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Zinc-Tin-Oxide Buffer Layer and Low Temperature Post Annealing Resulting in a 9.0 % Efficient Cd-free $\text{Cu}_2\text{ZnSnS}_4$ Solar Cell

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Abstract

$\text{Zn}_{1-x}\text{Sn}_x\text{O}_y$ (ZTO) has yielded promising results as buffer material for the full sulfur $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), with efficiencies continuously surpassing its CdS-references. ZTO can be deposited by atomic layer deposition (ALD) enabling tuning of the conduction band position through choice of metal ratio or deposition temperature. Thus an optimization of the conduction band alignment between ZTO and CZTS can be achieved. The ZTO bandgap is generally larger than that of CdS and can therefore yield higher currents due to reduced losses in the short wavelength region. Another advantage is the possibility to omit the toxic Cd. In this study the ALD process temperature was varied from 105 to 165 °C. Current-blocked devices were obtained at 105 °C while the highest open-circuit voltage and device efficiency was achieved for 145 °C. The highest fill factor was seen at 165 °C. The best efficiency reached in this study was 9.0 %, which, to our knowledge, is the highest efficiency reported for Cd-free full-sulfur CZTS. We also show that the effect of heat needs to be taken into

account. The results indicate that part of the device improvement comes from heating the absorber, but that the benefit of using a ZTO-buffer is clear.

1. Introduction

The earth abundant semiconductor material $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ (CZTSSe) has proven a viable solar cell absorber and several research groups have reached solar cell efficiencies above 10 % with a current record of 12.6 %.^[1-3] The material has a direct bandgap of 1-1.5 eV, tunable from pure selenide to pure sulfide, which makes it suitable for solar cell applications. The higher bandgap and the absence of the less-abundant Se, in principle make the pure sulfide, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), a better candidate.^[4] However, so far the efficiencies are slightly lower, with a record of 9.2 %.^[5, 6] One reason for this could be a non-ideal band offset between the buffer layer and the absorber for the higher bandgap material.^[7]

The standard buffer layer for CZTSSe solar cells is CdS, since this has been the preferred choice for the related $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ (CIGS) solar cells and generally gives good results also for CZTSSe. However, for a Se-free CZTS absorber, the band offset between absorber and CdS has been shown to be cliff-like, which is predicted to increase the interface recombination, and therefore decrease the open circuit voltage (V_{oc}) achieved from the device.^[7, 8] Accordingly, other buffer layer materials are investigated for these absorbers. The previously stated CZTS-records are actually both with CdS-based buffers but with addition of In and Zn respectively, to improve performance.^[5, 6] Previous work on alternative buffer layers for CZTSSe has been done on ZnO, Zn(O,S), ZnS(O,OH), (Zn,Mg)O, $\text{Zn}_{1-x}\text{Cd}_x\text{S}$, In_2S_3 and an “In-based” buffer.^[6, 9-14]

In this paper we are continuing our investigation on $\text{Zn}_{1-x}\text{Sn}_x\text{O}_y$ (ZTO) as a buffer for CZTS since this has yielded promising results, with efficiencies that continuously surpass its CdS-

reference, which is something that has not been seen for most other alternative buffers, beside the Cd-containing ones.^[15, 16] Another advantage with this buffer material, and many of the above mentioned, is that more light is transmitted in the UV-range, due to generally higher bandgaps than for CdS. This enables a higher maximum current from the solar cell. Additionally it is positive to be able to omit the toxic Cd.

The ZTO-layers are here deposited by atomic layer deposition (ALD), since this makes it possible to vary the bandgap of the films by changing Sn/(Zn+Sn)-ratio or process temperature. This enables optimization of the band alignment with the absorber.^[17] In this paper we focus on varying the process temperature, which was also done in our previous paper, however in that case lower temperatures were used, and the buffer layer composition and thickness fluctuated.^[15] The highest efficiency in the previous paper was 7.4 % and in this paper we present a 9.0 % efficient solar cell. This is to our knowledge the highest efficiency reported for Cd-free full-sulfur CZTS.

