progr. Photovolt: Res. Appl.* 20 (2012) 843–850
- 18 [9] M. Saad, A. Kassis, Thermally and light-activated current in $\text{ZnO}/\text{CdS}/\text{CuGaSe}_2$ single crystal solar
19 cells, *Renew. Energy* 33 (2008) 974-978
- 20 [10] H. Mirhosseini, J. Kiss, C. Felser, Behavior of $\Sigma 3$ grain boundaries in CuInSe_2 and CuGaSe_2
21 photovoltaic absorbers revealed by first-principles hybrid functional calculations, *Phys. Rev. Appl.* 4
22 (2015) 1-6

- 1 [11] M. Raghuwanshi, Influence of grain boundary chemistry on the properties of CIGS photovoltaic
2 cells, PhD Thesis, Rouen (2015)
- 3 [12] C.-S. Jiang, R. Noufi, K. Ramanathan, J.A. AbuShama, H.R. Moutinho, M.M. Al Jassim, Local
4 built-in potential on grain boundary of Cu(In,Ga)Se₂ thin films, *Renew. Energy* 1 (2005) 245-246
- 5 [13] J.T. Heath, J. D. Cohen, W.N. Shafarman, D. X. Liao, A.A. Rockett, Effect of Ga content on defect
6 states in CuIn_{1-x}Ga_xSe₂ photovoltaic devices, *Appl. Phys. Lett.* 80 (2002) 4540-4542
- 7 [14] A. Darga, W. Favre, M. Fruzzetti, J.-P. Kleider, B. Morel, D. Mencaraglia, P.Yu, H. Marko, L.
8 Arzel, N. Barreau, S. Noël, J. Kessler, Study of the electronic properties of wide band gap CIGSe
9 solar cells: Influence of copper, *J. Non Cryst. Solids* 358 (2012) 2428-2430
- 10 [15] S. Lany, A. Zunger, Limitation of the open-circuit voltage due to metastable intrinsic defects in
11 Cu(In,Ga)Se₂ and strategies to avoid these defects, Preprint. *Renew. Energy* (2008) 7-9
- 12 [16] S. B. Zhang, S.-H. Wei, A. Zunger, H. Katayama-Yoshida, Defect physics of the CuInSe₂
13 chalcopyrite semiconductor, *Phys. Rev. B - Condens. Matte. Phys.* 57 (1998) 9642-9656
- 14 [17] U. Rau, J.H. Werner, Radiative efficiency limits of solar cells with lateral band-gap fluctuations,
15 *Appl. Phys. Lett.* 84 (2004) 3735-3737
- 16 [18] J.R. Tuttle, D.S. Albin, R. Noufi, Thoughts on the microstructure of polycrystalline thin film
17 CuInSe₂ and its impact on material and device performance, *Sol. Cells* 30 (1991) 21-38
- 18 [19] R. Noufi, Y. Yan, J. Abu-Shama, K. Jones, M. Al-Jassim, B. Keyes, J. Alleman, K. Ramanathan,
19 Investigation of the microstructure of Cu(In,Ga)Se₂ thin films used in high-efficiency devices,
20 Preprint *Renew. Energy* (2002) 1-4
- 21 [20] Y. Yan, R. Noufi, K.M. Jones, K. Ramanathan, M.M. Al-Jassim, B.J. Stanbery, Chemical
22 fluctuation-induced nanodomains in Cu(In,Ga)Se₂ films, *Appl. Phys. Lett.* 87 (2005) 1-3

- 1 [21] T. Wada, N. Kohara, T. Negami, M. Nishitani, Growth of CuInSe_2 crystals in Cu-rich Cu-In-Se thin
2 films, *J. Mater. Res.* 12 (1997) 1456-1462
- 3 [22] D. Abou-Ras, S.S. Schmidt, R. Caballero, T. Unold, H-W. Schock, C.T. Koch, B. Schaffer, M.
4 Schaffer, P.-P. Choi, O. Cojocar-Mirédin, Confined and chemically flexible grain boundaries in
5 polycrystalline compound semiconductors, *Adv. Energy Mater.* 2 (2012) 992-998
- 6 [23] E. Simsek Sanli, Q.M. Ramasse, W. Sigle, D. Abou-Ras, R. Mainz, A. Weber, H.-J. Kleebe, P. A.
7 van Aken, Elemental redistributions at structural defects in $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films for solar cells, *J.*
8 *Appl. Phys.* 120 (2016) 205301
- 9 [24] T. Schwarz, G. Stechmann, B. Gault, O. Cojocar-Miredin, R. Wuerz, D. Raabe, Correlative
10 transmission Kikuchi diffraction and atom probe tomography study of $\text{Cu}(\text{In,Ga})\text{Se}_2$ grain
11 boundaries *Prog. Photovolt. Res. Appl.* (2017) 1-9
- 12 [25] E. Simsek Sanli, Q.M. Ramasse, R. Mainz, A. Weber, D. Abou-Ras, W. Sigle, P.A. van Aken,
13 Evidence for Cu_{2-x}Se platelets at grain boundaries and within grains in $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films,
14 *Appl. Phys. Lett.* 111 (2017) 32103
- 15 [26] D.F. Marron, Th. Glatzel, A. Meeder, Th. Schedel-Niedrig, S. Sadewasser, M.Ch. Lux-Steiner,
16 Electronic structure of secondary phases in Cu-rich CuGaSe_2 solar cell devices, *Appl. Phys. Lett.* 85
17 (2004) 3755-3757
- 18 [27] D.F. Marron, A. Meeder, U. Bloeck, P. Schubert-Bischoff, N. Pfander, R Wurz, S. M.Babu, Th.
19 Schedel-Niedrig, M.Ch. Lux-Steiner, Microstructural properties of CVD-grown CuGaSe_2 based thin
20 film solar cells, *Thin Solid Films* 431–432 (2003) 237-341
- 21 [28] H. Marko, L. Arzel, A. Darga, N. Barreau, S. Noël, D. Mencaraglia, J. Kessler, Influence of Cu off-
22 stoichiometry on wide band gap CIGSe solar cells, *Thin solid films* 519 (2011) 7228-7231

