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Crystallization properties of Cu2ZnGeSe4 Peer-reviewed author version

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Abstract: We have studied the crystallization reaction of polycrystalline Cu2ZnGeSe4 solar cell absorbers fabricated by H2Se selenization of sequentially deposited metal layer stacks. We have executed a stop experiment, stopping the crystallization reaction at different times during the process, then analyzing the subsequent X-ray diffraction patterns. We have found that mainly Cu3Ge and ZnSe phases form very rapidly at temperatures below 350°C. Depending on the order of the sequentially deposited metal layer stack, the formation reaction proceeds at different speeds. Putting the Ge layer in the bottom and the Cu layer on top leads to a very fast nucleation reaction of Cu2ZnGeSe4, leading to small grains that have obtained their final size already after 3 minutes of selenization at 460°C. The inverse stack with Ge on top and Cu in the bottom delays the nucleation of Cu2ZnGeSe4 grains, which obtain their final grain size only after 15 minutes of selenization at 460°C.

29/06/2018

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Dear Editor,

Please find herewith the manuscript of our publication entitled:

Crystallization properties of Cu₂ZnGeSe₄,

by G. Brammertz, T. Kohl, J. de Wild, M. Meuris, B. Vermang and J. Poortmans.

This work was presented at the Spring E-MRS meeting in Strasbourg in France and we would like to include it in the special issue for this meeting. Our work was presented as an oral contribution on Tuesday June 19th at 8:45 under abstract number A.IV.2.

We would like to ask the editor to kindly avoid one of the following researchers as reviewer for this contribution:

S. Schorr, HZB G. Gurieva, HZB

Kind regards,

Guy Brammertz et al.

Ref. No.: TSF-D-18-00932 Title: Crystallization properties of Cu2ZnGeSe4 Authors: Guy Brammertz; Thierry Kohl; Jessica de Wild; Marc Meuris; Bart Vermang; Jef Poortmans

Dear Editor,

We have fixed the following mechanical deficiencies:

- Text: please replace "e-beam" by "electron-beam".

- Reference 19 should read "[19] L. Choubrac, G. Brammertz, N. Barreau, L. Arzel, S. Harel, M. Meuris and B. Vermang, 7.6% CZGSe Solar Cells Thanks to Optimized CdS Chemical Bath Deposition, Phys. Status Solidi A 215 (2018) 1800043." [Stat. Sol. being standard abbreviation for statistic* solar]

- All graphs: all y-axis titles should be oriented to read from bottom to top. (They currently read from top to bottom.)

Kind regards,

Guy Brammertz et al.

Highlights

- Synthesis of thin film Cu₂ZnGeSe₄ layers by H₂Se selenization of stacked metals.
- Stack with Ge on top -> slower reaction (15 min).
- Stack with Ge on bottom > faster reaction (3 min).
- Copper germanide phase formed very rapidly in selenization process.

Crystallization properties of Cu₂ZnGeSe₄

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Abstract

We have studied the crystallization reaction of polycrystalline $Cu_2ZnGeSe_4$ solar cell absorbers fabricated by H₂Se selenization of sequentially deposited metal layer stacks. We have executed a stop experiment, stopping the crystallization reaction at different times during the process, then analyzing the subsequent X-ray diffraction patterns. We have found that mainly Cu₃Ge and ZnSe phases form very rapidly at temperatures below 350°C. Depending on the order of the sequentially deposited metal layer stack, the formation reaction proceeds at different speeds. Putting the Ge layer in the bottom and the Cu layer on top leads to a very fast nucleation reaction of $Cu_2ZnGeSe_4$, leading to small grains that have obtained their final size already after 3 minutes of selenization at 460°C. The inverse stack with Ge on top and Cu in the bottom delays the nucleation of $Cu_2ZnGeSe_4$, leading to a somewhat slower formation reaction and larger $Cu_2ZnGeSe_4$ grains, which obtain their final grain size only after 15 minutes of selenization at 460°C.

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Keywords: Copper zinc germanium selenide, Kesterite, Photovoltaics, Solar cell, Thin film, Crystallization, Selenization.

1. Introduction

Thin film solar cells based on Kesterite absorbers have shown strong progress in conversion efficiencies in the past decade, with Sn-based Kesterite solar cells now showing conversion efficiencies well in excess of 10 %. [1-6]. Part of the progress in Sn-based Kesterite solar cells was based on the discovery of Ge as being able to improve the crystallization properties of the absorber and thereby increasing the efficiency [6-12]. In this contribution we study the properties of pure Ge-based Kesterite solar cell absorbers Cu₂ZnGeSe₄ (CZGSe). Relatively little is known on the pure Ge-based Kesterite solar cell absorbers. Physical characterization has shown that it crystallizes readily in the Kesterite crystal structure [13-14] and shows a band gap in the 1.4 to 1.5 eV range [15-16] whereas recently solar cells with a conversion efficiency of about 6 % have been presented using a solution based process [17] and a vacuum process [18]. In this contribution we study the crystallization properties of CZGSe fabricated by using a two-step selenization process.

