

# Chemistry and dynamics of Ge in kesterite: towards band gap graded absorbers

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## Abstract

The selenization of metallic Cu-Zn-Sn-Ge precursors is a promising route for the fabrication of low-cost and efficient kesterite thin film solar cells. Nowadays, efficiencies of kesterite solar cells are still below 13 %. For Cu(In,Ga)Se<sub>2</sub> solar cells, the formation of compositional gradients along the depth of the absorber layer has been demonstrated to be a key requirement for producing thin film solar cells with conversion efficiencies above the 22 % level. No clear understanding has been reached so far about how to produce these gradients in an efficient manner for kesterite compounds, but among the possible candidates, Ge arises as one of the most promising ones. In the present work, we evaluate the potential of incorporating Ge in Cu<sub>2</sub>ZnSnSe<sub>4</sub> to produce compositional gradients in kesterites. Synchrotron-based in-situ energy-dispersive X-ray diffraction and X-ray fluorescence has been used to study the selenization of Cu-Zn-Sn-Ge metallic precursors. We propose a reaction mechanism for the incorporation of Ge atoms into the kesterite lattice after the formation of Cu<sub>2</sub>ZnSnSe<sub>4</sub>. Electron microscopy reveals that the annealing process leads to Cu<sub>2</sub>Zn(Sn,Ge)Se<sub>4</sub> absorber layers with an increase of Ge content towards the back contact with independence of the original location of Ge in the precursor layer. The effect of the Ge gradient on the optoelectronic properties of the absorber layer has been evaluated with room temperature cathodoluminescence. The implications of the results for the development of kesterite solar cells are discussed, with the aim of encouraging new synthesis routes for compositionally graded absorbers.

## 1. Introduction

Recent developments in the field of thin film solar cells based on Cu(In,Ga)Se<sub>2</sub> (CIGSe) have resulted in large progress in terms of record performances in the lab with efficiencies exceeding 22 %<sup>1-3</sup>. These efficiency levels have been achieved through producing absorber layers with variable band gap along its depth and with surface treatments<sup>3</sup>. These band gap variations in

CIGSe solar cells are achieved with synthesis processes designed to result in compositionally graded absorber layers<sup>1,2</sup>. The great advantage of compositionally graded absorber layers is that with composition, the position of the valence band and the conduction band can be modified along the thin film to minimize recombination losses and improve the performance of the solar cells<sup>1,4</sup>. An increased concentration of Ga in CIGSe towards the back contact helps in driving the photogenerated minority carriers to the heterojunction and reduces their recombination at the back contact. In CIGSe, this type of gradients leads to substantial improvements of open-circuit voltage ( $V_{OC}$ ) and charge carrier collection<sup>4,5</sup>.

Current efficiency levels of kesterites are below 13%<sup>6</sup>, owing to short minority carrier lifetimes in the sub-nanosecond regime<sup>7</sup>. Kesterite compounds like  $Cu_2Zn(Sn,Ge)(S,Se)_4$  as absorber for thin films solar cells have the potential to contribute to the increase of solar energy in large volumes using earth abundant elements such as Sn and Zn. The capability of these compounds to host various elements in the same atomic position, such as Sn and Ge in  $Cu_2Zn(Sn,Ge)Se_4$  (CZTGeSe), allows to tune the band gap of the compound by varying the composition similar to CIGSe. The band gap of these compounds is found to increase from  $\sim 1.0$  eV for  $Cu_2ZnSnSe_4$  (CZTSe)<sup>8</sup> to  $\sim 1.4$  eV for  $Cu_2ZnGeSe_4$ <sup>9,10</sup> and both crystallize in the kesterite type structure<sup>11,12</sup>. By synthesizing the solid solution CZTGeSe and by tuning the [Sn]/[Ge] ratio, the band gap energy of the compounds can be varied almost linearly with composition<sup>10,13</sup>. This band gap variation is expected to occur mainly by changes in the energy position of the conduction band minimum (CBM). This is because the CBM is mainly derived from the Ge or Sn 4s and the Se *p* states and the valence band maximum (VBM) is derived from the hybridization of Cu 3d and Se *p* states<sup>9</sup>. I.e., the CBM position can be potentially tuned within the absorber layers by controlling the depth distribution of Sn and Ge<sup>14</sup>.

In kesterites, the formation and control of band gap gradients by varying the anion composition (S and Se) has been identified as a challenging task<sup>15</sup>. Sulfur enrichment at the surface has been accomplished in a two stage process resulting in large gains of open circuit voltage  $V_{OC}$  and efficiencies of more than 12% owing to a band gap increase near the heterojunction interface<sup>16,17</sup>.

Several groups have reported substantial improvements in the performance of CZTSe solar cells by the incorporation of Ge. These improvements are mainly driven by 1) Increased  $V_{OC}$  and fill factor (FF) values<sup>13,18–24</sup>, 2) improved charged carrier collection<sup>13,18,19</sup> and 3) longer decay times in time resolved photoluminescence measurements (TRPL)<sup>13,23</sup>. However, the reasons for these improvements have rarely been attributed to a compositional gradient along the film. Instead, these improvements have been associated to other effects such as a) reduction of the concentration of deep defects<sup>18</sup>, b) improved crystallinity<sup>18,19</sup>, c) reduction of band tailing<sup>23</sup> and d) better control of elemental losses<sup>13</sup>.

To be able to optimize synthesis routes for the fabrication of graded CZT(Ge)Se absorber layers such as found in high efficiency CIGSe solar cells<sup>1</sup>, it is crucial to understand the chemistry and dynamics of Ge in kesterites compounds. Initial studies in the formation of Ge-Sn graded CZTGS absorbers from nanocrystal precursors have been reported by Kim *et al*<sup>25</sup>. Depletion of Ge towards the surface<sup>25</sup> or Ge accumulation towards the back contact has been observed<sup>13</sup>. However, the mechanism of formation of the Ge-Sn gradient during annealing remains

unclear. In this paper, the mechanism behind the synthesis of Sn-Ge compositionally graded kesterite absorbers is studied by in-situ energy-dispersive X-ray diffraction and X-ray fluorescence (EDXRD/XRF) which allows time resolutions of one spectrum every three seconds. The results presented here provide insights in the chemistry of the Ge incorporation in CZTSe and the gradient formation.