- 1 [29] S. Nishiwaki, S. Siebentritt, M. Giersig, M.Ch. Lux-Steiner, Growth model of grains in a Cu-
2 rich/Cu-poor bilayer process, *J. Appl. Phys.* 94 (2003) 6864-6870
- 3 [30] T. Godecke, T. Haalboom, F. Ernst, Phase equilibria of Cu-In-Se. I Stable states and equilibrium
4 stats of the $\text{In}_2\text{Se}_3\text{-Cu}_2\text{Se}$ system, *Z Metallkd* 91 (8) (2000) 622-634
- 5 [31] T. Haalboom, T. Gödecke, F. Ernst, M. Rühle, R. Herberholz, H. W. Schock, C. Berlharz, K.
6 W.Berz, Phase relations and microstructure in bulk materials and thin film of ternary system Cu-In-
7 Cu, *Proceedings of the Int. Conf. on Ternary and Multinary Compounds*, Inst. Phys. Conf. ser. No
8 152: Section B: Thin Film Growth and Characterization (1997) 249-252
- 9 [32] R. Herberholz, U. Rau, H. W. Schock, T. Haalboom, T. Gödecke, F. Ernst, C. Beilharz, K. W.
10 Benz, D. Cahen, Phase segregation, Cu migration and junction formation in Cu(In,Ga)Se_2 , *Eur.*
11 *Phys. J. AP* 6 (1999) 131-139
- 12 [33] L. S. Palatnik, E. K. Belova, Atroshch.Lv and Y. F. Komnik, *Sov Phys Crystallogr* 10 (4) (1966)
13 395
- 14 [34] J.C. Mikkelson, Ternary phase relations of the chalcopyrite compound CuGaSe_2 , *J. Electron. Mater.*
15 10 (1981) 541-558
- 16 [35] J. Kessler, J. Schöldström, L. Stolt, Rapid Cu(In,Ga)Se_2 growth using “End Point Detection”, *Conf.*
17 *Rec. IEEE Photovolt. Spec. conf.* 2000-January (2000) 509-512
- 18 [36] O. Lundberg, J. Lu, A. Rockett, M. Edoff, L. Stolt, Diffusion of indium and gallium in
19 Cu(In,Ga)Se_2 thin film solar cells, *J. Phys. Chem. Solids* 64 (2003) 1499-1504
- 20 [37] B. Namnuan, K. Yoodee, S. Chatraphorn, Probig diffusion of In and Ga in $\text{CuInSe}_2/\text{CuGaSe}_2$
21 bilayer thin films by X-ray diffraction, *J Crys. Growth* 432 (2015) 24-32
- 22 [38] F. Hergert, S. Jost, R. Hock, M. Purwins, A crystallographic description of experimentally
23 identified formation reactions of Cu(In,Ga)Se_2 , *J. Solid State Chem.* 179 (2006) 2394-2415

- 1 [39] J. Lehmann, S. Lehmann, I. Lauermann, T. Rissom, C.A. Kaufmann, M. Ch. Lux-Steiner, M. Bär,
2 S. Sadewasser, Reliable wet-chemical cleaning of natively oxidized high-efficiency Cu(In,Ga)Se₂
3 thin film solar cell absorbers, *J. Appl. Phys.* 116 (2014) 233502
- 4 [40] K.H Kim, K.H. Yoon, J.H Yun, B.T. Ahn, Effects of Se flux on the microstructure of Cu(In,Ga)Se₂
5 thin film deposited by a three-stage co-evaporation process, *Electrochem. Solid-State Lett.* 9 (2006)
6 382-384
- 7 [41] A. Rockett, Surface analysis of chalcopyrite materials for photovoltaics, *Progr. Photovolt. Res.*
8 *Appl.* 20 (2012) 575-581
- 9 [42] D. Papadimitriou, N. Esser, C. Xue, Structural properties of chalcopyrite thin films studied by
10 Raman spectroscopy, *Phys. Status Solidi* 242 (2005) 2633-2643
- 11 [43] W. Witte, R. Kniese, M. Powalla, Raman investigations of Cu(In,Ga)Se₂ thin films with various
12 copper contents, *Thin solid Films* 517 (2008) 867-569
- 13 [44] W. Witte, R. Kniese, A. Eicke, M. Pawolla, Influence of Ga content on the Mo/Cu(In,Ga)Se₂
14 interface formation, 2006 IEEE 4th World Conference on Photovoltaic Energy Conference,
15 Waikoloa, HI, (2006) 553-556
- 16 [45] C. Xue, D. Papadimitriou, Y.S. Raptis, W. Richter, N. Esser, S. Siebentritt, M. Ch. Lux-Steiner,
17 Micro-Raman Study of Orientation Effects of Crystallites on Cu-rich Thin Films, *J. Appl. Phys.* 96,
18 (2004) 1963-1966
- 19 [46] D. Drouin, A.R. Couture, D. Joly, X. Tastet, V. Aimez, R. Gauvin, CASINO V2.42—A fast and
20 Easy-to-use modeling tool for scanning electron Microscopy and microanalysis Users, *Scanning* 29
21 (2007) 92-101