2. Experimental details

The absorber layers were fabricated by a two-step selenization process shown schematically in Figure 1. As a first step the metal layers were sequentially evaporated onto a commercial Mo on soda lime glass substrate with a Na diffusion barrier. The substrate consists of a 5x5 cm² large, 3 mm thick soda lime glass substrate covered with 120 nm of Si(O,N) and 250 nm of Mo. Two different types of metal layer stacks were deposited on top of this substrate, one stack with Ge in the bottom of the stack and Cu on top, the other stack with Cu in the bottom and Ge on top. Solar cells were fabricated with the stack with Cu on top and the solar cell properties were presented elsewhere [19]. The exact layer thicknesses were Ge(180 nm)/Zn(125 nm)/Cu(170 nm) for the stack with Cu on top and Cu(170 nm)/Zn(135 nm)/Ge(200 nm) for the stack with Cu in the bottom. The layer thicknesses were chosen in such a way to end up with a slightly Cu-poor and slightly Zn-rich composition after a standard selenization process, as all reports on Sn-based Kesterite solar cells show that this is the region where best conversion efficiencies can be achieved. The metal stack evaporation was done in a Pfeiffer PLS 580 electron beam evaporation chamber, where the metal layer thickness was controlled with a quartz micro crystal for optimal reproducibility of the process. Following this metal layer deposition, the samples were annealed in an Annealsys

AS-150 anneal chamber in the presence of 10% H_2Se gas diluted in N_2 . The standard anneal consists of a ramping step of 1°C/sec in the presence of H_2Se , followed by 15 minutes of selenization at a temperature of 460°C. Optionally, a pre-anneal at somewhat lower temperature around 350°C can also be added to the process.

Scanning electron microscopy (SEM) images were acquired on a Philips XL 30 using an acceleration voltage of 20 kV and a secondary electron detector. The energy dispersive spectroscopy (EDS) measurements were made with an Oxford Instruments EDS detector attached to the tool operating at an acceleration voltage of 20 kV. X-ray diffraction (XRD) measurements were made on a Philips X'PERT Pro X-Ray diffractometer using a Cu K_{α} source in the Bragg-Brentano geometry.

3. Crystallization study 2-step selenization

Figure 2 shows the composition ratios Cu/(Zn+Ge) and Zn/Ge for the two stacks. For the stack with Ge on top, the Zn thickness was also varied, in order to find the optimum composition range. Typically, the Cu/(Zn+Ge) ratio as measured by EDS after selenization is around 0.9, whereas the Zn/Ge ratio varies between 1 and 1.5, depending on the Zn starting layer thickness. All the samples with the Ge on top show for a similar starting layer thickness a slightly lower Zn/Ge ratio, indicating that there is a certain amount of Ge loss during the selenization when the Ge starting layer is on top. This seems to be much less the case when the Ge is buried under the two other layers.

Figure 3 shows cross section SEM images of the two absorbers after a standard 15 minutes anneal at a temperature of 460°C. From the cross-section images, it is obvious that both stacks show good crystallization behavior. Nevertheless, the layer stack with Ge on top shows larger grain sizes as compared to the stack with the Cu on top. Unfortunately, the layer with Ge on top also leads to worse adhesion properties, inhibiting the fabrication of good solar cells as the layer delaminates during the wet chemical steps of the subsequent fabrication process. It seems therefore that the two stacks have their own advantages, the stack with Cu on top showing better stoichiometry control through very limited Ge loss during the selenization and better adhesion properties, and the stack with Ge on top showing larger grain sizes. We would of course like to better understand why this behavior is as such and possibly improve the grain growth also in the case of the stack with the Cu on top and

have therefore studied the selenization process in more detail. To figure out which phases are present in the samples at the different stages of the selenization process, we have carried out a stop experiment where the selenization was stopped after a certain time of the selenization process and the samples were then cooled down and removed from the selenization chamber to be analyzed by XRD. This study was made for the two stacks, the one with the Ge on top and the one with the Cu on top. The results of this detailed XRD study are presented here.

Two Bragg-Brentano XRD patterns of the fully selenized precursor layers are shown in Figure 4 along with the simulated patters for a Mo and a kesterite $Cu_2ZnGeSe_4$ layer. As becomes visible from the figure, all the XRD peaks that are expected for a CZGSe layer are observed, as well as the main Mo reflections. Besides the reflections of the CZGSe and the Mo, no other peaks can be clearly seen in the pattern, so the amount of secondary phases in the final layer is low, at least within the accuracy of the XRD. To find out how exactly the selenization process is proceeding as a function of time, we have stopped the selenization process at different times and removed the samples from the chamber to analyze them ex-situ with XRD. Figure 5 shows the temperature versus time profile of the selenization process that we used in our study and the 8 different points during the selenization at which we stopped the process and removed the sample for XRD measurements. The 8 different XRD measurements for the stack with the Ge on top (Cu-170 nm/Zn-135 nm/Ge-200 nm) are shown in Figure 6. For clarity, only the region from 42° to 47° is shown, where all the main phases that could be observed in the sample have a major reflection.