Due to the elevated temperature used in the ALD process, we also make additional experiments to decouple the possible effect of temperature treatment, from the effect of the buffer. We show that part of the changes in the series with ZTO-buffer comes from the heat treatment, but that there are also clear effects of the buffer change.

2. Results and discussion

2.1. Zinc-tin-oxide buffer temperature series

The process temperature in the ALD reactor was varied between 105 to 165 °C, samples A-D, and the effect on the cell performance was investigated. As described in the Experimental section, two references with standard CdS buffer are used for this series. The difference

between these is the absorber anneal batch, where one was annealed together with samples A and B, and the other one was annealed with samples C and D. This is due to that there may be small variations in device performance between anneal batches. As can be seen in **Table 1** and **Figure 1**, the V_{oc} is generally higher for the ZTO-devices compared to the CdS-references, and is highest for 145 °C process temperature. However, if taking the difference between the V_{oc} for the CdS-references into account, B and C show similar improvement of the voltage. The trend for the short circuit current (J_{sc}) is similar in-between the ZTO devices. However, for the current it is not possible to directly compare the ZTO-buffers with the CdS-references because of the large thickness difference between the two buffer types (roughly 10 versus 50 nm, see Table 1 and the Experimental section), which generates different reflection fringes, unless corrected by reflectivity measurements. Nevertheless, from a quantum efficiency (QE) measurement the benefit of a higher bandgap buffer can clearly be seen at the lower wavelengths, as depicted in **Figure 2**. The fill factor (FF) is similar for all samples besides a decrease for the ZTO deposited at 105 °C. Noteworthy is that the FF is best for the highest process temperature.

To determine the bandgaps of the buffers, spectroscopic ellipsometry measurements were performed on samples deposited on soda-lime glass (SLG) from the same ALD-runs as samples A-D. The resulting absorption coefficients were used to deduce the bandgap from linear extrapolation in Tauc plots, as shown in **Figure 3**. The data show the expected decrease in bandgap with increasing process temperature.^[18] For sample B and C we observe similar bandgaps, which is consistent with the observation that their V_{oc} values show equal increase compared to their respective CdS-references. The bandgaps are generally higher than the ones presented for ZTO on CIGS by Lindahl et al. due to the higher Sn-content in the buffers in the present case.^[18] This is in agreement with the trend shown in previous work by Lindahl et al.^[17] Previous results from ZTO-buffer on CIGS also suggest that the bandgap change

induced by the process temperature occurs mainly in the conduction band, while a change in Sn-content might affect both conduction and valence band.^[18, 19]

In the case of full-sulfur CZTS, the conduction band alignment with CdS has been shown to be negative, forming a so-called cliff, which leads to a lower V_{oc} than optimal.^[7] However, if the conduction band offset to the buffer is too positive there will instead be a barrier for the electrons at the buffer-absorber interface and the FF will drop. An optimal conduction band line up (for CIGS) is predicted for a small positive spike of 0.1-0.3 eV at the buffer-absorber interface.^[8] From the current-voltage (IV) curves for samples A-D shown in **Figure 4**, it is seen that sample A exhibit a blocking behavior with very low FF, which would agree with a too high barrier in the conduction band at the buffer-absorber interface. The V_{oc} is then increasing for sample B and C subsequently, while sample D, with the lowest buffer bandgap, has a tendency of lower V_{oc} again. This could indicate that the conduction band line up, going from sample C to sample D, is getting more cliff-like. Also the higher FF for sample D compared to sample C could be caused by a lower barrier at the buffer-absorber interface, if the barrier in sample C is still too high. However, the higher FF for sample D could also be a direct result of the higher process temperature, causing a better interface between buffer and absorber, either by an improved growth process or by modification of the absorber surface. As seen later, most of the samples that are just heat treated also show a slight improvement in FF, compared to non-heated references. However, in summary the IV results indicate that the best band alignment in this series was achieved for sample C, but that a more optimal band alignment for this particular CZTS absorber possibly could have been obtained for an intermediate temperature in-between those of sample C and D.

