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Surface modification through air annealing $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ absorbers

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Abstract

Recent studies demonstrate that air annealing can have a positive effect on the device performance of $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ [CZTSSe] solar cells. In this work air annealing of the selenium containing CZTSSe is compared to the pure sulfide CZTS. It is discovered that the selenium containing absorbers benefit from air annealing at higher temperatures than selenium free absorbers. The highest efficiency obtained utilizing the air annealing treatment on selenium containing absorbers is 9.7 %. We find that the band gap is narrowed when air annealing, which is partially explained by increased Cu-Zn disorder. Furthermore Zn enrichment of the surface after etching is identified as a possible cause of enhanced device performance. It is additionally observed that elemental selenium present on the CZTSSe surface is reduced in the air annealing treatment. Selenium removal is another possible explanation for the enhanced performance caused by the air annealing treatment.

1. Introduction

In recent years solar cells based on $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ [CZTSSe] have been the focus of intensive research. CZTSSe is closely related to the higher efficiency material $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGS). The relative scarcity of Ga and In is, however problematic if a high annual production volume is to be obtained [1]. In order to solve this issue materials without In and Ga are required and CZTSSe that only contains earth abundant elements is therefore an interesting alternative. Currently CZTSSe devices are, however, limited by a low open circuit voltage (V_{OC}) compared to the band gap of the material [2].

Several research groups have reported that low temperature annealing of the CZTSSe absorber prior to buffer layer deposition improves the device performance [3-8]. The typical approach employed in these studies is simply to perform the treatment by placing the sample on a hotplate. Most work has been focused on annealing of the bare CZTSSe absorber before further processing, while improvements have also been observed when annealing the CZTSe/CdS stack [3], as well as the complete device stack [3]. The studies in which the heat treatment is performed in an inert N_2 atmosphere focus on changes of the Na content in the absorber [6, 7] and in the CZTSSe/CdS buffer layer region [7]. It is argued that the annealing treatment can be used to obtain an appropriate level of Na [7]. In studies where the annealing treatment is performed in air, the focus is mainly directed to oxidation of grain boundaries [5, 8]. It is suggested that SnO_x formation in grain boundaries effectively passivate grain boundaries [5]. Another study find that oxygen substitutes for Se in the lattice near grain boundaries [8]. This lowers the valence band maximum and prevents holes from recombining in the grain boundaries. It is of course likely that both oxygen and Na plays a role when performing the annealing in air. In addition it has been noticed that the surface composition becomes poorer in Cu and richer in Zn when CZTSSe is annealed in either vacuum [3] or air (followed by ammonia etching) [9]. It has been argued that a Zn-rich and Cu-poor surface is beneficial and leads to

improved performance [3, 5, 9]. Most work on air annealing (AA) has been performed on CZTSSe or CZTSe, while only one study mentions the pure sulfide CZTS [7]. In this work we compare the effects of air annealing on pure sulfide CZTS and the selenium containing CZTSSe counterpart.

