Insights into the formation pathways of $\text{Cu}_2\text{ZnSnSe}_4$ using rapid thermal processes

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Abstract –

Recent advances in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSe) thin film photovoltaics open the possibility for the future industrialization of this technology. Nevertheless, major progresses in CZTSe have been achieved using conventional thermal processing annealing routes (CTP), which rely on time-consuming processes with tubular furnaces, incompatible with the requisites of fast methodologies for the Industry. Changing from conventional to rapid thermal processes (RTP) using halogen lamps as heating method is not at all obvious, since the system becomes kinetically controlled, and the CZTSe formation mechanisms as well as crystallization pathways can drastically change.

In this work we present the transfer of our kesterite production baseline ($\text{Cu}_2\text{ZnSnSe}_4\text{:Ge}$) from a conventional thermal process using a tubular furnace, towards a rapid thermal process using an adapted system, by comparing them and analyzing the differences between both processes in terms of formation mechanisms as well as photovoltaic absorber properties. For this purpose, the rapid annealing process is stopped at different steps, analyzing the compositional, structural and morphological properties of the CZTSe absorber at these different stages. Using a combination of XRF, SEM, Raman spectroscopy and XRD characterization techniques it is demonstrated that in contrast to CTP routes, when RTP is used, kesterite is being formed in large amounts in the very early stages. This suggests a fast formation of CZTSe promoted by the higher Se vapor pressure that can be quickly achieved with this methodology. The formation of kesterite seems to proceed via two competitive reactions (binaries vs ternary compound). Additionally, the fast reaction observed in the system avoids the possible Sn-loss in an efficient way. Through the optimization of this RTP treatment a device with 8.3% efficiency has been obtained (the total time of the thermal process is 12 min), comparable with the efficiencies obtained so far with CTP routes. Finally,

the consequences of all these changes for the future interpretation of the formation reaction mechanisms of kesterites are discussed.

Keywords: kesterite, $\text{Cu}_2\text{ZnSnSe}_4$, thin film solar cell, rapid thermal process, reaction mechanism

1. Introduction

Nowadays, the photovoltaic (PV) community is focusing more and more into obtaining maximum profit of sunlight via inexpensive, earth-abundant, readily available and non-toxic materials. Thin film PV is one of the most promising technologies to fulfil those objectives. Recently, $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) solar cell has held a record efficiency of 22.6% and CdTe of 22.1%¹, reinforcing the position of thin film technologies in the PV field. However, one of the main culprits of CIGS and CdTe technologies are the materials inside their structure. CIGS contains two critical raw materials (indium and gallium) and CdTe one (tellurium), which may develop into a shortage of supply in a relatively near future². In this scenario, a relatively new PV technology based on quaternary absorber compounds ($\text{Cu}_2\text{ZnSnS}_4$ -CZTS or $\text{Cu}_2\text{ZnSnSe}_4$ -CZTSe, or their corresponding solid solution $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ -CZTSSe) is becoming one of the most promising ones to overpass raw materials scarcity limitations, because only contains non-toxic earth abundant elements, showing a very high light absorption coefficient of over 10^4 cm^{-1} , an intrinsic p-type conductivity, and a direct band gap ranging from 1.0-1.5 eV depending on the S/Se content^{3,4}.

Kesterites share with the other thin film PV chalcogenide technologies a high degree of flexibility for the synthesis of good quality absorbers. In fact, several chemical⁵⁻⁹ and physical^{3,10-12} based routes have been successfully applied to the synthesis of kesterites, where most of them can be classified as sequential synthetic processes. In these so called sequential processes, during a first step a precursor is deposited by different techniques either from elemental sources, or binary, ternary, or multinary compounds; while in a second step the precursor is submitted to a thermal treatment normally under reactive conditions (with chalcogen in the atmosphere). During this reactive annealing, the desired compound is formed and then crystallized, so regularly both phenomena have to be controlled and optimized. In order to do that, it is quite common that reactive thermal annealing requires several stages at different temperatures and pressures, with the aim to decouple the synthesis process (that normally requires lower temperatures) and the crystallization process (that uses to require higher temperatures)^{10,13,14}. In this sense, and due to the multiple elements forming the material, together with the complexity of the synthesis/crystallization processes, the careful analysis of the formation mechanisms of kesterites has been of paramount importance from the beginning^{15,16}. This is among others very relevant for understanding the role of the different possible secondary phases during the kesterite formation, and in the properties of the resulting absorbers. Thus, Table 1 summarizes some of the most relevant works published in this subject¹⁵⁻²⁰, where it is clear that for the different possible materials and processes, relatively different pathways have been deduced.