## 2. Experimental section

Cu/Sn/Cu/Zn metallic stacks were sputtered on Mo coated soda lime glass substrates with compositional ratios of  $[Cu]/([Zn]+[Sn]) = 0.75$  and  $[Zn]/[Sn] = 1.20$  as determined with a calibrated X-ray fluorescence (XRF, Fischerscope XVD)<sup>18</sup>. An additional set of precursors were prepared with a 50 nm thick Ge layer thermally evaporated on top of the Cu/Sn/Cu/Zn metallic stacks<sup>19</sup>. The evaporation was performed in an Oerlikon Univex 250. To understand the growth mechanisms of kesterite compounds in the presence of Ge, different selenization processes were performed using a Cu/Sn/Cu/Zn stack with and without a 50 nm Ge layer on top of the precursor.

The precursors were annealed in selenium vapor inside a cylindrical graphite reaction box (reactor) placed inside a vacuum chamber<sup>26</sup>. For the reactive annealing, 200 mg of Se pellets were placed in a ceramic crucible next to the sample. The reactor was sealed with a motorised valve at a pressure of  $\sim 10^{-4}$  mbar and heated by halogen lamps. The temperature of the processes was controlled and recorded with a thermocouple located 5 mm above the sample. The heating rate was set to 20 K / minute which is similar to rates found for conventional tube furnaces. A two-step selenization process similar to the one used for achieving over 10% solar cells was studied with a first dwelling step at 400 °C for 30 minutes and a second one at 500 °C for 15 minutes<sup>19</sup>. The temperature profile for this process is shown in *Figure 1.a*. To evaluate shorter selenization times, an additional Cu/Sn/Cu/Zn/Ge sample was studied with a single heating ramp (20 K / minute) up to 500 °C and a dwell time of 10 minutes. During the cool-down step, the reactor valve was opened for five minutes at 350°C to remove potential residual vapor phases.

The annealing chamber<sup>26</sup> was coupled to the polychromatic EDDI beam line<sup>27</sup> of the BESSY II synchrotron facility. During the annealing, diffraction and fluorescence signals were recorded in an energy-dispersive high-purity Ge detector under a scattering angle of  $2\theta = 3.041 \pm 0.002$ . The relationship between the lattice plane spacing  $d_{hkl}$  of a crystalline phase and the photon energy  $E_{hkl}$  of the corresponding diffraction line follows the energy-dispersive Bragg law  $E_{hkl} = hc / (2d_{hkl} \sin\theta)$ , where  $h$  is Planck's constant and  $c$  the speed of light.

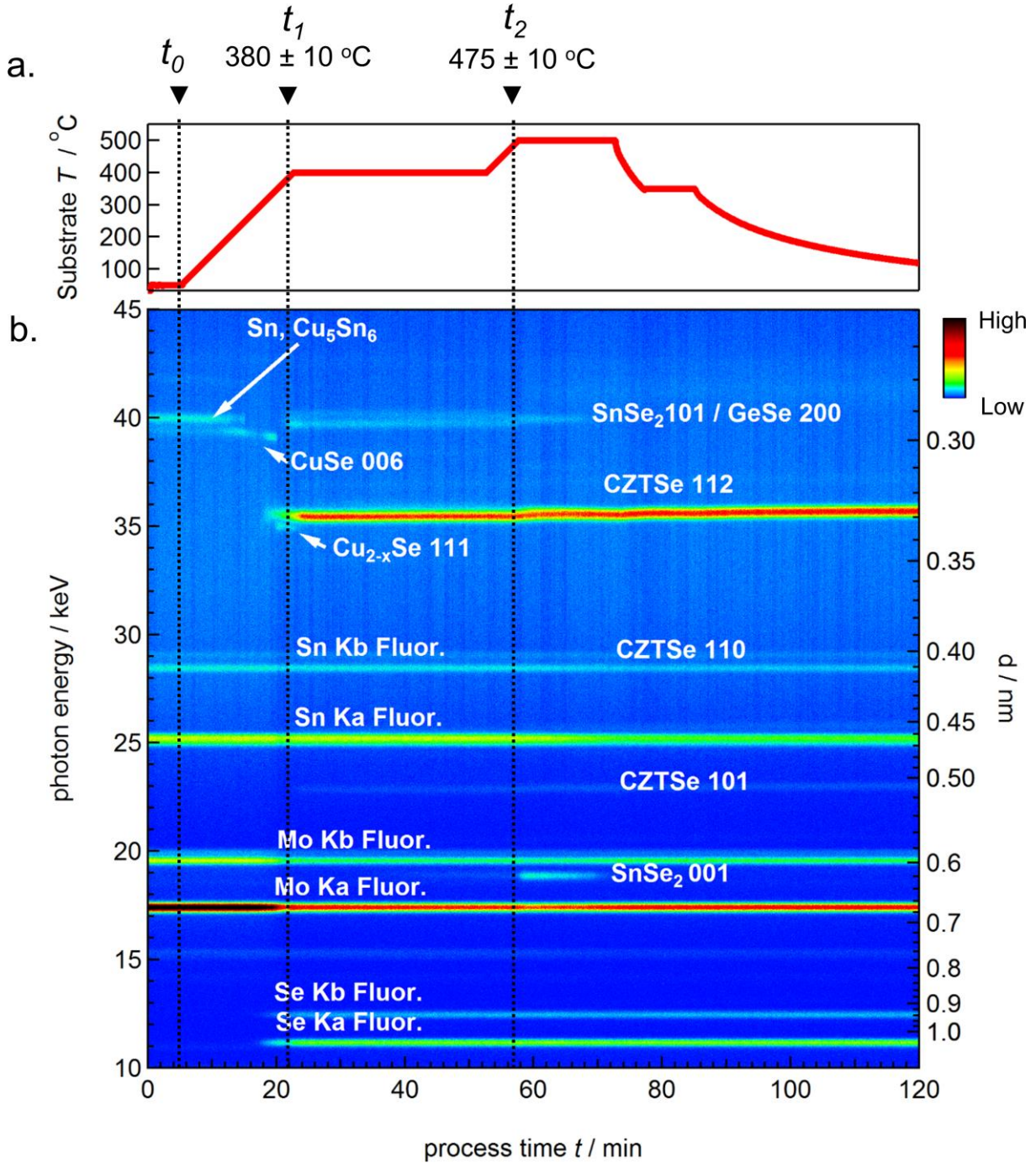
Elemental distributions were measured by means of energy-dispersive X-ray spectroscopy (EDX) conducted in Zeiss Ultraplus scanning electron microscope equipped with an Oxford Instruments XMax 80 mm<sup>2</sup> silicon drift detector on polished cross-sectional samples. For EDX elemental-distribution maps (net counts), 7 kV acceleration voltage and 90 pA probe current were used.