- 1 [47] T. Maeda, W. Gong, T. Wada, Crystallographic and optical properties and band structures of
2 CuInSe_2 , CuIn_3Se_5 , and CuIn_5Se_8 phases in Cu-poor Cu_2Se – In_2Se_3 pseudo-binary system J. Appl.
3 Phys. 55 (2016) 04ES15
- 4 [48] C. Beilharz, Charakterisierung von aus der Schmelze gezüchteten Kristallen in den Systemen
5 Kupfer-Indium-Selen und Kupfer-Indium-Gallium-Selen für photovoltaische Anwendungen, Shaker
6 Verlag (1999)
- 7 [49] H. Dittrich, U. Prinz, J. Szot, H. W. Schock, Analysis of reaction kinetics of selenized CuInSe_2 and
8 CuGaSe_2 thin films, Proc. 9th EC Photovoltaic Solar Energy Conf. (1989) 163-166
- 9 [50] S. Kim, W.K. Kim, R. M. Kaczynski, R.D. Acher, S. Yoon, T.J. Anderson, O. D. Crisalle, E.A.
10 Payzant, S.S. Li, Reaction kinetics of CuInSe_2 thin films grown from bilayer InSe/CuSe precursors,
11 J. Vac. Sci. Techn. A Vacuum, Surfaces, Films 23 (2005) 310-315
- 12 [51] W. K. Kim, E.A. Payzant, S. Kim, S.A. Speakman, O. D. Crisalle, T.J. Anderson, Reaction kinetics
13 of CuGaSe_2 formation from a GaSe/CuSe bilayer precursor film, J. Cryst. Growth 310 (2008) 2987–
14 2994
- 15 [52] Polyxeni Tsoulka, Adrien Rivalland, Ludovic Arzel, Nicolas Barreau, Improved CuGaSe_2 absorber
16 properties through a modified co-evaporation process, Thin Solid Films (2020), “accepted”
- 17 [53] Polyxeni Tsoulka, Local inhomogeneities in polycrystalline wide band gap $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin-
18 films, PhD Thesis, Nantes (2019)
- 19 [54] M. Marudachalam, R.W. Birkmire, H. Hichri, J.M. Schultz, A. Swartzlander, M.M. Al-Jassim,
20 Phases, morphology, and diffusion in $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ thin films, J. Appl. Phys. 82 (1997) 2896-2905
- 21 [55] N. Barreau, T. Painchaud, F. Couzine-Devy, L. Arzel, J. Kessler, Recrystallization of CIGSe layers
22 grown by three-step processes: A model based on grain boundary migration, Acta Mater. 58 (2010)
23 5572-5577

- 1 [56] F. Couzinie-Devy, N. Barreau, J. Kessler, Re-investigation of preferential orientation of
2 Cu(In,Ga)Se₂ thin films grown by the three-stage process, Prog. Photovolt: Res. Appl. 19 (2011)
3 527-536
- 4 [57] J. Kessler, C. Chityuttakan, J. Lu, J. Schöldström, L. Stolt, Cu(In,Ga)Se₂ Thin films Grown with a
5 Cu-Poor/Rich/Poor Sequence: Growth model and structural considerations, Prog. Photovolt: Res.
6 Appl. 11 (2003) 319-331
- 7 [58] G. Hanna, J. Mattheis, V. Laptev, Y. Yamamoto, U. Rau, H.W. Schock, Influence of the selenium
8 flux on the growth of Cu(In,Ga)Se₂ thin films, Thin Solid Films 431–432 (2003) 31–36
- 9 [59] N. Ott, G. Hanna, U. Rau, J.H. Werner, H.P. Strunk, Texture of Cu(In,Ga)Se₂ thin films and
10 nanoscale cathodoluminescence, J. Phys. Condens. Matter 16 (2004) 85-89
- 11 [60] S. Ishizuka, A. Yamada, P.J. Fons, H. Shibata, S. Niki, Structural tuning of wide-gap chalcopyrite
12 CuGaSe₂ thin films and highly efficient solar cells: differences from narrow-gap Cu(In,Ga)Se₂, Prog.
13 Photovolt. Res. Appl. 22 (2013) 821-829
- 14 [61] V. Deprédurand, T. Bertram, D. Regesch, B. Henx, S. Siebentritt, The influence of Se pressure on
15 the electronic properties of CuInSe₂ grown under Cu excess, Appl. Phys. Lett. 105 (2014) 172104
- 16 [62] M. Marudachalam, H. Hichri, R. Klenk, R.W. Birkmire, W.N. Shafarman, J. M. Schultz Preparation
17 of homogeneous Cu(In,Ga)Se₂ films by selenization of metal precursors in H₂Se atmosphere Appl.
18 Phys. Lett. 67 (1995) 3978-3980

19
20
21
22

1 **List of figures**

2 Figure 1: SEM surface images of the CIGSe layers: #01 with $x=0.30$ (left) and #02 with $x=0.60$ (right)
3 without post-deposition treatment

4 Figure 2: SEM surface images of CIGSe films, after the KCN surface etching and annealing under
5 vacuum: #01 with $x=0.30$ (left) and #02 with $x=0.60$ (right)

6 Figure 3: Raman analysis of the CIGSe films #01 with $x=0.30$ (a) and #02 with $x=0.60$ (b). The black
7 lines correspond to the Raman spectra of the samples without any post-deposition treatment. The red
8 lines represent the samples after the KCN etching and annealing. The peak that corresponds to the
9 copper selenide phase is highlighted in yellow

10 Figure 4: XRD analysis of $x=0.30$ (#01, (a)) and $x=0.60$ (#02, (b)) CIGSe layers grown on
11 SLG/SiN/Mo. The black lines illustrate the diffractogram of the final CIGSe layers obtained after the
12 end of the two-stage co-evaporation process and they did not undergo any post-deposition process. The
13 red lines show the diffractogram obtained for the CIGSe samples after the KCN surface etching and
14 annealing under vacuum for 30 days at 350°C