Temperature dependent current voltage analysis (IVT) gives the activation energy of the dominant recombination path when extrapolating the $V_{oc}(T)$ to 0 K.^[20] If the energy value is

lower than the bandgap of the absorber it is typically assumed that the devices are limited by interface recombination.^[20] In **Figure 5**, $V_{oc}(T)$ is plotted for sample C, D and their CdS-reference. The extrapolation to 0 K gives activation energies of 1.27, 1.24 and 0.99 eV respectively. However, the linear regions for extrapolation are small, which causes an uncertainty in the values, especially for sample C. The difference between the two types of buffer layers is nevertheless clear. The increase of activation energy indicates that the interface recombination is reduced for the ZTO samples. This, together with the improved V_{oc} compared to the CdS-references, the IV-curves for the experimental set and the bandgaps determined by ellipsometry, suggests that the band alignment is improved for the ZTO samples compared to the CdS-reference. However, the values for ZTO are still lower than the bandgap obtained from the QE band edge, which was 1.49-1.51 eV, and also lower than the measured room temperature photoluminescence (PL) peak at 1.31-1.32 eV (not shown). This implies that the devices are still limited by interface recombination. The activation energies obtained here are also lower than in our previous study, where the best sample had an activation energy of 1.36 eV.^[15] This decrease may come from a more defective interface, but might also indicate that the band alignment in the current series could have been further improved.

From X-ray reflectivity measurements (XRR) on SLG/quartz, that was included in the same ALD-runs as samples A-D, thicknesses between 11-13 nm are obtained (see also Table 1). However, investigation of sample D with transmission electron microscopy (TEM) indicates that the buffer may be thinner when it is grown on the actual absorber. For this sample the estimated thickness was 5-10 nm from TEM (see Supporting Information). The same trend has previously been seen for CIGS, where the ZTO grown on CIGS absorber is thinner, compared to when grown on a glass reference, for example 76 nm versus 87 nm for 2000 ALD cycles at 120 °C.^[21]

In our previous paper with ZTO on CZTS the thickness varied, but in the present study the same thickness was kept for the different ZTO-buffer deposition temperatures. However, we could still observe the same trends in device parameters, confirming that the trends are coming from the change of buffer properties, rather than a thickness variation. It should also be noticed that the buffers in this paper are much thinner than in the previous publication (around 12 nm compared to 40-100 nm), which demonstrates that well performing solar cells can be made for a wide range of ZTO-buffer layer thicknesses.

TEM investigation showed no indication of interdiffusion between buffer and absorber, however, due to the thin layer thickness more thorough characterization would have to be done to rule this out. Future experiments are planned to characterize the interface between the CZTS and the ZTO.

2.2. Post annealing series

Several groups have recently reported on changes of CZTSSe devices due to post annealing, already for low temperatures and short times, down to 100-150 °C and 30 min.^[22, 23] Since this is similar to what the samples A-D experience during the ALD process, additional experiments were carried out in an attempt to decouple the influence of the ZTO-buffer from possible anneal effects of the CZTS absorber.

First a series with a post anneal of the absorber was done. The absorber (non-etched) was placed in a chamber and heated to the process temperature (105, 125, 145 and 165 °C respectively) for 40 min in 2 Torr N₂ atmosphere. The samples were then etched and processed together in the same CdS-bath. The device characterization show small improvements on all parameters for 125, 145 and 165 °C while the sample heated to 105 °C