2. Experimental

Soda lime glass coated with 300 nm Mo by sputtering was used as substrates. Cu-Zn-Sn-S precursors were deposited onto the substrates by sputtering from binary CuS, ZnS, and SnS targets in an argon atmosphere. The composition of the precursors was measured by x-ray fluorescence. Precursors used for selenization experiments had $\text{Cu}/(\text{Zn}+\text{Sn}) = 0.96$ and $\text{Zn}/\text{Sn} = 1$ while precursors used for the sulfurization experiments had the composition ratios $\text{Cu}/(\text{Zn}+\text{Sn}) = 0.97$ and $\text{Zn}/\text{Sn} = 1$. When performing the selenization four $2.5 \times 2.5 \text{ cm}^2$ precursors from the same precursor deposition were loaded in a graphite box with a volume of 15 cm^3 containing 114 mg Se. The graphite box was then introduced into a preheated tube furnace with an argon background pressure of 35 kPa. When samples were transferred to the hot zone the temperature of the box increased to 560°C in about 90 s. The samples were allowed to dwell for 4 minutes and cooled down to 200°C in 170 s. During the selenization process sulfur in the precursor is exchanged for selenium leading to $\text{S}/(\text{S}+\text{Se}) \approx 0.25$ (estimated from the quantum efficiency (QE) band gap). The sulfurization was performed in the same system, but instead the box was loaded with 40 mg of sulfur. A temperature of 580°C , dwell time of 13 min, and background pressure of 46 kPa was used for the sulfurization. One reference sample was taken aside and the three remaining absorbers were exposed to an air annealing treatment. This was done by placing the sample onto a preheated hotplate at a set temperature for 10 min. Set temperatures of 100°C , 200°C , and 300°C were tested in this study. The temperature of the sample surface was measured to be within 10°C of the set value with a thermocouple. After the AA treatment the samples were removed from the hot plate and allowed to cool to room temperature (few seconds cooling time). A part of each sample was brought into the X-ray photo electron spectroscopy (XPS) chamber rapidly after the AA treatment, while a part of the sample was used for device fabrication. The samples were placed in a 5 vol% ammonia solution for 5 minutes before thiorea and Cd acetate solutions were added to start the CdS buffer layer deposition. About 70 nm CdS is deposited. The devices were completed by deposition of a i-ZnO (80 nm)/Al:ZnO (210 nm) bilayer by sputtering followed by mechanical scribing to define cells with an area of 0.1 cm^2 . All samples within each series were processed in the same CdS and window layer batch. Dark and illuminated current-voltage measurements were performed in a one-sun solar simulator (Newport, ABA) and external quantum efficiency was measured in a homebuilt setup under weak illumination (about 5 % of 1 sun). XPS measurements were performed after air annealing of the absorbers and repeated after etching the absorbers in 5 vol% ammonia for 5 minutes to investigate what is left on the surface before the CdS buffer layer is deposited. XPS measurements were performed in a Quantum 2000 from Physical Electronics with monochromatic an Al αK (1486.7 eV) excitation source, a beam size of $200 \mu\text{m}$ and a pass energy of 23.5 eV. The XPS binding energy calibration had been performed against metal standards. Photoluminescence (PL) measurements were performed at room temperature in a Renishaw inVia confocal Raman microscope equipped with an InGaAs CCD detector using a 785nm laser. The entire experiment was repeated with two minor differences. Instead of ammonia etching the samples were etched for 2 min in 5 % KCN before CdS deposition. In the repeated experiment a Ni/Al/Ni grid and a cell area of 0.5 cm^2 was used. Since the general trends observed when repeating the experiment is the same as the results presented here, these are left out of the paper.

3. Results

Figure 1(A) shows the effect of air annealing on sulfurized CZTS. It is noticed that the reference sample not exposed to the AA treatment shows relatively poor performance especially low V_{OC} and fill factor (FF). With an efficiency of 2-3 % this sample performs worse than typical devices produced with the baseline process that are typically above 6 % (see e.g. reference [10, 11]). For the samples treated with the air annealing of 100°C and 200°C a significant FF and V_{OC} increase is observed as well as a small increase in short circuit current (J_{SC}). As a result the device efficiency is improved to

6.8 %, which is comparable to typical baseline samples. One could therefore argue that the air annealing treatment can recover poor absorbers. Interestingly the efficiency is reduced if an even higher annealing temperature of 300 °C is used. At this temperature a detrimental effect becomes dominant and counteracts the beneficial effects observed at lower temperature.

Figure 1: (A) Device parameters for CZTS absorbers air annealed at different temperatures. (B) Device parameters for CZTSSe absorbers air annealed at different temperatures.

Figure 1(B) shows the device behaviour obtained after selenization of the sulfur containing precursor i.e. CZTSSe. In this case we observe a somewhat different trend. Air annealing at 100 °C leads to slight degradation of the devices mainly due to reduced V_{oc} . When annealing at 200 °C the devices reach up to 6.8 % efficiency, significantly better than the 4.5 % reference. Increasing the temperature further to 300 °C yielded an additional increase of the efficiency up to 9.1 % mainly due to improved FF. This dramatic performance improvement is very noteworthy and confirms the benefit of the air annealing treatment. By routinely air annealing a part of the absorber for a large quantity of samples, an advantage of the annealing treatment has been often seen. The highest efficiency obtained so far utilizing the air annealing treatment on our CZTSSe absorbers is 9.7 % (V_{oc} :446 mV, J_{sc} :32.7 mA/cm², FF:67 %).