15 Figure 5: Schematic representation of the copper selenide surface segregation and bulk precipitation in
16 the case of *i*) In-rich CIGSe and *ii*) Ga-rich CIGSe absorber layers. At the In-rich sample after the end of
17 the CIGSe growth the copper selenide has entirely segregate at the surface of the film. Hence the
18 removal of the copper selenide phases from the surface leaves a homogeneous CIGSe film without any
19 detrimental Cu-rich secondary phases. At the Ga-rich sample, the duration of the deposition process is
20 not sufficient to homogenize the film and make the copper selenide compounds segregate at the surface.
21 As a result, after the end of the deposition process, there are Cu-enriched bulk precipitates within the
22 bulk of the absorber layer, that they cannot be removed by the KCN treatment. A long annealing under
23 vacuum is then required for the Ga rich absorber to make the entire Cu_3Se segregate at the surface

24 Figure 6: SEM surface images of CGSe Cu-rich layer (#03) deposited on Mo, (a) after the co-
25 evaporation without post-deposition treatment, (b) after annealing at 350°C for 24h under vacuum and
26 (c) high-magnification image of the sample after annealing at 350°C for 24h

27 Figure 7: Left: SEM surface image coupled with EDS surface cartography (at 5kV acceleration voltage)
28 of the In-free CGSe film (#03) after annealing. Right: The elemental concentration of the two grains
29 highlighted by the dotted circles in the SEM image. The red curve in the EDS spectrum corresponds to a
30 stoichiometric CGSe region while the yellow curve represents a Cu-enriched region and the presence of
31 copper selenide secondary phases

32 Figure 8: XRD analysis of a CGSe sample (#04, $y=0.95$) grown on SLG/Mo by two-stage co-
33 evaporation process (Cu-RO). The diffractogram does not present any Cu_3Se peak. The y axis represents
34 the logarithm of the intensity

35 Figure 9: SEM-EDS cross-section elemental profile of a CGSe sample (#04, $y=0.95$) grown on Mo by a
36 two-stage co-evaporation process (Cu-RO). The EDS measurement was performed at 10 kV beam
37 acceleration voltage

38 **List of tables**

39 Table I: Summary of the elemental concentration $x=[\text{Ga}]/([\text{Ga}]+[\text{In}])$ and $y=[\text{Cu}]/([\text{Ga}]+[\text{In}])$ measured
40 by EDS at 20 kV acceleration voltage, the substrate, the CIGSe co-evaporation process and the post-
41 deposition treatment (KCN etching and annealing) of each sample. The y_R , y and y_A denote the Cu
42 content at the end of the Cu-rich stage, after the end of the co-evaporation process and after the
43 annealing respectively. The error at the atomic percentage is ± 0.03

1
2
3
4
5
6
7
8
9
10

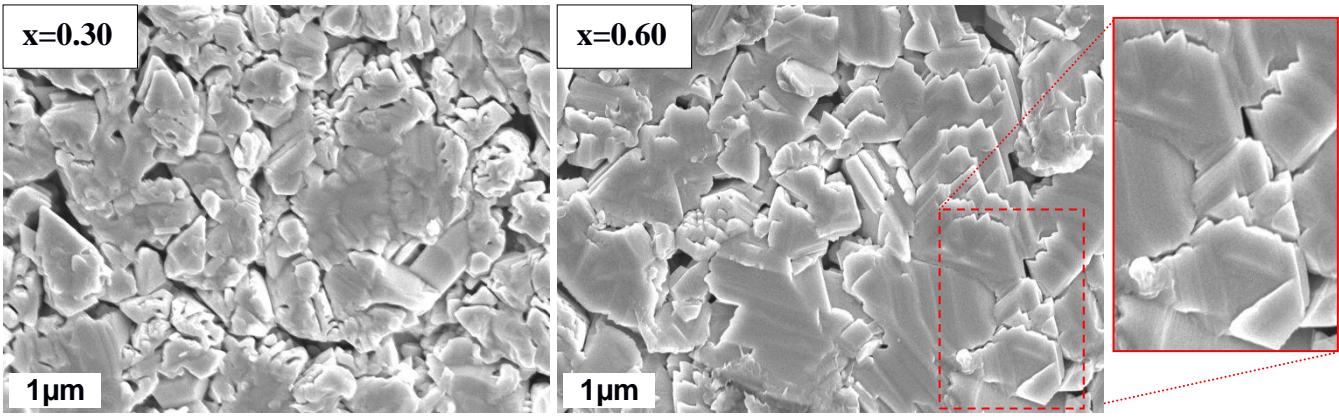


Figure 1: SEM surface images of the CIGSe layers: #01 with $x=0.30$ (left) and #02 with $x=0.60$ (right) without post-deposition treatment

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

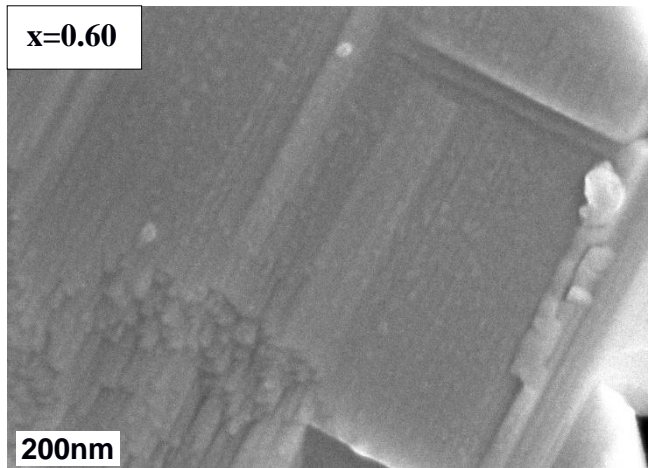
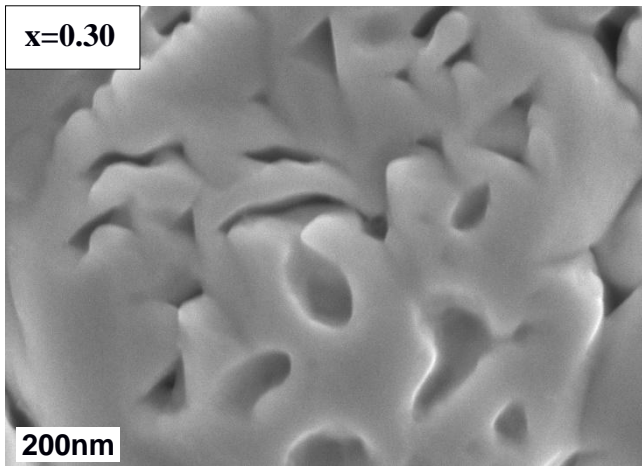