Cathodoluminescence (CL) hyperspectral maps were measured with a Zeiss Merlin SEM equipped with a Delmic Sparc CL detection system. Point exposure time on the InGaAs array detector was 3s for a 10kV acceleration voltage and a 10nA beam current.

### 3. Results and discussion

#### 3.1. Real-time phase analysis

##### 3.1.1. Selenization of the metallic precursor and formation of the kesterite phase



**Figure 1.** a) Substrate temperature during the process. b) Color-coded representation of the EDXRD/XRF intensities as a function of photon energy and process time recorded during the selenization of a metallic Cu/Sn/Cu/Zn/Ge stack. The right axis shows the lattice plane distances  $d$  calculated from the photon energy values using the Bragg equation. The Mo Sn and Se fluorescence signals and the reflections of the following phases are indicated in the plot: CuSe (PDF- 86-1239),  $\text{Cu}_{2-x}\text{Se}$  (PDF- 073-2712 ), CZTSe (PDF- 070-8930),  $\text{SnSe}_2$  (PDF- 01-089-2939), Sn (PDF- 01-086-2266),  $\text{Cu}_5\text{Sn}_6$  (PDF- 01-072-8761) and GeSe (PDF- 01-071-4730).

EDXRD/XRF data recorded during the two-step selenization of the sample with a 50 nm Ge capping layer are shown in Figure 1. The plot shows color-coded diffraction and fluorescence

signals as a function of photon energy, lattice plane distance  $d$  and process time  $t$ . (A similar plot for the sample without Ge can be found in the Supplementary Information, *Figure S1*).

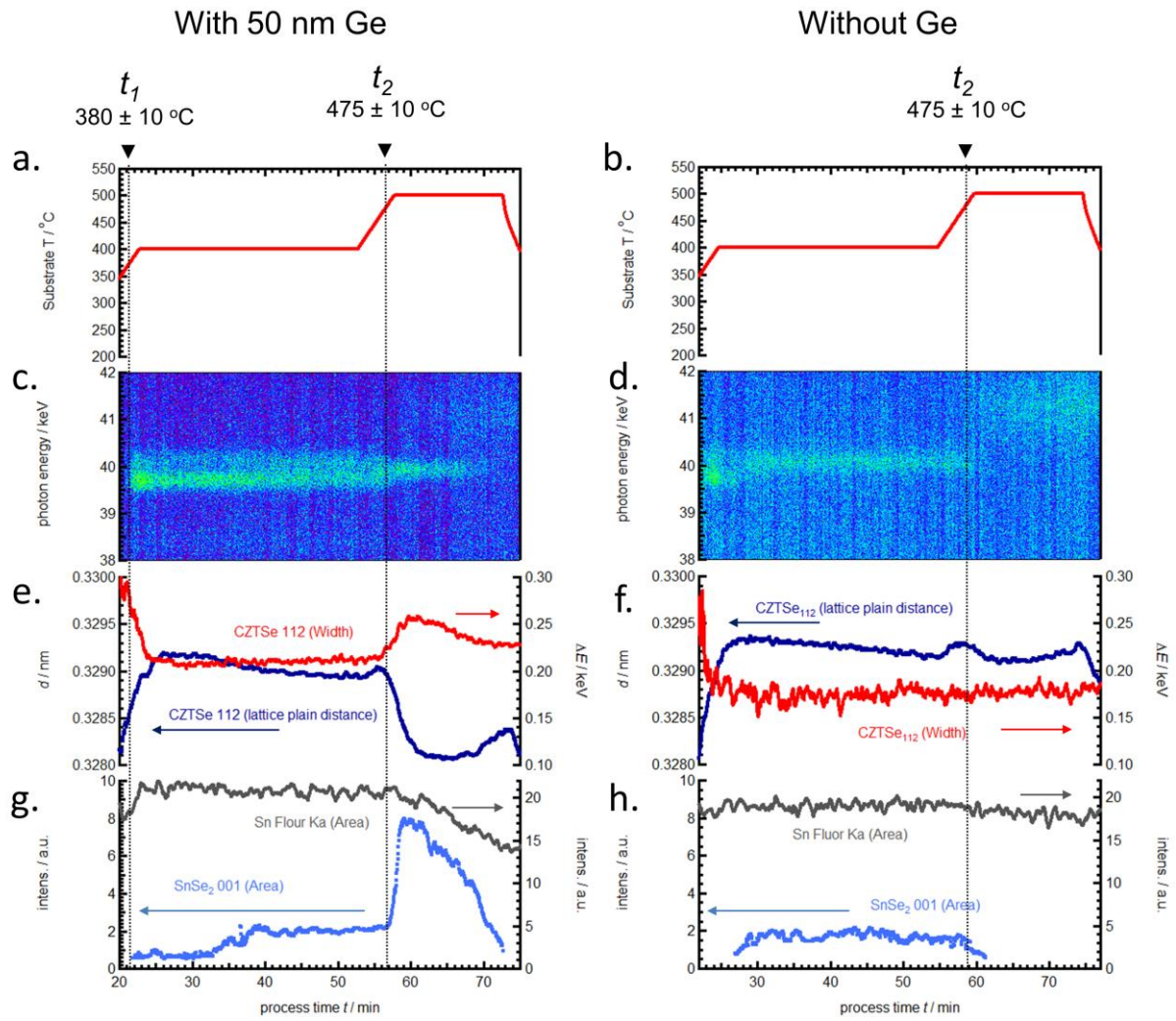
At the beginning of the process ( $t_0$  - *Figure 1*), a diffraction signal of the metal precursor (overlapping peaks of Sn and  $\text{Cu}_5\text{Sn}_6$ ) can be observed at around 40 keV, along with the fluorescence signals of Se, Mo and Sn. The diffraction signal of the metal precursor starts to vanish at temperatures around the melting point of Sn  $\sim 231^\circ\text{C}$  (15 min process time)<sup>28</sup>. Shortly after this, the fluorescence signals of Se start to appear, indicating the beginning of the first reactions with Se in the film. As the Se fluorescence signals increase in intensity, the Mo signals decrease. This can be explained by the attenuation of these signals due to the Se incorporation.

