Crystallization properties of $\text{Cu}_2\text{ZnGeSe}_4$ based solar cells

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Abstract

We have studied the crystallization reaction of polycrystalline $\text{Cu}_2\text{ZnGeSe}_4$ solar cell absorbers fabricated by H_2Se 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 XRD spectra. We have found that mainly Cu_3Ge 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 $\text{Cu}_2\text{ZnGeSe}_4$, 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 $\text{Cu}_2\text{ZnGeSe}_4$, leading to a somewhat slower formation reaction and larger $\text{Cu}_2\text{ZnGeSe}_4$ grains, which obtain their final grain size only after 15 minutes of selenization at 460°C . $\text{Cu}_2\text{ZnGeSe}_4$ -CdS-based solar cells were fabricated which showed a maximum power conversion efficiency of 5.7%.

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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 $\text{Cu}_2\text{ZnGeSe}_4$ (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 properties of CZGSe fabricated by using a two-step selenization process. We first study the crystallization behavior of the thin film CZGSe fabricated using first metal deposition followed by a selenization step, from which we conclude on a more optimized starting layer stack structure. Then, the solar cell properties of the optimized CZGSe absorber layer are discussed in detail, trying to identify the causes limiting the conversion efficiency in these devices.

2. Sample fabrication 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 $5 \times 5 \text{ cm}^2$ 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. 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 e-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% H₂Se gas diluted in N₂. The standard anneal consists of a ramping step of 1°C/sec in the presence of H₂Se, 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. 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 energy dispersive X-ray spectroscopy (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, due to the formation of volatile GeSe and GeSe₂ species. This seems to be much less the case when the Ge is buried under the two other layers.

Figure 3 shows cross section secondary electron microscopy (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 quite 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 X-ray diffraction (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 in the following paragraph.

3. Crystallization study 2-step selenization

A Bragg-Brentano XRD spectrum of a fully selenized precursor layer is shown in Figure 4.

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 seen in the spectrum, 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 e-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 Cu_3Ge peak becomes visible in the spectrum. 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. 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 $\text{Cu}_2\text{ZnGeSe}_4$ is formed yet. Then, after 2 minutes anneal at 460°, the $\text{Cu}_2\text{ZnGeSe}_4$ 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 $\text{Cu}_2\text{ZnGeSe}_4$ 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 spectrum 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 Cu_3Ge 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 Cu_3Ge and ZnSe peaks are already reducing, a clear Cu_9Se_5 peak appears and it seems that a $\text{Cu}_2\text{ZnGeSe}_4$ phase is also already forming. At the end of the ramp to 460°C the $\text{Cu}_2\text{ZnGeSe}_4$ phase is very clearly present, whereas the ZnSe, Cu_9Se_5 and Cu_3Ge phases are all reducing in intensity. Already after a 2 minute anneal at 460°C, the Cu_3Ge and Cu_9Se_5 phases disappeared and only a small trace of the ZnSe can be observed. No further large changes in the spectra 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 $\text{Cu}_2\text{ZnGeSe}_4$ 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 $\text{Cu}_2\text{ZnGeSe}_4$ and larger final grain sizes.

As a consequence, it seems that it is beneficial to have the Cu and Ge close to each other, in order to facilitate the formation of the Cu_3Ge phase as the Cu diffuses to the Ge very rapidly anyway. In addition, it seems beneficial to have a Ge layer on top and the Cu as far in the back as possible, to inhibit the fast formation of Cu_9Se_5 , which leads to fast nucleation of $\text{Cu}_2\text{ZnGeSe}_4$ crystals. We have therefore made a new layer stack, where the Cu and Ge layers

are close to each other, the Cu is partly buried in the back and a Ge layer is on top. The resulting stack is Cu(85 nm)/Ge(90 nm)/Zn(125 nm)/Cu(85 nm)/Ge(100 nm). In the following paragraph we will present the electrical and physical properties of this new optimized layer stack.