Figure 2: SEM surface images of CIGSe films, after the KCN surface etching and annealing under vacuum: #01 with $x=0.30$ (left) and #02 with $x=0.60$ (right)

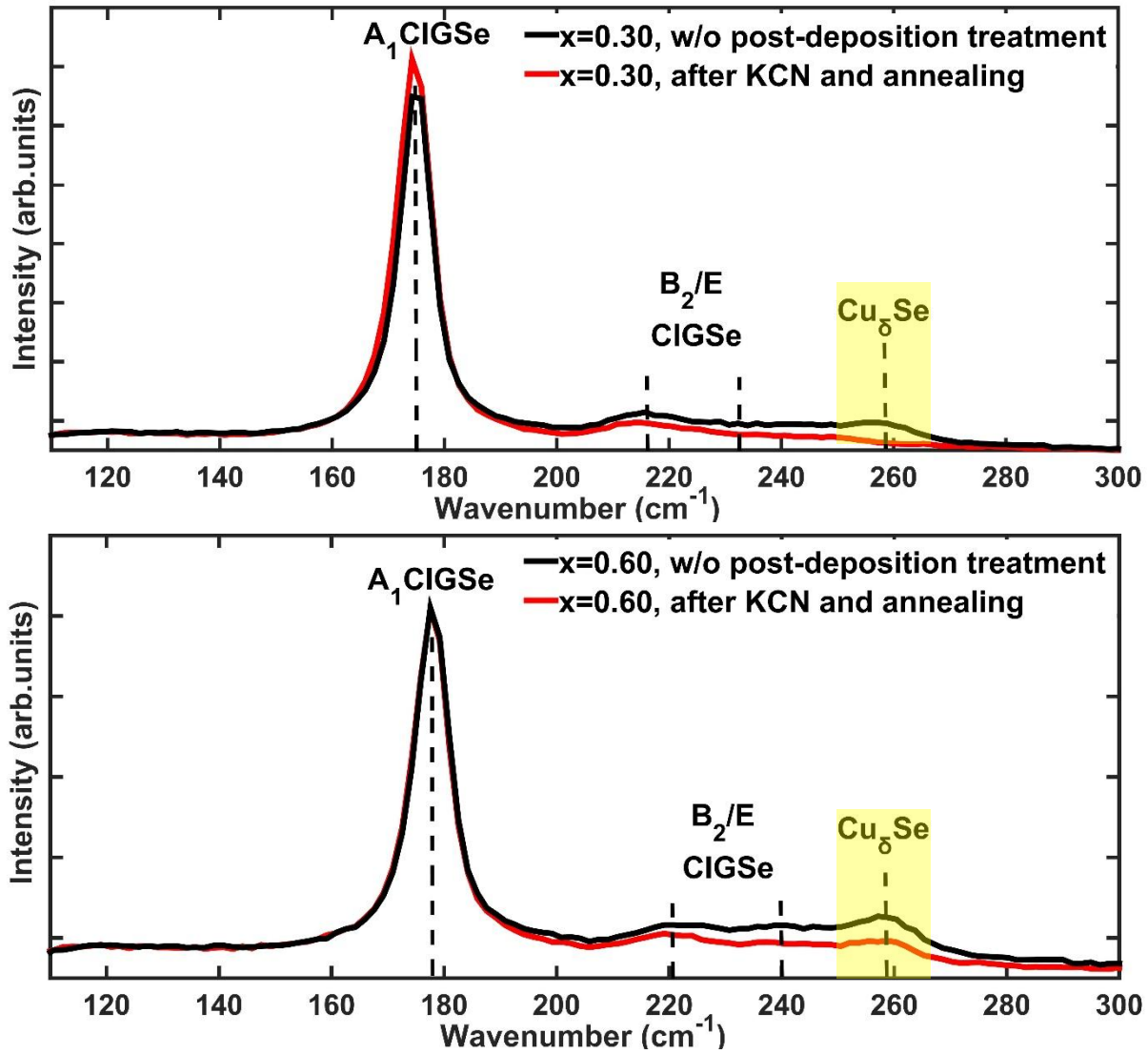


Figure 3: Raman analysis of the CIGSe films #01 with $x=0.30$ (a) and #02 with $x=0.60$ (b). The black lines correspond to the Raman spectra of the samples without any post-deposition treatment. The red lines represent the samples after the KCN etching and annealing. The peak that corresponds to the copper selenide phase is highlighted in yellow