The first crystalline binary phase observed is CuSe (PDF - 86-1239)<sup>29</sup> which can be tracked by the 006 reflection appearing at around 39 keV. This signal disappears at around  $\sim 340^\circ\text{C}$  (20 min process time). At this time, a reflection corresponding to the  $\text{Cu}_{2-x}\text{Se}$  (PDF - 073-2712) phase arises at photon energies around 35 keV. Simultaneously, a diffraction signal near the expected position of CZTSe 112 at 35.5 keV appears, indicating the initial formation of the CZT(Ge)Se phase. While this reflection cannot be unambiguously attributed to kesterite due to similar peak positions of CT(Ge)Se and ZnSe, the simultaneously rising of the peak near the position of CZT(Ge)Se 101 (23 keV) confirms the formation of the kesterite phase<sup>30</sup>.

The early formation of Cu-Se binaries has been proposed to be promoted by a fast diffusion of Cu towards the surface of the film compared to the other elements<sup>30</sup>. This mechanism has also been proposed for CIGSe where Cu has a higher diffusivity than In and Ga and reaches the surface of the film where it starts reacting with the Se vapor<sup>31</sup>.

Slightly after the appearance of the diffraction signal of CZT(Ge)Se 112, a broad double peak feature emerges at 39 keV at around  $\sim 380^\circ\text{C}$  ( $t_1 = 22 \text{ min}$  - *Figure 1 and 2*). These two peaks can be attributed to the reflections of GeSe 200 (PDF- 01-071-4730) and  $\text{SnSe}_2$  101 (PDF- 01-089-2939) and are present during the whole dwell time at  $400^\circ\text{C}$ . *Figure 2.c* and *d* show a magnification of the double peak feature for the sample with 50 nm of Ge added and without Ge for comparison. For the sample without Ge, the double shoulder peak cannot be seen and just a low intensity peak at around 40 keV is present (*Figure 2.d*), confirming that for the sample with Ge the low energy side of the double peak was arising from a Ge containing phase (*Figure 2.c*). Without loss of Sn, the presence of Sn-Se binary phases is expected considering that the precursors used for this study have Cu-poor composition<sup>32</sup>.



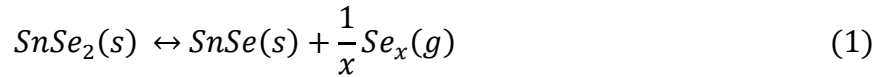


**Figure 2.** Plots in the left column (a, c, e and g) are related to the selenization process of the Cu/Sn/Cu/Zn/Ge stack and in the right column (b, d, f and h) are related to the selenization of the Cu/Sn/Cu/Zn stack. All plots are a function of the process time (x axes). a) and b) show the temperatures measured for the selenization processes. c) and d) show a magnification of the color coded EDXRD signals with photon energies from 38 to 42 keV. e) and f) show the calculated lattice plane distance (dark blue: left y-axis) and the width (red: right y-axis) of the CZT(Ge)Se 112 diffraction signal. g) and h) show the values of the area of the 001 SnSe<sub>2</sub> diffraction signal (light blue: left y-axis) and the Sn K $\alpha$  fluorescence (grey: right y-axis).

### 3.1.2. Ge incorporation and SnSe<sub>2</sub> segregation

At around  $\sim 475^\circ\text{C}$  in the second ramping step, the signal of the 200 reflection of GeSe vanishes ( $t_2 = 57 \text{ min}$  – see Figures 1 and 2). Simultaneously, the intensity of a previously faint signal at 19 keV attributed to SnSe<sub>2</sub> 001 increases substantially (as shown in Figure 1.), indicating the segregation of this phase. The evolution of the integral intensity of this reflection is plotted in Figure 2.g. In contrast, an increase in intensity of this signal is not observed for the selenization of the Cu/Sn/Cu/Zn sample without Ge (Figure 2.h). Interestingly, for the sample with Ge, the SnSe<sub>2</sub> 101 reflection ( $\sim 40 \text{ keV}$ , Figure 2 c) does not show such an increase in intensity at  $t_2 = 57 \text{ min}$  as observed for the 001 SnSe<sub>2</sub> signal, suggesting that the segregated phase exhibits strong preferential orientation. Figure 2 g and h also show the evolution of the Sn K $\alpha$  fluorescence signal. For the sample with Ge a clear decrease in the Sn K $\alpha$  intensity can be seen as the 001 SnSe<sub>2</sub> signal decreases during the dwell time at  $500^\circ\text{C}$ . The parallel decline indicates