have worse performance than the unheated reference, as seen in **Figure 6**. This sample also has the highest spread between the different cells. Capacitance-voltage (CV) measurements were performed on this series and shows that the doping is slightly higher for the 105 °C sample, $2.2 \cdot 10^{17} \text{ cm}^{-3}$ compared to values around $7 \cdot 10^{16} \text{ cm}^{-3}$ for the other samples. This could be a reason for the degraded electrical properties, as was observed by Xie et al. for similar changes in absorber doping.^[23] However, the effect of a change in absorber doping may vary from detrimental to beneficial depending on several parameters, such as the initial absorber doping, absorber quality, doping level of the buffer and properties of the interface. Many of these properties could be affected by the heat treatment and thus additionally change the electrical behavior in opposite directions. The tendency that a non-heated reference and samples post annealed at a higher temperature show similar doping levels, while samples annealed at lower temperatures have higher doping has also been seen by Hironiwa et al. and Xie et al., but for somewhat different anneal conditions and temperatures.^[22, 23]

To further investigate the influence of post-annealing and surface treatment, additional experiments were performed. This time the experiment was done in the ALD-system but without depositing any ZTO-film. The highest process temperature, 165 °C, was chosen for this study. The samples were etched in KCN before inserted, just as they were in the case of ZTO-deposition. Then the samples were heated in the ALD-system in same way as they would have for a ZTO-deposition. They were then kept in the ALD for 15 min in 2 mbar flowing N₂ atmosphere. One sample was only heated, but the next sample got the same treatment but additionally was exposed to the same amount of Zn-precursor as was used in the ZTO-process. The last sample was instead exposed to the Sn-precursor. Directly after each heat treatment the sample was coated with the normal CdS-buffer and finished to solar cells in the same way as the main series.

The three different treatments give cells with similar electrical properties, judging from the IV curves, as seen in **Figure 7**. There is a larger V_{oc} improvement for the post annealed samples in this series than what was seen in the previous heat treatment experiment. As before, a slight FF increase is observed, but in this series only one of the samples (the Zn-treated one) showed a very small improvement on J_{sc} , measured in IV. These results indicate that the treatment with Zn/Sn-precursor does not have any additional effect on the solar cell performance.

However, looking at the QE curves (**Figure 8a**), the J_{sc} improvement for the Zn-treated sample appears more clearly and a better collection for long wavelengths is observed. The difference between the results from IV and QE could depend on that the QE is not performed under full illumination. Looking at the ratio of biased QE and unbiased QE (Figure 8b) we see that, for the other samples, the long wavelength region is increased with bias, which indicates that they have a short diffusion length and a narrow space charge region. This region was already higher for the Zn-treated sample and in this case the increase with bias is less, which could be explained by that the Zn-treated sample already had a larger space charge region. The results from this series thus show that the heating is the main contributor for changes in device properties, but that there is also an effect of a modified surface with Zn-treatment.

Raman measurements with 532 and 785 nm lasers were performed on most of the finished cells but no clear trends connected to the post annealing treatment could be seen.

2.3. Post annealing effects

The above results indicate that any step after the absorber deposition that include heating, even at a low temperature and short time, may affect the solar cell behavior. This makes it challenging to compare cells that have different thermal histories.

The extra series done here indicated that up to 60 mV of the V_{oc} improvement could come from the heat treatment alone, and that the poor behavior for the 105 °C sample may depend partly on the absorber deterioration seen with heat treatment at that temperature. However, the IV measurements for the ZTO-series clearly show the effect of the band alignment, as well as the QE shows the benefit of the higher bandgap material.

Several papers have been published about the effect of post annealing of CZTSSe.^[22-27] However due to the complexity of the starting material, especially the S/Se-ratio and the various kind of impurities caused by the many different deposition methods used, and additionally due to the many kinds of post annealing chosen, such as different atmosphere type and pressure, different temperatures and performed at different stages of the solar cell fabrication, there is no general conclusion regarding a reason for the changes seen, and possibly this might also differ from case to case.

There could be numerous reasons for the absorber to be affected by these rather short, low temperature heat treatments. Without extensive material and electrical characterization it is hard to decipher what is the origin of the changes. Suggested explanations in literature are, for example, changes in the Cu-Zn disorder, changes in absorber surface composition, re-distribution of Na and oxidation of grain boundaries.^[22, 26, 28, 29] In our case the annealing was done in an inert atmosphere which should limit the risk of oxidation, however oxygen can of course never be completely avoided.