Nowadays, there is a general agreement that the synthesis route of kesterites proceeds either via the previous formation of binary (Cu-X, Zn-X and Sn-X binaries, X = S and/or Se), or ternary

(mainly Cu-Sn-X phase, X = S and/or Se) compounds, which react at a given temperature to form the corresponding quaternary phase. The formation of the pure Se-based kesterite compound seems to proceed at lower temperatures ($\sim 350\text{ }^{\circ}\text{C}$)^{15,17,20} than the formation of the pure S counterpart ($\sim 500\text{ }^{\circ}\text{C}$)^{16,18,19}. Nevertheless, there is no general indication of when or why the formation precedes either via the reaction of binary compounds like in references 15, 17 and 19; or via the reaction of ternary Cu-Sn-X compounds with ZnSe like in references 14, 16 and 18. In principle, as is clear from Table 1 this is fully independent of the chalcogen (S/Se).

Table 1. Summary of some of the most relevant papers published in the literature analysing the formation mechanisms of kesterites.

Ref.	Material	Process	Precursor	Annealing process	Reaction pathway	T _F (°C)*
15	CZTSSe	Chemical: Hydrazine based slurries	Cu ₂ S-S/SnSe ₂ -Se/Zn slurries Spin coating	Hot Plate at 540 °C	$Cu + Sn + Zn + X \text{ or alloys}$ $\rightarrow \text{Binary chalcogenides} \rightarrow Cu_2ZnX_3 + ZnX \rightarrow Cu_2ZnSnS_4, X = S, Se$	350
16	CZTS	Physical: Sputtering (metallic stacks)	Sn/Cu/Zn metallic stacks	Graphite box (S+Sn) at 550 °C	$[Cu_2S + SnS]_{(liq)} + ZnS + S_{2(gas)} \rightarrow Cu_2ZnSnS_4$	480
17	CZTSe	Chemical: Ethanol based inks	Cu (II) and Zn nitrates, Sn (IV) chloride. Knife coating. Se top capping layer.	Graphite dome with enough Se at 550 °C	$(Cu, Zn, Sn) \xrightarrow{\sim 190^\circ C} CuSe_x \xrightarrow{\sim 340^\circ C} Cu_2SnSe_3 + Cu_2ZnSnSe_4 \xrightarrow{\sim 420^\circ C} Cu_2ZnSnSe_4$	340
18	CZTS	Chemical: electro-deposition of metals	Cu and Zn metallic electrodeposited.	Graphite box with S and Sn at 550 °C as maximum T	$2ZnS_{(s)} + Cu_{2-x}S_{(s)} + SnS_{(g)} + 1/2S_{2(g)} \rightarrow Cu_2ZnSnS_{4(s)} + ZnS_{(s)}$	>500
19	CZTS	Physical: sputtering (sulphides)	ZnS, SnS ₂ and Cu by sputtering	Tubular furnace (N ₂ /H ₂ S 95%/5%) at 550°C as maximum T	$Cu_2S + SnS_2 \xrightarrow{350^\circ C} Cu_2SnS_3$ $Cu_2SnS_3 + ZnS \xrightarrow{500^\circ C} Cu_2ZnSnS_4$	500
20	CZTSe	Physical: sputtering (metals)	Cu, Zn and Sn metals by co-sputtering	Graphite box with elemental Se at a maximum T of 600 °C	$\alpha Cu + \beta Cu_xSn_y + Zn + 2Se_2 \rightarrow Cu_2ZnSnSe_4$	>350
20	CZTSe	Physical: sputtering (metals)	Cu, Zn and Sn metals by co-sputtering	Three zones furnace using elemental Se with a cracking zone at a maximum T of 600 °C	$\alpha' Cu_{2-z}Se + ZnSe + SnSe + \gamma' Se_2 \rightarrow Cu_2ZnSnSe_4$	300