that the Sn loss occurring in this sample mainly arises from the SnSe<sub>2</sub> phase. Sn loss is a mechanism which has been studied in kesterites, and has been associated to processes with longer dwelling times and where the Se partial pressure was low<sup>33–36</sup>. The poor capability of the annealing reactors to maintain high S and Se partial pressure with time due to leakage or vapor absorption in the reactor walls has also been associated with Sn loss<sup>37</sup>. The evaporation of SnSe<sub>2</sub> occurs incongruently as represented by *reactions 1* and *2*<sup>38</sup>. Under high Se partial pressure, SnSe<sub>2</sub> would be stabilized as the reaction 1 would proceed towards the left hand side. The decrease of the intensity of the SnSe<sub>2</sub> reflection indicates a decrease of the Se partial pressure in the system, similarly observed for SnS<sub>2</sub> by in-situ Raman spectroscopy measurements<sup>37</sup>.

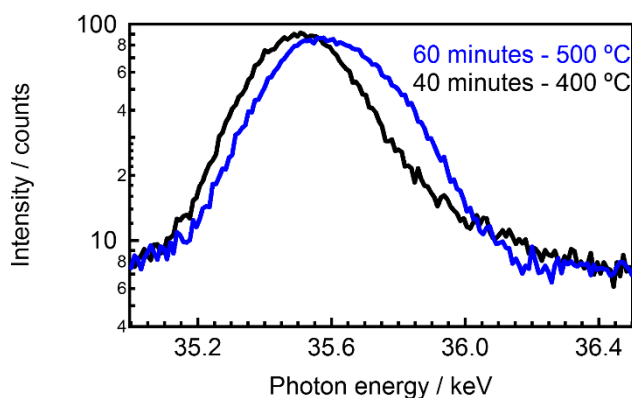


To study the incorporation of Ge into the kesterite phase the calculated peak width and the lattice plane distances of the 112 reflection of the CZT(Ge)Se phases of the samples with and without Ge are shown in *Figure 2.e* and *f* respectively. During the 400 °C step of the annealing process, the *d* values of CZT(Ge)Se 112 for both samples are very similar, with slightly smaller values for the Ge-containing sample (*Figure. 2.e*), suggesting that the amount of Ge incorporated into the tetragonal CZT(Ge)Se structure is rather small at this stage. However, during the transition at *t*<sub>2</sub> = 57 min where the GeSe reflection vanishes and SnSe<sub>2</sub> segregates, a steep decrease of *d* for the sample with 50nm of Ge occurs (*Figure 2e*). This shift is not observed in the sample without Ge, implying that the decrease is due to the incorporation of Ge into the CZT(Ge)Se lattice.

Ge atoms, which are smaller than Sn, occupy Sn positions in the kesterite-type structure, inducing a decrease of the lattice plane distance *d*<sup>10</sup>. The detection of the SnSe<sub>2</sub> 101 signal prior to the incorporation of Ge at *t*<sub>2</sub> = 57 min suggests that the CZTSe lattice is saturated with Sn. To be able to incorporate Ge atoms into the CZTSe lattice, Sn atoms would need to leave the structure. We propose that the replacement of Sn by Ge in the kesterite structure leads to the further segregation of SnSe<sub>2</sub> observed by the increased intensity of the SnSe<sub>2</sub> 001 signal, as discussed in Sec. 3.3.

Broadening of a diffraction peak can arise from different sources such as low values of the domain size, increase of microstrain<sup>39,40</sup>, or compositional gradients<sup>41</sup>. At the point where the CZT(Ge)Se 112 signal shifts to lower *d*-values, indicating incorporation of Ge (*t*<sub>2</sub> = 57 min – *2.e*), the width of the 112 peak clearly increases. *Figure 3* shows the diffraction signal of the 112 of the CZT(Ge)Se phase before (400 °C, 40 minutes) and after the Ge incorporation (500 °C, 60 minutes). The widening of the peak is asymmetric and more pronounced at the high-energy side. This asymmetric broadening can be explained by the formation of domains which have higher Ge concentration and therefore lower *d*-values than the main part of the film. In *Figure 2e* it can be seen that after the Ge incorporation – detected by the shift of the 112 peak to lower *d*-values –, the broadening of the peak achieves its maximum and then it decreases progressively during the 500 °C dwell time. This decrease of the width of the peaks is correlated

with an increase of  $d$ . Both variations can be explained by the interdiffusion of Ge and Sn which leads to a decrease of the Ge/Sn gradient in the CZTGeSe phase. However, the final width of the peak is still significantly broader ( $\sim 0.23$  keV) and more asymmetric compared to the reference sample without Ge ( $\sim 0.18$  keV). This difference in widths suggests that a compositional gradient still exist at the end of the process, which is analyzed in more detail in the next section.



**Figure 3** 112 reflection of the CZT(Ge)Se phase of the Cu/Sn/Cu/Zn/Ge stack at 400 °C - 40 minutes (black) and 500 °C - 60 minutes (blue).