Figure 2: Quantum efficiency measured under weak illumination of CZTSSe for samples air annealed at different temperatures. Included with circular symbols are the photoluminescence spectra measured on the absorbers of the same samples.

In an attempt to get some insights into the reason for the improved device performance QE and PL measurements were performed on the samples. For the QE measurements the trends were similar for both CZTS and CZTSSe samples (figure 2 only includes CZTSSe). For the selenized samples an

enhanced QE level throughout most of the range is observed for samples air annealed at 200 °C and 300 °C. At the same time a shift of the band gap to lower energies is observed as the temperature of the air annealing is increased. From a linear extraction of the QE edge a shift of 15 meV at 200 °C and 35 meV at 300 °C compared to reference is estimated. This shows that the treatment causes a small band gap narrowing. The PL peak also shifts to lower energies (18 meV at 200 °C and 35 meV at 300 °C) in agreement with the decreased band gap. In the QE measurement (figure 2) a peak is observed for ASe in the range 400-480 nm. This peak is only present under bias light illumination, and is considered to be an artefact possibly related to presence of laterally distributed shunt paths and photoconductive CdS [12].

XPS measurements were performed on the CZTS and CZTSSe absorber surface without air annealing treatment as well as samples air annealed at 100 °C, 200 °C, and 300 °C. The samples were then etched in ammonia after which the XPS analysis was repeated. Due to the vast amount of data all spectra are not included here and instead the results will be briefly described. The measurements gave very similar results for both CZTS and CZTSSe. When performing the air annealing an oxide layer is formed consisting of SnO_x , ZnO , and $\text{Na}_2\text{S}(\text{e})\text{O}_3$, $\text{Na}_2\text{S}(\text{e})\text{O}_4$. It cannot be excluded that other selenium oxide compounds could be present as well. After etching of the absorbers these oxide layers are removed, leaving no trace of Na and $\text{S}_x(\text{e})\text{O}_y$ behind. A small trace of SnO_x could be seen for absorbers air annealed at 300 °C. Some changes on the surface of the absorber are highlighted in figure 3.

Figure 3: XPS spectra of (A) the Zn 2p^{3/2} peak for the CZTSSe reference sample that is not air annealed before and after ammonia etching compared to the same measurements on a sample air annealed at 300 °C. (B) The Se 3d peak measured on samples after ammonia etching. A reference sample is compared to samples air annealed at different temperatures. (B-inset) shows the ratio of the fitted peak area of the Se 3d doublet related to Se in CZTSSe (54 eV) and the 3d doublet in elemental Se (55 eV).

Figure 3(A) shows the Zn 2p^{3/2} peak for the reference sample before and after ammonia etching. This is compared to the sample air annealed at 300 °C. It is noticed that the peak is almost unaltered when etching the reference. On the other hand the peak is strongly increased when etching the AA sample. Comparing the two etched surfaces a large increase of Zn in the AA sample is seen. Exactly the same trend is observed for the pure sulfide (not shown).

Figure 3(B) shows the selenium 3d peak of the absorbers air annealed at different temperatures after ammonia etching. The selenium 3d peak is fitted with two pairs of doublets, both having the

constraint that the doublet separation is fixed at 0.86 eV and the area ratio fixed at 2/3. For the dominating doublet the $3d^{5/2}$ component is centred on 54 eV. This corresponds with the expected peak position observed in CuInSe_2 [13] and can be assigned to Se in CZTSSe. The second doublet needed to fit the spectrum has a $3d^{5/2}$ component centred at around 55 eV, and may be ascribed to elemental selenium [14]. The ratio of the peak areas for the two components $\text{Se}_{\text{CZTSSe}}/\text{Se}_{\text{elemental}}$ is included in the inset of figure 3B. It is clear that the contribution to the Se 3d peak from elemental selenium is reduced as the annealing temperature is increased.

4. Discussion

As described in the introduction several effects of air annealing have been observed in literature. The best described effects are passivation of grain boundaries, modification of the surface composition, and diffusion of Na. These effects certainly all play a role in the experiment performed here, though they are not all explicitly studied. Some of the effects of the air annealing can, none the less, be identified from the experiments performed here.