Further analysing the reported mechanisms of Table 1, it seems that when metallic precursors are used, the formation of kesterites preferably proceeds directly via the reaction of binary compounds and in general no ternary compounds are observed. On the contrary, if the chalcogen is already present in the precursor from the very beginning of the annealing, the reaction formation proceeds preferably including ternary compounds (Cu-Sn-X, Cu-Zn-X).. This could be a clear advantage of this last pathway, because a simplified formation schema, with less number of molecules involved in the synthesis, can represent a lower risk of secondary phases remaining after the end of the formation reaction. All this has been almost exclusively studied for conventional thermal processes (CTP), i.e. for annealing routes involving furnaces with radiative heating using electrical resistances. These processes are characterized for being slow with total synthesis/crystallization times in the range of 2-3 hours or even longer, and are ideal for research purposes but not for industrial applications.

Conversely, rapid thermal processes (RTP), based in the fast heating of the annealing system using halogen lamps is extensively used in the conventional PV industry, because its substantial reduction of the time required for the synthesis and crystallization process, minimizing the processing time and energy consumption. In kesterites, RTP annealing has been barely studied. Some reports demonstrate its potential²¹⁻²³, reducing the total duration of this critical step from hours to several minutes. Additionally to the shorter process times, in this type of processes higher chalcogen vapour pressures can be achieved from the very beginning. All these fundamental changes are expected to have a non-negligible impact in the formation mechanisms of kesterites.

Taking this into account, in this work we optimize and analyse an RTP annealing for the synthesis of CZTSe absorbers, using metallic stacks deposited by sputtering as precursors. Different parameters of the annealing are investigated. The phase evolution during the annealing process is analysed in a break-off experiment, where the RTP process has been stopped at different stages. By combining advanced characterization techniques such as multi-wavelength Raman spectroscopy, X-ray diffraction, X-ray fluorescence and glow discharge optical emission spectroscopy (GDOES). The formation mechanisms are investigated and compared with standard thermal routes. We observe remarkable differences that open interesting new perspectives for the optimization of rapid thermal processes applied to the kesterite synthesis.

2. Experimental Section

For the synthesis of CZTSe by a sequential process, SLG/Mo/Cu/Sn/Cu/Zn metallic precursor stacks were deposited by DC-magnetron sputtering (Alliance Concept Ac-450) onto Mo coated soda-lime glass substrates. The compositions of the films were near the range of those reported as ideal for high-efficiency solar cell devices; namely Cu-poor and Zn-rich: Cu/(Zn+Sn)= 0.77, Zn/Sn =1.21, Cu/Zn = 1.41, Cu/Sn = 1,71.

Precursors (2.5x2.5 cm² in area) were then selenized by RTP using an AnnealSys AS-ONE-100 furnace in a semi-closed system made up by a graphite box with a reaction volume of 3.8 cm³. Approximately, 20 mg of elemental Se (Alfa Aesar, 99.999% purity) were placed into the box next to the substrates, and after two evacuate and purge cycles (base vacuum of 3x10⁻² mbar), the Ar flow was increased until obtaining 1 mbar total pressure inside the furnace. Then, the

reactive annealing was conducted in a two-step process; 1) heating from room temperature to 400°C (ramp 180 °C/min, dwell time 3 minutes), 2) heating up to 500°C (ramp 60 °C/min, dwell time 5 minutes). During the second step, the pressure is raised to 900 mbar. After the second step, the setup cools down below 80°C (also at 900 mbar). The whole annealing process takes only 12 minutes, with an additional 8 minutes approximately for the cool down. For the break-off experiment, the annealing process was interrupted at different temperatures and times as is shown in Figure 1, corresponding to different stages of the thermal treatment. The samples were then cooled down quickly for further characterization.