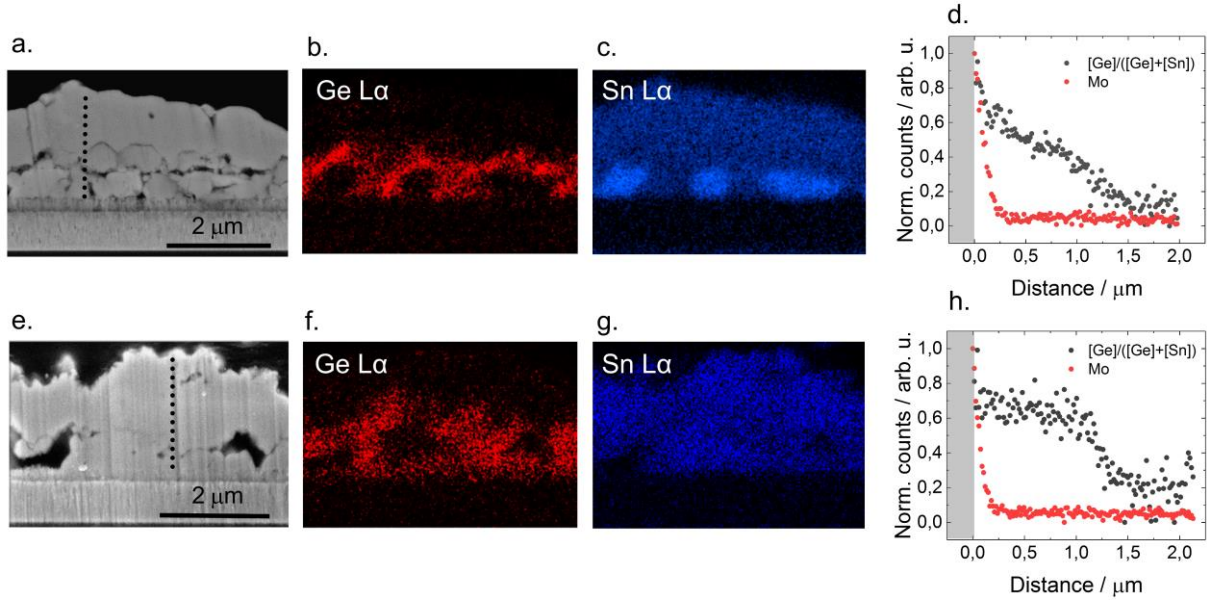
### 3.2. Microstructural and chemical distribution

To confirm and improve the understanding of the SnSe<sub>2</sub> segregation due to Ge incorporation in the CZTS(Ge)Se lattice, a selenization process with a single annealing step at 500 °C for 10 minutes was performed with a Cu/Sn/Cu/Zn/Ge stack. The qualitative phase evolution of this process observed by EDXRD/XRF was similar to the one shown in *Figure 1* (see Supplementary Information *Figure S2*). However, the total disappearance of the SnSe<sub>2</sub> 001 signal could not be observed here, indicating that a Se pressure high enough to prevent the decomposition of SnSe<sub>2</sub> to SnSe + Se (reaction 1) was maintained throughout the process. During the one-step selenization the total time at temperatures where the Se is in vapor phase was shorter (10 minutes at 500 °C) than in the two step processes presented in *Figures 1* and *2* (30 minutes at 400 °C + 15 minutes at 500 °C). Therefore, a higher Se pressure at the end of the one-step process is expected.

To evaluate the chemical distribution of the films after annealing, cross sectional SEM images and EDX compositional maps were acquired for the samples with Ge from both annealing processes (two-steps - 30 minutes at 400 °C, 15 minutes at 500 °C and one-step - 10 minutes at 500 °C) which are shown in *Figure 4*. In the sample annealed with a single step at 500 °C, an increase of Sn and Se counts in certain regions near the back contacts can be observed. In those locations there are no Ge counts, leading to the conclusion that these are the regions where the accumulation of SnSe<sub>2</sub> occurred. In the vicinity of the SnSe<sub>2</sub> phase, an increase of counts of Ge can be seen. This supports our previous assumption that SnSe<sub>2</sub> forms during the incorporation of Ge into the CZTSe lattice by replacement of Sn. The Ge counts are significantly reduced towards the surface of the film as shown in the [Ge]/([Ge]+[Sn]) profiles depicted in *Figure 4d*.



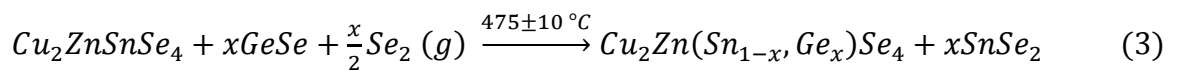
For the sample annealed with the two-step process, no accumulation of SnSe<sub>2</sub> can be observed as expected from the EDXRD data. The distribution of Ge counts is also increased towards the back contact (*see Figure 4h*), showing that the Ge/Sn gradient proposed in the previous section due to the peak widening occurs in the vertical direction (normal to the sample substrate). Also, voids in the interface with the back contact can be seen. The voids can be a consequence of the loss of SnSe<sub>2</sub> observed in the in-situ EDXRD/XRF data.



**Figure 4.** Secondary electron (SE) image and elemental EDX maps and line-scans showing the evolution of the normalised  $[Ge]/([Ge]+[Sn])$  ratio for the Cu/Zn/Sn/Ge samples selenised with (a,b,c and d) one-step - 10 minutes at 500 °C and (e, f, g and h) two-steps - 30 minutes at 400 °C and 15 minutes at 500 °C. The dotted lines in a and e represent the regions where the line-scans were performed. The shadowed areas in d and h represent the back contact region.

### 3.3. Growth mechanism and Ge-Sn interdiffusion

On the basis of in-situ EDXRD/XRF measurements and the results of the morphological and chemical analysis, we propose a mechanism for the Ge incorporation into the CZT(Ge)Se lattice for the type of samples and processes used in this study. This mechanism is schematically depicted in *Figure 5*. As previously observed for the selenization of Cu-Zn-Sn-S nanoparticles precursors, the formation of Cu-Se phases precedes the formation of CZT(Ge)Se<sup>30,42</sup>. The formation of CZTSe - with barely any incorporation of Ge in the lattice -, GeSe and a small amount of SnSe<sub>2</sub> occurs at temperatures around 380 °C (*Figure 5.a*). In the temperature range from 380-475 °C, CZTSe coexists with GeSe and some traces of SnSe<sub>2</sub>. At around 475 °C, GeSe reacts with CZTSe forming CZTGeSe and segregating SnSe<sub>2</sub> (*Figure 5.b*) as described by *reaction 3* where  $x$  is equivalent to the  $[Ge]/([Ge]+[Sn])$  ratio in the CZTGeSe compound formed.