One of the effects, which is considered of minor importance, is the change of the band gap seen in figure 2. The reason for the reduced band gap could be related to the Cu-Zn disorder in the material [15]. When heating the samples above the critical temperature for the order-disorder transition and rapidly cooling it down it is expected that the Cu-Zn disorder is increased. The critical temperature is about 200 °C for CZTSe [15] and 260 °C for CZTS [16]. Based on Raman measurements (not shown) it is possible to estimate the order in the sulfurized samples [16]. Using the ratio of the two A-modes at 290 cm^{-1} and 305 cm^{-1} the order parameter of $S = 0.18$ is estimated for the reference sample that was not air annealed and $S = 0.1$ after air annealing at 300 °C. We do observe changes in the Raman spectrum of CZTSSe as well (a shift and decrease of a peak at 240-245 cm^{-1}) but due to limited research on the topic we are currently uncertain if this is associated with Cu-Zn order. A reduced order is however expected in both cases, which would give a small band gap narrowing. The fact that a shift is also observed below the critical temperature indicates that there are also other effects involved that are not currently understood. Even though the disorder in the material is increased by air annealing of the samples the performance is increased. This indicates that the disorder is not the main limitation for the devices. Several competing effects are taking place when air annealing, and while disorder is expected to be detrimental, other effects like e.g. grain boundary and surface passivation could happen simultaneously. It is noticed that the PL peak intensity increases with annealing temperature. The luminescence intensity is governed by the competition between radiative and non-radiative recombination. The increase in PL intensity can therefore be interpreted as a sign of reduced non-radiative recombination, which is in agreement with the observation of higher V_{OC} values for the air annealed samples. For the three air annealed samples the PL yield scales with the measured V_{OC} . It is worth noticing that the V_{OC} is increased due to air annealing while the band gap is reduced. This leads to a reduction of the voltage deficit $E_{\text{g}}[\text{QE}]-V_{\text{OC}}$ by about 110 meV when comparing the reference (ASe) to the sample air annealed at 300°C (DSe). From XPS measurement we found an increase of the Zn in the surface region (figure 3 (A)). A Zn enrichment of the surface has been previously observed in a similar AA study [9]. It has also been observed that Zn terminated growth of co-evaporated CZTSe leads to better device performance [17]. It can therefore be speculated that the AA has a similar effect. One of the most likely explanations for the benefit of a Zn enriched surface is an increase of the surface band gap and therefore formation of a larger hole barrier at the junction [17]. This would lead to a reduced interface recombination which is also in agreement with the observation that the QE is improved for all wavelengths (figure 2).

It was noticed in figure 3(B) that the amount of elemental selenium on the surface is decreased with increased air annealing temperature. The elemental selenium on the absorber surface is expected to be detrimental if the selenium covers a too large fraction of the surface area [18]. For CIGS it was observed that the presence of selenium on the absorber surface reduced the QE for all wavelengths

[18]. Both surface passivation and/or selenium removal could therefore be the cause of increased QE of AA samples. The fact that the selenium containing absorbers benefit from a higher annealing temperature than the pure sulfides (figure 1) could also be related to the removal of elemental Se. It is conceivable that a higher temperature is needed to obtain a beneficial effect of Se removal. The presence of elemental selenium on the surface is strongly process dependent. In our case the selenium condenses on the surface when the graphite box cools down. It would be expected that this effect could similarly be of importance for other research groups using a similar technique.

5. Summary

The effect of air annealing on the absorber before buffer layer deposition was investigated for CZTS and compared to CZTSSe. It was observed that the treatment affects device performance differently. The Se containing materials benefit from a higher annealing temperature compared to pure sulfides. The highest efficiency obtained after air annealing of a selenium containing absorber is 9.7 %. A band gap reduction is seen after air annealing, which can partly be explained by increased Cu-Zn disorder. In agreement with previous studies it was observed that the composition of the absorber surface is strongly altered by air annealing. Particularly the increase in Zn content in the surface layer seems to be beneficial. For the selenium containing absorbers the air annealing additionally aids to remove elemental selenium from the surface. This is certainly a process dependent effect, but could be a part of the reason for the improved device performance.

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