The different explanations and the likelihood that they cause the effects seen here are further discussed in the supporting information. In summary, for these two series it is not possible to conclude with certainty which phenomenon that causes the changes seen with post annealing treatment. For the Cu-Zn disorder our previous experiments indicates that major changes only

occur for longer times or higher temperatures.^[28] Additionally, the absorber bandgap should be affected by the ordering process and no such shift is seen here. The changes in doping for the temperature series points towards changes in the Na-distribution, while the changes in QE for the Zn-treated sample indicates that surface composition of Zn has an influence of the device properties, however, in this case it was not seen in the IV-measurements. Most probably both effects can occur and also influence the results we see for the ZTO-series, causing part of the degraded performance for sample A and part of the V_{oc} improvement for samples B-D. The results also points towards that there might be two different temperature optima, one for the treatment of the absorber bulk, and possibly top surface, and one for the buffer properties, affecting both growth conditions and bandgap.

2.4. Record cell

Several additional runs with ZTO-buffer on CZTS were done and the IV for the best cell made during the experiments is shown in **Figure 9**, and is noted in Table 1 as sample E. The ALD process temperature was 145 °C, same as for sample C in the main series, with the differences that the pulse length of the nitrogen purge was 800 ms instead of 2000 ms and that the number of cycles was 250 instead of 500. This resulted in a ZTO-composition of $\text{Sn}/(\text{Zn}+\text{Sn})=0.28$ and a thickness of 10 nm (measured on quartz). The bandgap was determined to be 3.5 eV by ellipsometry and IVT gave an activation energy of 1.29 eV. Anti-reflective (AR) coating (MgF_2 , 110 nm thick) was evaporated on the device, which resulted in a record efficiency of 9.0 %. This is to our knowledge the highest efficiency reported for Cd-free full-sulfur CZTS.

The higher efficiency for this sample comes partly from better absorber performance, the CdS-reference has an efficiency of 7.2 % (without AR) which is higher than the references for the main series, see Table 1. This could be due to the slightly different Cu/Sn-ratio of the

absorber (see Experimental section). Additionally, the higher activation energy for the dominant recombination path, compared to sample C and D, suggests that the interface recombination is decreased for this sample, which could originate from better interface properties or that the band alignment is slightly better for sample E. This is also supported by the higher FF for sample E compared to sample C, especially in comparison with respective CdS-reference. The bandgap determined by ellipsometry for this buffer is in-between the values for sample C and D which further strengthens the hypothesis that the optimal band alignment lies within this range.

Compared to the best cell from our previous paper it is mainly the current that has been improved, and looking at the J_{sc} for the CdS-references (17.1 versus 20.5 mA) the improvement seems to originate mostly from a better absorber. The difference between these absorbers is primarily composition and a slightly changed annealing process.^[15]

3. Conclusion

ZTO-buffer was used for CZTS solar cells, as a replacement for the standard CdS-buffer. The ZTO-buffer was deposited by ALD and by varying the process temperature it is possible to adjust the band alignment with the absorber. In this paper the ALD process temperature was changed from 105 to 165 °C. Current-blocked devices were obtained at 105 °C while the highest V_{oc} and device efficiency was achieved for 145 °C. The highest FF was seen at 165 °C.

Part of the change in solar cell behavior was shown to come from the heat treatment that the absorber experienced in the ALD process. This is a valuable conclusion when comparing and evaluating CZTSSe samples that have different thermal histories.

It is however again clear that ZTO is a very promising buffer material for CZTS solar cells, continuously surpassing its CdS-references. In this paper the highest efficiency presented was 9.0 % (ZTO with AR). This is to our knowledge the highest efficiency reported for Cd-free full-sulfur CZTS.