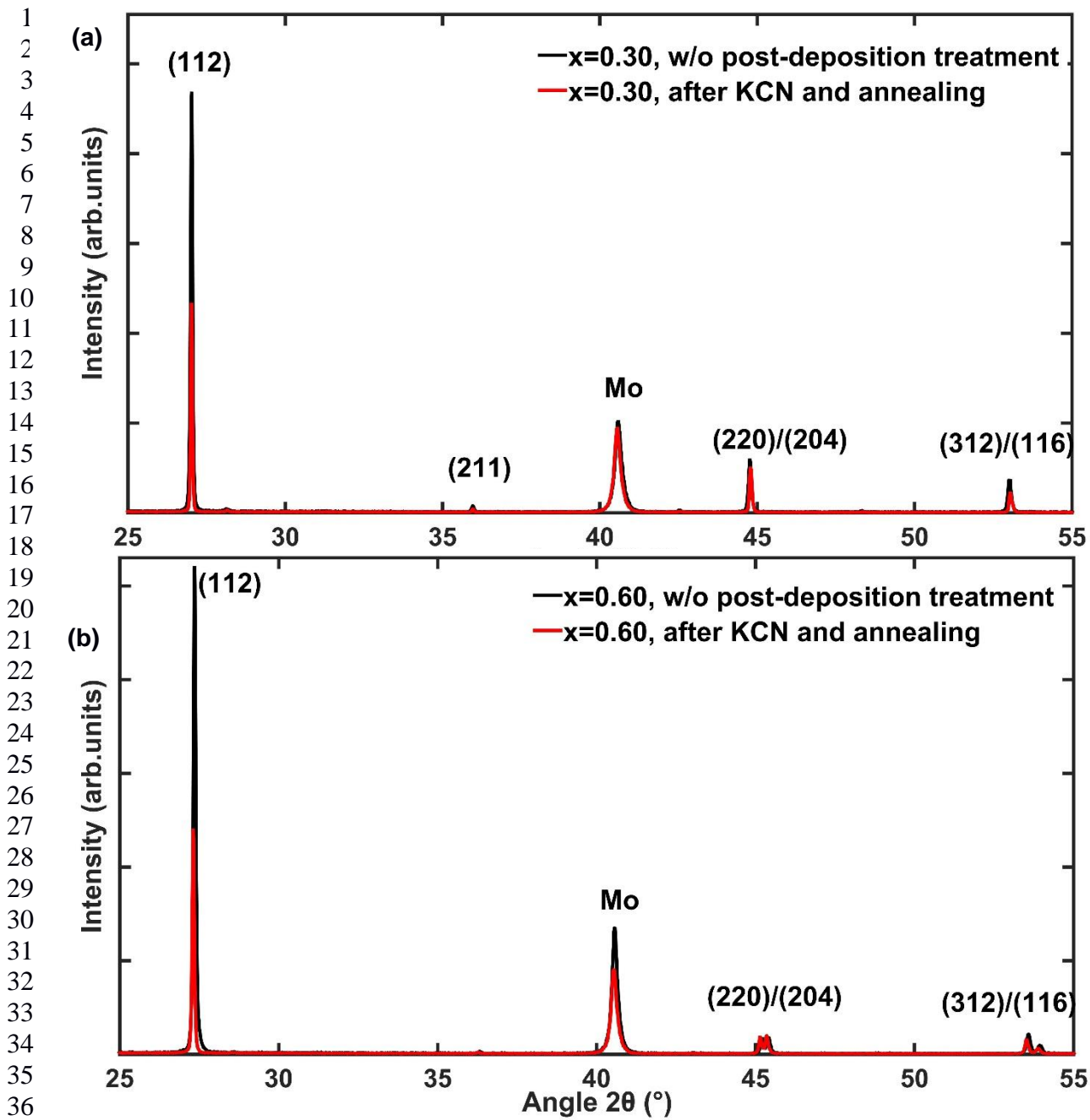
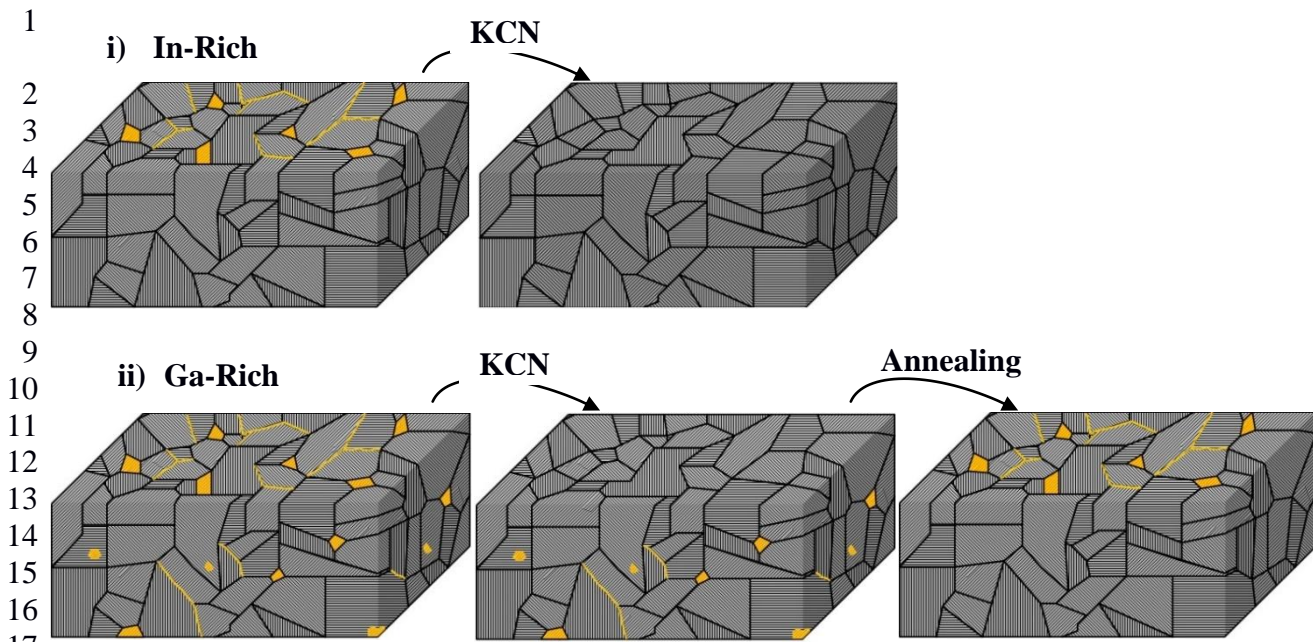