Precursor stacks and annealed CZTSe films from the break-off experiment were characterized by X-Ray fluorescence (XRF), for its compositions. In addition, a phase analysis was performed by combining x-ray diffraction (XRD) and Raman spectroscopy (RS). XRD measurements were performed using a PANalytical X'pert ProMPD diffractometer with Cu-K α -radiation ($\lambda=1.54056\text{\AA}$) and a secondary graphite monochromator. Multi-wavelength Raman characterization has been carried out using 325nm, 442nm, 532nm and 785nm laser wavelengths as a source of excitation. Raman scattering measurements were performed in back scattering configuration using a Horiba Jobin Yvon fHR-640 spectrometer for the wavelengths 325nm, 442nm and 532nm and an iHR-320 spectrometer for the 785nm wavelength. Spectrometers are coupled with Raman probes developed at IREC and a low noise CCD detector cooled to -70°C. Excitation and light collection were made using a macro optic system with a laser spot diameter of the order of 50 μm . In order to avoid thermal effects in the spectra, the power density on the surface of samples was kept below 150 W/cm². The position of all spectra has been corrected taking into account the first order Raman spectrum of monocrystalline silicon as a reference measured before each acquisition and imposing its position at 520 cm⁻¹. Cross-section images were obtained in selected samples by using scanning electron microscopy (SEM-ZEISS Series Auriga microscope) for its thickness calculation. A depth profiling analysis of some selected samples was performed by GDOES measurements using a Horiba Jobin Yvon GD Profiler 2 Spectrometer, equipped with an anode diameter of 4 mm and 19 element channels.

Once the kesterite absorbers were synthesized and characterized, solar cell devices were fabricated with selected samples. First, and in order to remove the possible presence of secondary phases (mainly ZnSe and SnSe), the films were etched in H₂SO₄ + KMnO₄ and (NH₄)₂S solutions^{24,25}. Next, a CdS buffer layer was deposited via chemical bath deposition (CBD) with a thickness of approximately 50 nm²⁶. Then, i-ZnO (50 nm) and In₂O₃:SnO₂ (ITO, 200 nm) layers were deposited by pulsed DC-magnetron sputtering (Alliance Concept CT100). Finally, 3x3 mm² cells were mechanically scribed to complete device fabrication and were optoelectronically characterized by measuring both the J-V characteristics under simulated AM1.5 illumination (AAA Abet 3000 Solar Simulator) and the external quantum efficiency (EQE- Bentham Instruments PV300 Photovoltaic characterization System).

3. Results

Figure 1 (left) shows the temperature profile used in this work, in which the different temperatures where the process was stopped in the break-off experiments are indicated

(points from A to I), covering the full temperature and time ranges for the RTP annealing. Figures 1 (right) show the corresponding cross section SEM images of selected samples.

Figure 1. Temperature profile with the different points where the annealing was stopped for the break-off experiment (left side). Cross section SEM images of devices from selected samples (right hand).

We will focus on the evolution of morphology for the samples from point E on, i.e. from the point in which Se starts to be significantly incorporated into the precursor as we will show later. At point E, the thickness of the precursor has increased almost twice with respect to the metallic stack one (see Fig. S1a of Supporting Information (SI)), suggesting that almost all the Se necessary for the synthesis of kesterite has been integrated into the precursor. In fact, XRF analysis performed on all the samples (see the evolution of the concentration of the different elements determined by XRF in the Fig. S2 of the SI), confirms that the selenization of the metallic precursors is completed and only rather small quantities of Se are further incorporated later on and/or at higher temperatures. This is also confirmed by GDOES measurements that show non-significant variation of Se content in samples F, G, H and I (see Fig 6 SI).

Following the steps of the RTP annealing (from point F up to point I), helps to clearly increase the grain size (first in the surface near region and afterwards these grains grow towards the back interface) and to reduce the rough superficial structures. Compared to conventional thermal processes (with generally slower heating ramps, longer dwelling times and lower Se partial vapour pressures), in the RTP annealing the chalcogen is incorporated much faster, but proper crystallization is only achieved during the second ramp at higher temperature, as is also characteristic for conventional processes¹⁶. Nevertheless, in the RTP case only 5 minutes at 500°C are enough for the formation of large crystals, suggesting that the Se vapour pressure in the reaction chamber is still high enough to assist a fast crystallization. (See in Fig. S1b a very well crystallized absorber made by the described RTP process). Thus, compared to the conventional process, RTP annealing accelerates the incorporation thanks to the high Se vapour pressures present. This has a clear impact on the crystallization (large crystals are formed in shorter times), but probably this feature has an impacting on phase evolution during kesterite formation, too.