4. Experimental Section

Sample preparation: Soda lime glass substrates are coated with 350 nm Mo by sputtering. On top a co-sputtering process is used to prepare a 1 μm homogenous film of Cu, Zn, Sn and S. Three targets (CuS, ZnS and SnS, all with purity 99.99 %) are used in a 0.67 Pa Ar-atmosphere. The composition of the samples are Cu/Sn=1.94-1.95 and Zn/(Cu+Zn)= 0.35-0.37 for the two first series, and Cu/Sn=1.89-1.90 and Zn/(Cu+Sn)=0.38 for the second extra series and the record cell.

The films are then sulfurized in a graphite box with additional S-powder, inside a tube furnace under a static Ar pressure of 350 Torr. The anneal time is 780 s at 580 °C. Four samples fit in one anneal run. For the main series, sample A-B and their reference are annealed together, and sample C-D and their reference are annealed in the next anneal run. For the post annealing series the samples heated at 105 and 145 °C comes from the same anneal run, and the samples heated at 125 and 165 °C and the reference sample from the next run.

The films are etched for 2 min in 5 wt% KCN, rinsed in deionized water and then immediately transferred into the ALD-system, a Microchemistry F-120. The samples are heated to the reaction temperature for 30 min and then the ZTO-layers are grown by diethyl zinc $[\text{Zn}(\text{C}_2\text{H}_5)_2]$, tetrakisdimethylaminotin(IV) $[\text{Sn}(\text{N}(\text{CH}_3)_2)_4]$ and deionized water. N_2 is used as carrier gas. The growth cycle is Zn/Sn-precursor: N_2 : H_2O : N_2 and the pulse lengths are

400/400:2000:400:2000 ms respectively. A 1:2 ratio of Zn:Sn cycles is used. The growth rate is slightly lower for lower process temperatures, so to keep the same thickness within the series, the number of cycles was varied from 500 to 800, giving a variation in deposition time between 40 to 65 min.

A ZnO/ZnO:Al transparent top contact is sputtered on and the devices are finished by evaporating a Ni:Al:Ni-grid. Finally 0.5 cm^2 cells are defined by mechanical scribing. Reference samples with CdS-buffer were made in the same way, besides that the ALD buffer deposition step was exchanged to our standard chemical bath deposition process, as described by Lindahl et al., giving a CdS layer of about 50 nm.^[30]

Measurements: Devices were characterized by IV measurements in a class A solar simulator from Newport. External QE was measured in a homebuilt setup calibrated with an external Si calibration cell from Hamamatsu. The bandgap from QE was retrieved by plotting (photon energy $\cdot (\ln(1-\text{QE}))^2$) versus photon energy, making a linear fit to the low energy side of the spectrum and interpreting its intersection with the x-axis as the bandgap.

SLG substrates were included in the buffer deposition runs and used to evaluate the thickness by XRR in a Philips X'pert MRD diffractometer. The bandgaps of these samples were determined by spectroscopic ellipsometry using a Woollam VASE instrument. Wavelengths from 260 to 1700 nm and angles of incidence of 65, 70 and 75° were measured. Reflections off the back of the glass substrate were largely reduced through use of an index matched, diffusive tape, with remaining contributions taken into account in the model used for the data analysis. In the model, isotropic optical constants were assumed for all layers. Tabulated data were employed for the glass substrate while an oscillator model including two polynomial spline functions was used to fit the optical constants of the ZTO-layer in a Kramer-Kronig

consistent manner. For the record cell these measurements were instead performed on quartz substrate.

Composition of both absorber precursor and buffer were measured by X-ray fluorescence (XRF) calibrated by Rutherford backscattering spectrometry (RBS) measurements. For the buffer, the composition measurements were carried out on the SLG/quartz pieces mentioned above.

The thickness and quality of the buffer layers was evaluated by TEM. The analysis were performed in a FEI Tecnai F30 ST, equipped with detectors for energy dispersive X-Ray spectroscopy and electron energy loss spectroscopy, which were both used for analysis of the layers. All analysis was performed at 300 kV acceleration voltage. Electron transparent cross-sections were prepared in a FEI Strata DB235 Focused Ion Beam, using the in situ lift-out technique. The ion beam energy was decreased stepwise from 30 keV down to 5 keV during the preparation, to minimize damage from the ion beam to the material.