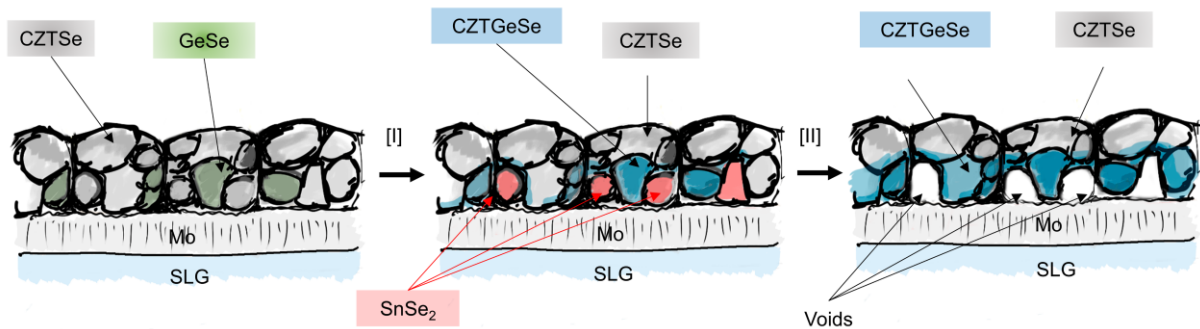
The reaction is adjusted under the assumption that the number of moles of GeSe incorporated to the CZT(Ge)Se phase is equal to the number of moles of SnSe<sub>2</sub> segregated. If the sample is annealed at a high temperature, loss of SnSe<sub>2</sub> with time can be observed, resulting in the

formation of voids (*Figure 5.c*). The segregation of  $\text{SnSe}_2$  could possibly be avoided by reducing the amount of Sn deposited in the precursor. This could also have the implication that the CZTSe phase formed at around  $380^\circ\text{C}$  grows in a Cu-rich regime, since the Cu/Sn ratio would be increased. The consequences of growing the absorber in a Cu-rich regime are still unclear and require further studies.

EDX and SEM analysis suggests that *reaction 3* takes place near the back contact, where the segregation of the textured  $\text{SnSe}_2$  occurs and where the Ge accumulation is observed. A key question for the understanding of the formation of the Ge gradient is how the Ge moves from the surface of the original precursor to the back of the film. The real-time measurements showed that first selenide that forms is Cu-Se, followed by Ge-poor CZTSe (possible also ZnSe or  $\text{Cu}_2\text{SnSe}_3$ ). Only then the Ge reacts with Se to form GeSe. We conclude that the formations of Cu-Se and CZTSe are enabled by the up-diffusion of Cu and subsequently Zn and Sn towards the surface to react with Se from the gas phase, which has been also observed for the selenization of CZTS nanoparticles<sup>30</sup>. This means that Cu, Zn and Sn diffuse through the Ge layer which leads to an effective downwards movement of Ge. If instead we would assume that Se diffuses into the film to form Cu-Se and CZTSe while Ge stays at the surface, the formation of Ge-Se would be expected as the first reaction. However, the real-time measurements show that GeSe forms in a later stage. This reaction is similar to the selenization of metallic Cu-In-Ga precursors, where first Cu and In react with Se to form Cu-Se, In-Se and finally  $\text{CuInSe}_2$  on top of the remaining Ga, leading to accumulation of Ga at the back of the film<sup>31</sup>.

At the boundaries where reaction 3 takes place, the CZTGeSe domains have higher Ge/(Ge+Sn) ratio than at the surface of the film (*Fig. 4*). After the reaction occurs, the Ge atoms can diffuse in the CZT(Ge)Se grains, increasing the  $[\text{Ge}]/([\text{Ge}]+[\text{Sn}])$  ratio towards the surface. According to the evaluation of the evolution of the 112 CZT(Ge)Se peak width (*Figure 2e.*) the Sn-Ge interdiffusion occurs for around 10 minutes until the decrease of the peak width saturates. This finding indicates that the final compositional profile has been reached.

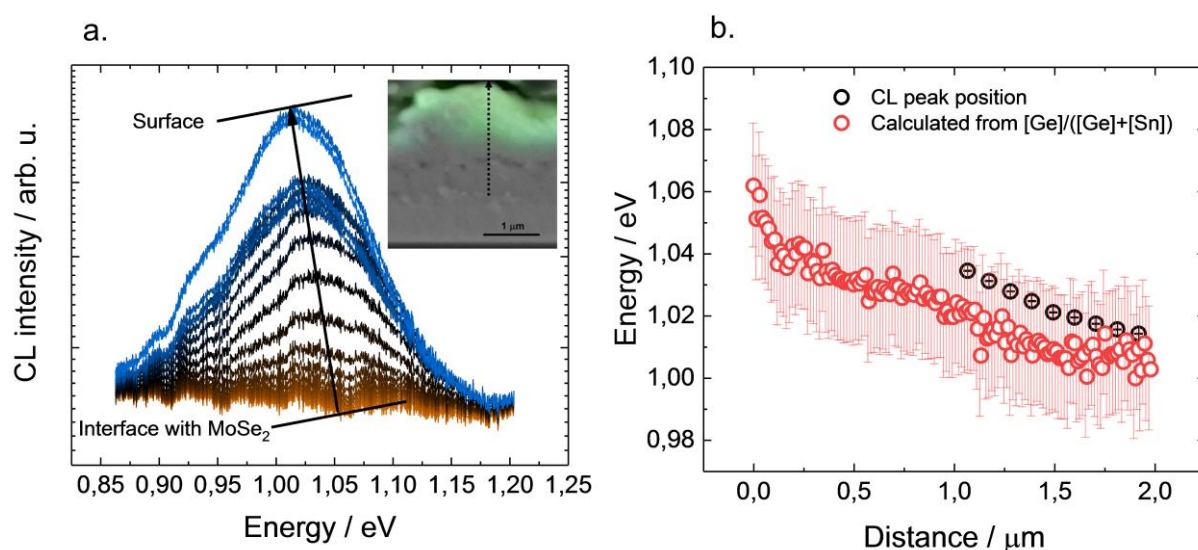
- I. Ge incorporation in CZTSe and segregation  $\text{SnSe}_2 \rightarrow T \sim 475^\circ\text{C}$
- II. Ge diffusion in CZTSe and  $\text{SnSe}_2$  loss  $\rightarrow f(T, t)$