In order to investigate this, XRD analysis was performed in the complete set of samples. Figure 2 (a) shows the diffractograms evolution corresponding to all the samples, while Figure 3(b) shows the evolution of the relative XRD intensity for the different detected phases. This relative XRD intensity was normalized with respect to the (110) reflection of Mo, which is supposed to be constant for all the samples. It is important to remark that the main XRD peaks of the ZnSe, Cu_2SnSe_3 (CTSe) and $\text{Cu}_2\text{ZnSnSe}_4$ (CTZSe) phases almost coincide at room temperature, making the distinction extremely complicated²⁷. While this impedes the detection of ZnSe/ Cu_2SnSe_3 secondary phases, there are several additional characteristic peaks with low intensity for the tetragonal kesterite phase with lower symmetry, which allow to clearly identify the latter. These are for example the peaks at 22.1° , 28.3° , 35.2° , 36.1° corresponding to diffraction planes (119), (103), (202), (121) respectively. In consequence and to our surprise, already in point E, i.e. at the very beginning of the first dwell time at 400°C , we were able to detect peaks corresponding to the CZTSe tetragonal kesterite phase, alongside with SnSe. There are no evidences of other phases.

This is in contrast to samples prepared in a conventional thermal process with very similar conditions (see Fig. 3 of the SI, point E), where no evidence of kesterite formation is found. We rather observe several secondary phases including, even, metallic ones. This implies that in the RTP process the formation of kesterite phases occurs faster, starting at lower temperatures and/or shorter times. Again, we relate this to the higher Se vapour pressures achievable with this setup. Besides this, the RTP process seems to produce kesterite with acceptable crystalline quality even at 400°C .

The evolution of the diffractograms of the different samples describes the phase formation in the bulk during the annealing process. From room temperature (RT) to point D, we see transformation of the metallic phases from a highly textured Sn phase and Cu-Sn, Cu-Zn alloys towards a Cu-Sn alloy, accompanied by a reduction of the peaks of the Sn and Cu-Zn phases. The reduced intensities of the Zn related phases are attributed to the formation of ZnSe with low crystallinity. The diffractogram of point F is very similar to the one of point E, with a slightly increased intensity of the CZTSe peaks, while the peaks corresponding to SnSe are decreased in favour of increasing SnSe_2 peaks. We postulate that here SnSe formed during the first dwell time gets further selenized to SnSe_2 . Finally, for points G, H and I (corresponding to different times during the second dwell time at 500°C), the intensity and the full width at half maximum (FWHM) of the characteristic CZTSe peaks remain practically constant. Additionally, a thin MoSe_2 layer is formed, as expected. Highly (400) textured and non-textured SnSe is detected, but its origin is most probably the condensation of remaining gaseous Sn-Se during the user-forced cooling down process²⁵. Following this line of arguments, the actual quaternary kesterite phase is already completely formed during the first dwell time at 400°C , and the second dwell time at 500°C is predominantly necessary for an improved crystallization of the absorber.

Figure 2. a) XRD diffractogram and (b-e) Raman using 4 different excitation wavelengths (325 nm, 442 nm, 532 nm and 785 nm) of the different samples produced in the break-off experiment (detailed diffractograms and Raman spectra are reported in the Figure 3 and 4 of the SI).

Figure 3. a) Evolution of the absolute area most relevant phases detected by Raman spectroscopy (surface). b). XRD normalized to the intensity of the (110) reflection of Mo (bulk)