The starting layer shows a Zn and a Cu peak, but no trace of a Ge peak, so the Germanium seems to be amorphous after the electron beam deposition. Already after the ramp at 1°C/s to 350° C, the Zn and Cu peaks are very strongly reduced and a prominent Cu₃Ge peak becomes visible in the pattern. Therefore, it is most likely that the Cu, which is the most mobile species in the stack, has already diffused through the Zn to the Ge layer to form a Copper germanide phase. By diffusing through the Zn to the Ge, the Cu has likely left holes at the backside behind, possibly leading to the worse adhesion properties that we observe for this stack. At the end of the 12 minutes pre-anneal at 350°C, the Cu germanide peak is slightly reduced and a not yet very well defined ZnSe peak starts to appear, which at the end of the ramp to 460°C intensifies, as the Cu germanide peak is strongly reduced in intensity, but no Cu₂ZnGeSe₄ is formed yet. Then, after 2 minutes anneal at 460°, the Cu₂ZnGeSe₄ phase

appears and the ZnSe starts to reduce in intensity. In addition, a Cu_9Se_5 phase also appears. After 5 minutes anneal at 460°C, the $Cu_2ZnGeSe_4$ peak intensifies and the ZnSe phase is reduced in intensity. After 15 minutes, the ZnSe peak is strongly reduced in intensity, but does not disappear completely. No further changes in the pattern can be observed after 32 minutes of selenization.

Figure 7 shows the same type of data for the stack with the Cu layer on top (Ge-180 nm/Zn-125 nm/Cu-170 nm). Similarly to the other stack, a Cu₃Ge phase already forms after the temperature ramp step to 350°C, so the Cu already diffused at least partly through the Zn to the back of the sample. As opposed to the other stack, here ZnSe is already formed in quite large quantities at the end of the ramp to 350°C. At the end of the 12 minutes pre-anneal at 350°C, the Cu₃Ge and ZnSe peaks are already reducing, a clear Cu₉Se₅ peak appears and it seems that a Cu₂ZnGeSe₄ phase is also already forming. At the end of the ramp to 460°C the Cu₂ZnGeSe₄ phase is very clearly present, whereas the ZnSe, Cu₉Se₅ and Cu₃Ge phases are all reducing in intensity. Already after a 2 minute anneal at 460°C, the Cu₃Ge and Cu₉Se₅ phases disappeared and only a small trace of the ZnSe can be observed. No further large changes in the patterns can then be observed after 5, 15 and 32 minutes of selenization.

It seems therefore that the top Ge layer inhibits the rapid formation of ZnSe and Cu_9Se_5 , which in the case of the stack with Cu on top leads to a very fast and early crystallization of the $Cu_2ZnGeSe_4$ and consequently small grains. In the case of the stack with the Ge on top, mainly the formation of Cu_9Se_5 is delayed, leading to a later crystallization of the $Cu_2ZnGeSe_4$ and larger final grain sizes.

4. Conclusions

We have synthesized polycrystalline $Cu_2ZnGeSe_4$ solar cell absorbers by selenization of a metal layer stack. Studying the XRD patterns of the absorber at different times during the

selenization process allowed to get insight into the crystallization reaction that happens during the selenization process. It was discovered that mainly Cu_3Ge and ZnSe phases already form very rapidly at temperatures below 350°C. The formation of $Cu_2ZnGeSe_4$ happens then through the reaction of Cu_9Se_5 , Cu_3Ge and ZnSe phases. Depending on the stack, the formation reaction proceeds at different speeds. Putting the Ge layer in the bottom and the Cu layer on top leads to a rapid formation of Cu_9Se_5 and ZnSe and a very fast nucleation reaction of $Cu_2ZnGeSe_4$, leading to small grains. The inverse stack with Ge on top and Cu in the bottom delays the formation of Cu_9Se_5 and subsequently the nucleation of $Cu_2ZnGeSe_4$, leading to a somewhat slower formation reaction and larger $Cu_2ZnGeSe_4$ grains.

Acknowledgments

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7.6% CZGSe Solar Cells Thanks to Optimized CdS Chemical Bath Deposition, Phys. Status
Solidi A 215 (2018) 1800043.

Figure Captions

Figure 1. Schematic representation of the two-step selenization process.

Figure 2. Cu/(Zn+Ge) and Zn/Ge ratio for both the stacks with Ge (circles) and Cu on top (diamonds) as a function of Zn starting layer thickness.

Figure 3. Cross section SEM images of the two absorbers after a 15 minute selenization process at 460 °C. Figure 3 (a) shows the absorber with the Ge top layer, whereas figure 3 (b) shows the absorber with the Cu top layer.

Figure 4. XRD patterns of the two fully selenized absorber layer stacks on a Mo/glass substrate. The simulated patterns for a Mo and a kesterite Cu₂ZnGeSe₄ layer are also shown.

Figure 5. Schematic representation of the temperature versus time of the selenization process. The blue dots indicate the times at which the sample was removed from the selenization chamber to do an XRD measurement.

Figure 6. XRD pattern measured for the samples with the Ge layer on top for the 8 different times during the selenization process.

Figure 7. XRD pattern measured for the samples with the Cu layer on top for the 8 different times during the selenization process.





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Soda lime glass