Figure 4: XRD analysis of $x=0.30$ (#01, (a)) and $x=0.60$ (#02, (b)) CIGSe layers grown on SLG/SiN/Mo. The black lines illustrate the diffractogram of the final CIGSe layers obtained after the end of the two-stage co-evaporation process and they did not undergo any post-deposition process. The red lines show the diffractogram obtained for the CIGSe samples after the KCN surface etching and annealing under vacuum for 30 days at 350°C



19 **Figure 5:** Schematic representation of the copper selenide surface segregation and bulk precipitation in
 20 the case of i) In-rich CIGSe and ii) Ga-rich CIGSe absorber layers. At the In-rich sample after the end
 21 of the CIGSe growth the copper selenide has entirely segregate at the surface of the film. Hence the
 22 removal of the copper selenide phases from the surface leaves a homogeneous CIGSe film without any
 23 detrimental Cu-rich secondary phases. At the Ga-rich sample, the duration of the deposition process is
 24 not sufficient to homogenize the film and make the copper selenide compounds segregate at the surface.
 25 As a result, after the end of the deposition process, there are Cu-enriched bulk precipitates within the
 26 bulk of the absorber layer, that they cannot be removed by the KCN treatment. A long annealing under
 27 vacuum is then required for the Ga rich absorber to make the entire Cu_5Se segregate at the surface
 28

1
2
3
4
5
6
7
8
9
10
11
12
13
14

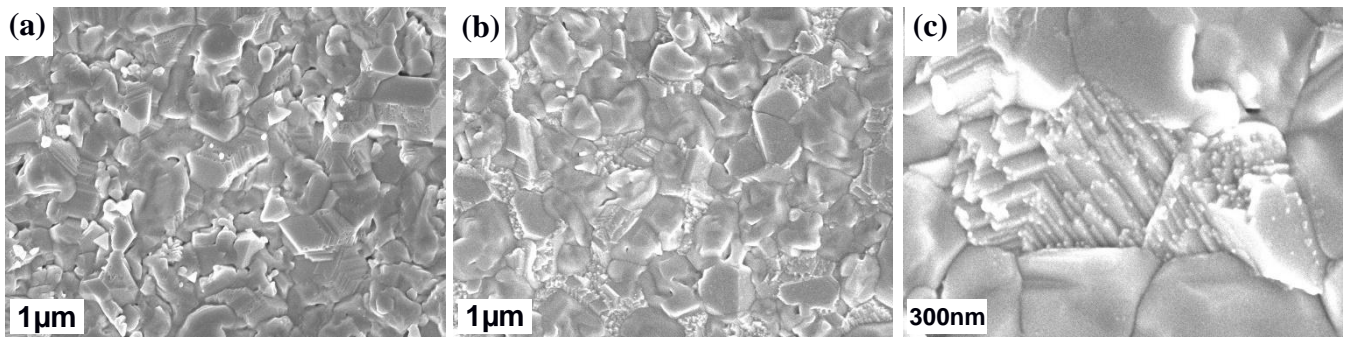


Figure 6: SEM surface images of CGSe Cu-rich layer (#03) deposited on Mo, (a) after the co-evaporation without post-deposition treatment, (b) after annealing at 350°C for 24h under vacuum and (c) high-magnification image of the sample after annealing at 350°C for 24h