**Figure 5.** Schematic model showing the incorporation of Ge in CZTSe and the segregation of  $\text{SnSe}_2$ . The model also illustrates a potential route for  $\text{SnSe}_2$  loss, voids formation and Ge-Sn interdiffusion in the CZT(Ge)Se grains. In the sketch,  $T$  and  $t$  stand for temperature and time respectively.

### 3.4. Implications for kesterite solar cells and recommendations for synthesis and characterization

The results presented in the previous sections clearly demonstrate that during selenization a Sn-Ge gradient with increasing Ge concentration towards the backside of the film forms, even though the Ge was deposited on the precursor surface. The beneficial effects observed in some Ge incorporated kesterite absorbers in literature might also be related to this effect. Bearing this in mind, we suggest that future research should strongly consider the phenomenon of Sn-Ge compositional gradients and careful characterization of elemental depth profiles is highly encouraged to support the interpretation of the optoelectronic properties of the samples.



**Figure 6.** *a)* Cathodoluminescence (CL) spectra acquired in a line-scan (dotted arrow in the inset) of the cross section view of the sample selenized with one-step - 10 minutes at 500 °C. An arrow is depicted for visual guidance of the evolution of the maxima of the CL spectra from the back surface to the top surface of the film. The inset shows a SE image of the cross section of the sample overlaid with the CL signal acquired (in green). *b)* CL peak position and  $E_g$  calculated from the compositional gradient as a function of the distance from the back contact.

The influence of the Ge to Sn ratio on the optoelectronic properties of the sample selenized with one-step and 10 minutes at 500 °C was evaluated with CL at room temperature at the cross section of the film. The evolution of the CL spectra as a function of depth of the absorber layer is depicted in *Figure 6a*. The intensity of the CL signal is represented in the inset of the figure overlaid with the SEM image as green color. No CL signal could be detected in the region with increased Ge concentration and where the segregation of SnSe<sub>2</sub> occurs. We speculate that the decrease in luminescence in this region could be due to several factors, for example: 1) decrease in carrier concentration in this region, which has been observed in literature in Ge rich kesterites<sup>18</sup> and thus affecting the luminescence yield<sup>43</sup>; 2) Carrier losses due to the presence of SnSe<sub>2</sub> in this region, shown to be detrimental for the performance of kesterite solar cells<sup>44</sup>. A red-shift of the maxima of the CL spectra as the signal comes originates from the middle of the film (1 μm) towards the top surface of the film demonstrating the influence of the compositional gradient on the optoelectronic properties of the absorber layer (*Figure 6b*). For visual comparison, the band gap ( $E_g$ ) values calculated from the EDX signals scaled to an average value of  $[Ge]/([Ge]+[Sn]) = 0.11$  as measured by XRF in an absorber layer processed with an

identical precursor are also shown in *Figure 6b*<sup>18</sup>. The XRF measurement is also in good agreement with the average composition calculated from the EDXRD data (see Supplementary Information *Figure S3*). For the  $E_g$  calculation from the composition, a bandgap of 1.0 eV is assumed for  $\text{Cu}_2\text{ZnSnSe}_4$  and 1.4 eV for  $\text{Cu}_2\text{ZnGeSe}_4$  with a linear increase with Ge content<sup>9</sup> and error bars with an amplitude of 40 meV to account for variations of bandgap with Cu concentration<sup>45</sup>. The figure shows that within the error bars the gradient of the CL peak position corresponds to the  $E_g$  gradient derived from the Ge and Sn distributions.

This work demonstrates that absorber layers with increased Ge concentration towards the back contact are obtained even if Ge is deposited at the top of the precursor layers without the need of a preliminary designing of the elemental distribution as attempted by other groups<sup>25</sup>. By analogy with the knowledge developed for Ga-In dynamics in CIGSe, it can be expected that in addition to increasing the temperature and annealing time, the use of Se containing precursors might help promoting the Sn-Ge interdiffusion<sup>46</sup>. Future research should focus on how to manipulate the Sn-Ge gradient to optimize the optoelectronic properties of the absorber layer.

#### 4. Conclusion

We studied the formation mechanism of CZT(Ge)Se absorbers layers through selenization of metallic precursors via in-situ EDXRD/XRF and propose a reaction mechanism that explains the incorporation of Ge and segregation of  $\text{SnSe}_2$ . The incorporation of Ge occurs after an initial formation of CZTSe. CZTSe reacts with GeSe to form CZTGeSe and  $\text{SnSe}_2$  at around 475 °C. Our results show that the reaction occurs near the back contact, inducing compositional Sn-Ge gradients in the film. The influence of the gradient on the optoelectronic properties has been evaluated with CL showing a gradual red shift of the emission towards the surface of the film as the Ge content decreases. These compositional gradients could be used for back contact interface passivation and to reduce recombination mechanisms in kesterite absorber layers.

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#### Supporting Information.

Additional temperature and EDXRD/XRF data recorded during different selenizations and a modification of figure 6.b. “This material is available free of charge via the Internet at <http://pubs.acs.org>.”

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