Raman spectroscopy with four different excitation wavelengths (325nm, 442 nm, 532 nm, 785 nm) was performed in order to complement the previous analysis. The use of various excitation wavelengths leads to pre-resonant conditions for different compounds and enhances the ability to detect several secondary phases present²⁸. Figure 2(b-c) shows the Raman spectra obtained in the different samples for the four excitation wavelengths. In particular, under UV excitation (325 nm) the ZnO phase signal is strongly enhanced²⁹, together with a non-bandgap resonant enhancement of the CZTSe³⁰. Under blue excitation (442 nm) we enhance the detection of ZnSe^{31,32}, and with red excitation (785 nm) the detection of Sn-Se³³ and ternary Cu-Sn-Se phases³¹. Figure 3(a) depicts the evolution of the absolute intensity for the Raman peaks recorded at the absorber surface (<300nm) using the signal acquired with the most favourable excitation wavelength for each phase. During the first ramp (from point A up to point E), ZnO, ZnSe, SnSe and Cu₂SnSe₃ are clearly detected, with CuSe traces only at point E. This is unexpected, as in literature CuSe(S) is found most frequently alongside with SnSe(S) or SnSe(S)₂ in the case that the formation reaction proceeds via the reaction of binary compounds¹⁶. Alternatively, Cu₂SnSe(S)₃ is found when the formation of kesterites proceeds via the reaction of this ternary phase with ZnSe¹⁷. The intimate mixing of all these phases and the presence of both, Sn-Se and Cu-Sn-Se coexisting in the bulk of the same absorber suggests that most probably these two reaction pathways are competing and contributing both to the formation of kesterites under the studied conditions. As is clear, somewhere between the point D (350 °C) and point E (400 °C) the kesterite starts to be formed, in good agreement with previous published data^{17,20}. In our case, the heating ramp is 180 °C/min, i.e. to go from point D to point E only takes approximately 17 seconds. This implies that once the minimum formation temperature is reached, the precursor phases react very quickly with selenium in the RTP and form the kesterite almost immediately.

At point E, the selenization has not been completed yet. We find strong contributions from ternary Cu-Sn-Se compounds and ZnSe and only few quantities of Cu-Se and Sn-Se binary phases are left. At point F, we can consider that the reaction is almost finished, the kesterites is formed and only some secondary phases remain: ZnSe due to the Zn-rich composition, and SnSe probably in the MoSe₂/CZTSe interface³¹ and the surface due to condensation during the cooling down process from pre-evaporated material²⁵. Additionally, a clear contribution of the SnSe₂ (under resonant conditions with 785nm excitation) is observed that is arguably correlated with the superficial structures observed in the corresponding SEM image (Figure 1). After point F, i.e. once the temperature is increased to 500 °C, no reduction of the Raman FWHM is observed for the CZTSe phase. This contrast with conventional thermal processes, where in the last step a clear improvement of the crystal quality with the annealing time has been reported³⁴. On the other hand, an accurate analysis (using the Raman non-bandgap resonant conditions with 325nm excitation) shows a clear modification with time of the bands at 175 cm⁻¹, 233 cm⁻¹ and 250 cm⁻¹ (Figure 4). Modifications of these peak intensities have been attributed to changes in the V_{Cu} and Zn_{Sn} point defect concentrations which have strong impact in the final optoelectronics properties³⁰.

Figure 4. Raman spectra under UV non-bandgap resonant conditions (325nm) for samples E to I together with a reference sample annealed using an optimized conventional thermal process.

We now return to the possible formation mechanisms, and compare the results obtained here with those reported in the literature. For low chalcogen vapour pressures and/or a low availability of chalcogen (e.g. no chalcogen in the precursors), the formation of kesterites proceed mainly by the reaction of binary compounds [see Refs. 16 and 21] where the kesterite was synthesized under equivalent conditions]. In this case a tri-molecular reaction is required, enhancing the probability of formation and presence of secondary phases at the end of the annealing.

On the other hand, under high chalcogen vapour pressure like in this work, or high availability of chalcogen from the very beginning of the annealing (like the precursors already containing chalcogen in their composition); the reaction preferably proceeds via the formation of ternary Cu-Sn-Se compounds [see Refs. 15 and 19]. This implies that a bi-molecular reaction between Cu-Sn-Se and Zn-Se is favoured, minimizing the risk of secondary phases formation. Figure 6 summarizes the pathways that are competing and contributing in this case to the formation of CZTSe:

Figure 5. Schematic representation of the two competing formation mechanisms.