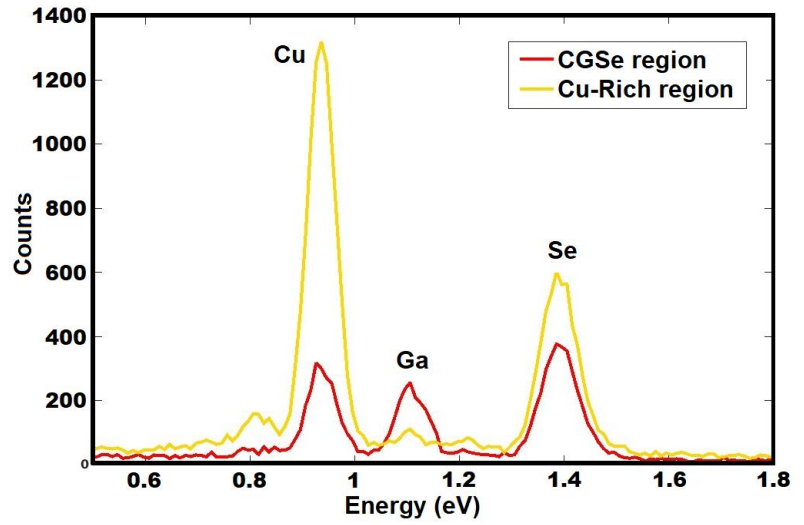
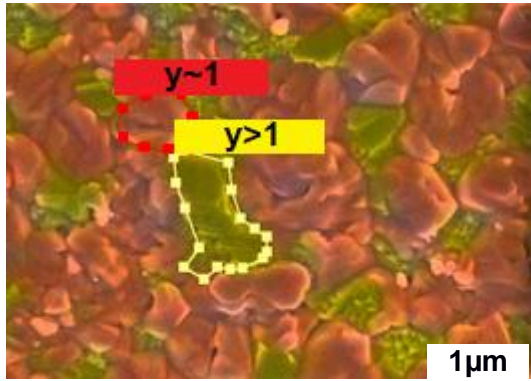
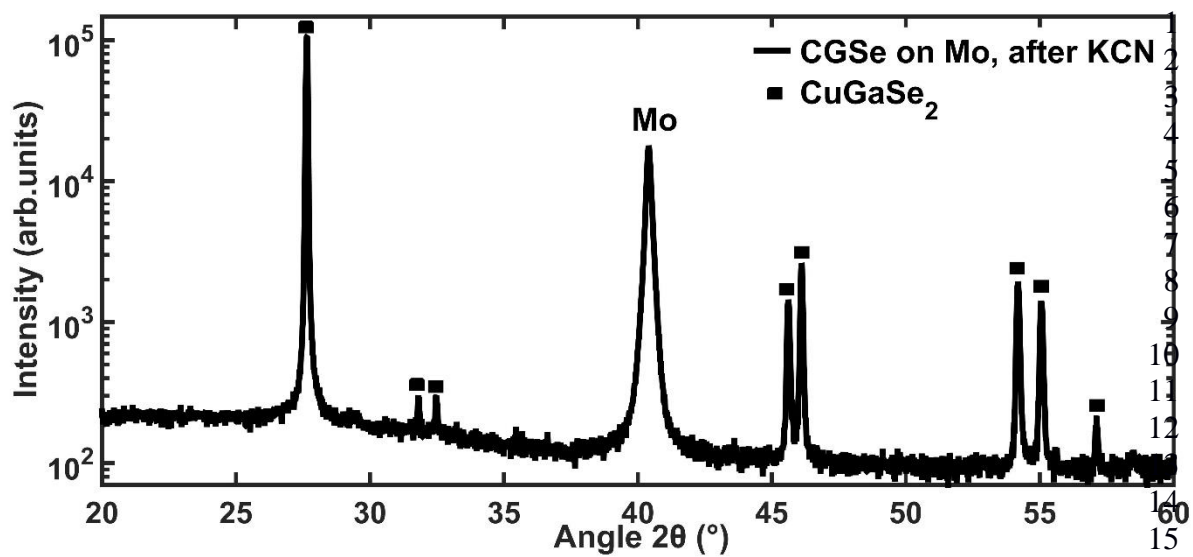
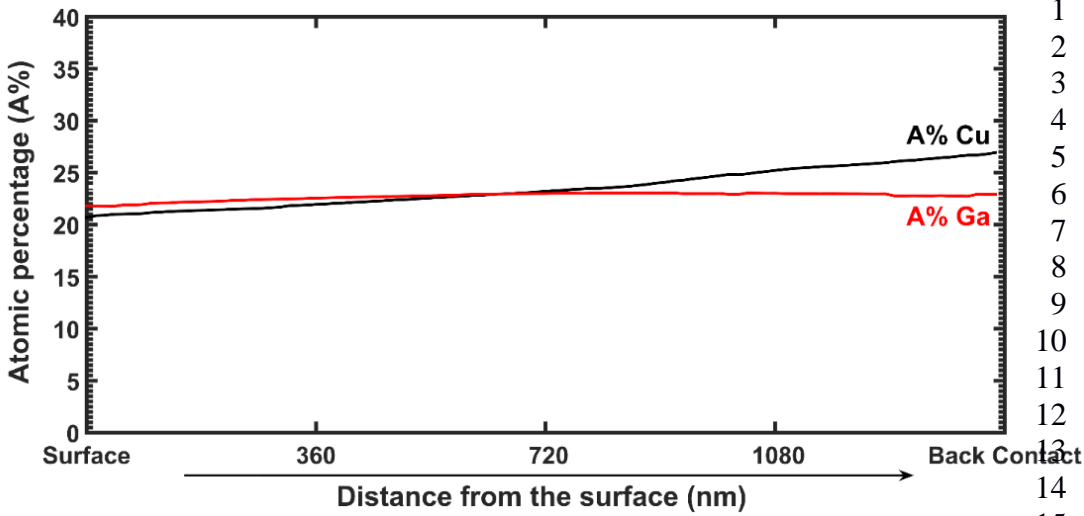


Figure 7: Left: SEM surface image coupled with EDS surface cartography (at 5kV acceleration voltage) of the In-free CGSe film (#03) after annealing. Right: The elemental concentration of the two grains highlighted by the dotted circles in the SEM image. The red curve in the EDS spectrum corresponds to a stoichiometric CGSe region while the yellow curve represents a Cu-enriched region and the presence of copper selenide secondary phases



16 **Figure 8:** XRD analysis of a CGSe sample (#04, $y=0.95$) grown on SLG/Mo by two-stage co-
 17 evaporation process (Cu-RO). The diffractogram does not present any Cu_3Se peak. The y axis represents
 18 the logarithm of the intensity
 19



1 **Figure 9:**
 2 *SEM-EDS*
 3 *cross-section*
 4 *elemental*
 5 *profile of a*
 6 *CGSe*
 7 *sample (#04,*
 8 *y=0.95)*
 9 *grown on*
 10 *Mo by a*
 11 *two-stage*
 12 *co-*
 13 *evaporation*
 14 *process (Cu-*
 15 *RO). The*

16 *EDS measurement was performed at 10 kV beam acceleration voltage*
 17
 18

1 **Table I:** Summary of the elemental concentration $x=[Ga]/([Ga]+[In])$ and $y=[Cu]/([Ga]+[In])$
2 measured by EDS at 20 kV acceleration voltage, the substrate, the CIGSe co-evaporation process and
3 the post-deposition treatment (KCN etching and annealing) of each sample. The y_R , y and y_A denote the
4 Cu content at the end of the Cu-rich stage, after the end of the co-evaporation process and after the
5 annealing respectively. The error at the atomic percentage is ± 0.03
6

sample	x	y_R	y	y_A	Substrate	Co-evaporation process	KCN etching	Annealing ¹
#01	0.30	1.36	0.98	0.92	SLG/ Si _x N /Mo	Cu-RO	YES	30 days
#02	0.60	1.39	0.87	0.86	SLG/ Si _x N /Mo	Cu-RO	YES	30 days
#03	1.00	-	1.50	-	SLG/Mo	Cu-R	NO	24 hours
#04	1.00	-	0.95	-	SLG/ Mo	Cu-RO	YES	-

7 ¹For the annealing of 30 days the samples were sealed under vacuum in quartz tubes. The annealing of
8 24 hours was carried out in a chamber under vacuum

9