PL and Raman measurements were performed on full devices in a Renishaw inVia confocal Raman microscope with a Si CCD detector. The measurements were performed in room temperature. For PL a 532 nm laser was used and for Raman 532 and 785 nm laser was used. The PL was corrected for system spectral response using an Avantes calibrated light source.

IVT from 100 to 330 K and CV at room temperature were measured by placing the sample on a liquid nitrogen cryostat connected to a Lakeshore 325 auto tuning temperature controller, and using a Keithley 2041 SourceMeter and an Agilent 4284A LCR meter. White light LED was used as the light source and its intensity was calibrated to match the J_{sc} previously

measured with IV. The temperature independence of the ideality factor was checked for the values included in the linear extrapolation of V_{oc} to 0 K.

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Figure 1. Device parameters for cells with ZTO-buffers, deposited at different process temperatures in the ALD (samples A-D), and their CdS-references. The left CdS-reference belongs to samples A-B and the right CdS-reference to samples C-D. Stars show the record efficiency achieved (sample E with anti-reflective coating) and its CdS-reference.

Figure 2. QE for the samples with ZTO-buffer together with their respective CdS-reference.

Figure 3. Bandgap determination of the ZTO-films on glass by spectroscopic ellipsometry.

Figure 4. IV-curves of the best cells from the devices with ZTO-buffers deposited at different process temperatures in the ALD. Dashed lines show dark IV of respective sample.

Figure 5. Open circuit voltage, extracted from temperature dependent IV, for samples C, D and their CdS-reference. Extrapolation to 0 K, to get the activation energy of the dominant recombination path, gives 1.27, 1.24 and 0.99 eV, respectively.

Figure 6. Device parameters for the post annealed series, with the unheated reference to the left.

Figure 7. IV-curves for the surface treatment series and its unheated reference. Dashed lines show dark IV of respective sample.

Figure 8. a) QE-curves for the surface treatment series and its unheated reference. b) Ratio between QE measured at -0.5 V and 0 V for the same samples.

Figure 9. IV curve for the ZTO record cell (with AR) and its CdS-reference (without AR). Device parameters are given for the record cell. Dashed lines show dark IV of respective sample.

Table 1. ALD process parameters, resulting film properties and device parameters (best cell) for samples A-E and their CdS-references.

Sample name	ALD process temp. [°C]	Sn/(Sn+Zn) in ZTO (XRF calibrated with RBS)	Thickness [nm] (XRR on glass/quartz)	Bandgap [eV] (ellipsometry on glass/quartz)	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	Eff [%]
CdS ref A-B	-	-	-	-	0.560	18.1	59.3	6.0
A	105	0.27	11	3.8	0.536	15.9	32.2	2.7
B	125	0.27	12	3.6	0.627	17.4	57.6	6.3
C	145	0.26	12	3.6	0.655	18.8	57.4	7.1
D	165	0.22	13	3.3	0.636	17.8	63.5	7.2
CdS ref C-D	-	-	-	-	0.584	19.1	59.4	6.6
E (incl. AR)	145	0.28	10	3.5	0.679	21.6	61.4	9.0
CdS ref E (no AR)	-	-	-	-	0.608	20.5	58.0	7.2

Table of contents entry

$\text{Zn}_{1-x}\text{Sn}_x\text{O}_y$ is applied as a buffer layer for $\text{Cu}_2\text{ZnSnS}_4$ solar cells and show better performance than the CdS-references. Deposition by atomic layer deposition enables tuning of the conduction band alignment by changing process temperature. Also $\text{Cu}_2\text{ZnSnS}_4$ can be affected by the temperature but the results indicate that, even if part of the improvement comes from heating, there are clear benefits with zinc-tin-oxide-buffer.

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