In order to demonstrate the impact of the different stages on the properties and characteristics of the devices, solar cells were prepared with the most relevant samples. As was expected, devices prepared with absorbers from A up to F, do not give any working solar cell. All of them were shunted, probably because the presence of very large amounts of secondary phases as is clear from the XRD and Raman spectroscopy analysis, together with the poor crystallization of the kesterite phase when present. On the contrary, samples G, H and I leads to working devices as is presented in Figure 5. Additionally, in this Figure, the short circuit current density (j_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and efficiency (η) are presented with some statistics. The solar cell prepared with the absorber G, exhibit low efficiency mainly due to the low V_{oc} and FF. The difference of only 100 seconds and 100 K between point F and point G seems therefore to be enough to go from no working devices to working ones. This means that the crystallization/defect reordering observed by Raman spectroscopy under 325nm excitation wavelength (Figure 4) is also very fast for the RTP process with relatively high Se pressures. Nevertheless, at point G, the absorber properties (defects concentration and type, and presence of a residual SnSe_2 secondary phase) are still not good enough to ensure a high performance. Additionally, relatively small grains are observed in the SEM that can contribute to the low V_{oc} and FF. An inadequate concentration and type of defects and density and the presence of a large number of grain boundaries, which are probably not well passivated, can deteriorate the charge transport properties of the absorber and explain the bad performance.

After only 150 additional seconds at 500 °C, both the V_{oc} and the FF are largely improved (and in consequence the efficiency). The j_{sc} is also slightly increased. This large improvement is basically explained by the better crystalline quality of the absorber thanks to the fast grain size growth, as well as the complete consumption or minimization of secondary phases. Longer crystallization times seems to have a limited impact on the improvement of the performance of the devices, suggesting that times as short as 150 s at relatively high temperatures can be enough to crystallize the CZTSe absorber and fully exploit the potential of the RTP annealing.

Figure6. J-V illuminated curve of devices obtained from absorbers produced during the break-off experiments (points G, H and I). Evolution of the different optoelectronic parameters of the same three points.

Finally, with further optimization of the precursor composition and device preparation, via a fine tuning of the cationic ratios and a better substrate cleaning, we prepared a device with 8.3% efficiency using the RTP thermal routine presented in Figure 1. Figure 7 shows the J-V illuminated curve and the corresponding external quantum efficiency of this champion device, obtained with an annealing process of only 12 minutes of total duration (20 minutes including the cooling down process). If we compare this device with others previously reported by our group using the CTP annealing (10.1%, 10.6%, 8.2%, 11.8%)^{10,13,26,34}, we can conclude that the V_{oc} is at the same level, and only j_{sc} and FF are slightly lower. Please note that these absorbers have been prepared without any additional Ge layer. The j_{sc} is somehow lower than expected. One plausible cause is the rather small absorber thickness (1.2 μ m) for these absorbers; also no anti-reflection coating was applied. The lower FF can be probably related to the necessity to adapt and optimize the back and front contacts for the characteristics of the absorbers obtained with this type of thermal treatment and the fact that no metallic grids were applied.

Figure 7. *j*-*V* illuminated curve (under AM1.5G conditions, no anti-reflection coating or metallic grid), and external quantum efficiency of the champion cell.

4. Conclusions

The formation pathways of CZTSe absorber by using a RTP annealing were investigated. The higher vapour pressures achieved with this rapid process have shown to have a dramatic impact on the formation pathways of the kesterite absorber. While the selenization of metallic precursors in conventional thermal processes proceeds predominantly via binary compounds, this contrasts to what is observed for the RTP. A competing mechanism between the route implying binaries and the one implying the formation of Cu-Sn-Se ternary compound is observed here. We therefore present first evidences for the dependence of the reaction pathway on the selenium partial pressure. A pathway involving binary selenides is preferred for relatively low Se vapour pressures during annealing, and a pathway involving the Cu-Sn-Se ternary compound predominates for relatively high vapour pressures. In between (as is apparently our case), both mechanisms can compete. The consequences on the devices show that non-working solar cells are obtained for poorly crystallized absorbers, even if the formation reaction of the kesterite phase seems to be completed. During the crystallization at 500°C, the j_{sc} of the corresponding devices is quickly raised during heat up, while the V_{oc} and FF improve rapidly during the first minutes together with the crystal quality. Through the optimization of this RTP annealing we report an 8.3% efficient device, prepared with an annealing time of only 12 min, demonstrating the compatibility of the materials with possible future industrial processes.

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