4. Properties of the optimized layer stack

We have made a 15 minute anneal at 460°C in a flow of 10% H₂Se in N₂ of the new optimized multilayer stack. For this stack the adhesion properties were good and no delamination during the wet chemical steps could be observed. The XRD spectrum at the end of the selenization is similar to the other two stacks, with only Cu₂ZnGeSe₄ and Mo peaks visible and maybe a few small traces of ZnSe. Figure 8 shows the photoluminescence spectrum and the photoluminescence decay curve of the sample. The photoluminescence signal was acquired with a Hamamatsu C12132 time-resolved photoluminescence system. A pulsed 532 nm laser light source was used with a repetition rate of 15 kHz, an average power of 50 mW and an illumination area on the sample of about 3 mm diameter. We made a gaussian fitting to the experimental photoluminescence spectrum and we could identify three different components in the signal. A low energy component at around 1.2 eV, another component at around 1.37 eV and a third one around 1.45 eV. These peaks can be seen going up and down in intensity when the intensity of the illumination is varied. It is difficult to estimate at present what the different components of the PL signal are due to. The photoluminescence signal decays at first very rapidly, basically at the same rate as the instrument response of the tool, and once the signal reached an about hundred times lower level decays with a lifetime of about 2 to 3 ns. Solar cells were fabricated out of this optimized absorber layer using a standard process flow consisting of CdS deposition by chemical bath deposition followed by the deposition of 120 nm of intrinsic ZnO and 230 nm of Al-doped ZnO. Then an Al metal grid was deposited and the cells were isolated into 0.5 cm² cells using manual needle scribing. The current density versus voltage behavior of the best cell is shown in figure 9.

A conversion efficiency of 5.7 % could be measured under AM1.5G illumination. Especially the shunt resistance (R_{sh}) in the dark is very high with a value of $17.5 \text{ k}\Omega \text{ cm}^2$. The open circuit voltage (V_{oc}) and the fill factor (FF) on the other hand are a bit on the low side, which seems to be mainly due to non-optimal carrier collection leading to a strongly bias dependent photocurrent. This non-optimal carrier collection could of course be related to the relatively short lifetimes observed for the photoluminescence signal, giving an indication about the minority carrier lifetime, which seems to be rather short. Because of the low leakage currents in the dark, the diode ideality factor ($A = 1.92$) and reverse saturation current density ($J_0 = 2.5 \cdot 10^{-9} \text{ A/cm}^2$) could easily be extracted from the dark J-V curve. A capacitance voltage measurement of the best cell was acquired as well and the doping in the absorber was derived by using a Mott-Schottky plot at a measurement frequency of 100 kHz. The results are shown in Figure 10 as a function of the position in the absorber. As becomes visible from the measurement, the doping in the absorber is rather low, of the order of 10^{15} cm^{-3} .

5. Conclusions

We have synthesized polycrystalline $\text{Cu}_2\text{ZnGeSe}_4$ solar cell absorbers by selenization of a metal layer stack. Studying the XRD spectra 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 $\text{Cu}_2\text{ZnGeSe}_4$ 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 $\text{Cu}_2\text{ZnGeSe}_4$, 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 $\text{Cu}_2\text{ZnGeSe}_4$, leading to a somewhat slower formation reaction and larger $\text{Cu}_2\text{ZnGeSe}_4$ grains. An optimized layer stack having at the same time Ge and Cu close to each other and a top Ge layer has led to optimized absorber properties. Solar cells were fabricated with this

absorber layer and these showed power conversion efficiencies of 5.7%, limited mainly by a strongly bias dependent photocurrent.

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Figure Captions

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

Figure 2. $\text{Cu}/(\text{Zn}+\text{Ge})$ 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 spectrum of a typical CZGSe sample on a Mo/glass substrate.

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 spectra measured for the samples with the Ge layer on top for the 8 different times during the selenization process.

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

Figure 8. Photoluminescence spectrum (a) and photoluminescence decay curve (b) of the optimized $\text{Cu}_2\text{ZnGeSe}_4$ sample. A peak fit to the photoluminescence signal with three Gaussian components is also shown.

Figure 9. Current density versus voltage behavior of the best device in the dark and under AM1.5G illumination.

Figure 10. Doping in the absorber as derived from a Mott-Schottky plot.