<http://www.diva-portal.org>

Postprint

This is the accepted version of a paper published in *Physica Status Solidi (a) applications and materials science*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the original published paper (version of record):

Larsen, J K., Scragg, J J., Frisk, C., Ren, Y., Platzer-Björkman, C. (2015)
Potential of CuS cap to prevent decomposition of Cu₂ZnSnS₄ during annealing
Physica Status Solidi (a) applications and materials science, 212(12): 2843-2849
<https://doi.org/10.1002/pssa.201532420>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-263983>

Potential of CuS cap to prevent decomposition of $\text{Cu}_2\text{ZnSnS}_4$ during annealing

Jes K. Larsen, Jonathan J.S. Scragg, Christopher Frisk, Yi Ren, and Charlotte Platzer-Björkman

¹ Ångström Solar Center, University of Uppsala, 75121 Uppsala, Sweden

Received ZZZ, revised ZZZ, accepted ZZZ

Published online ZZZ (Dates will be provided by the publisher.)

Keywords Thin films, solar cells, $\text{Cu}_2\text{ZnSnS}_4$, cap layer

One of the challenges associated with processing of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is the thermal decomposition reaction that causes loss of S and SnS from the absorber surface. To reduce the decomposition a sufficiently high SnS and S partial pressure must be supplied during annealing. The absorber surface can alternatively be protected with a thin cap. Aiming to obtain a more flexible process, CZTS precursors were capped with a thin CuS layer before annealing. The cap was subsequently removed with a KCN etch before device finishing. It was found that the cap coverage decreased during annealing, exposing a part of the absorber surface. At the same time, the initially Cu poor absorber took up Cu from the cap, ending up with a stoichiometric Cu content. Devices made from capped precursors or precursors annealed without sulfur had poor device characteristics. An increased doping density of almost one order of magnitude could be the reason for the very poor performance. CuS is therefore not a suitable cap material for CZTS. Other cap materials could be

investigated to protect the CZTS absorber surface during annealing.

A thin CuS cap is deposited on CZTS to protect its surface from decomposition during annealing.

Copyright line will be provided by the publisher

1 Introduction In recent years $\text{Cu}_2\text{ZnSnS}_4$ [CZTS(e)] has gained a lot of attention as a promising absorber for thin film solar cells. A record efficiency of 12.6% has been demonstrated with a process based on spin coating of a hydrazine based solution and subsequent annealing [1]. In order to achieve high efficiency it is essential to control the annealing process. One of the challenges is the well-known thermal decomposition reaction that causes loss of S and SnS from the absorber surface according to the chemical equilibrium [2]:

To prevent the decomposition a sufficiently high SnS and S partial pressure must be supplied during annealing. Aiming to yield more flexibility in the annealing process, this paper investigates an alternative approach to prevent

surface decomposition. It will be investigated if a thin cap covering the surface of the CZTS layer during the annealing can protect the surface. Ideally the cap material should fulfill certain criteria in order to be an attractive choice. The list of requirements includes 1) the cap should not react with CZTS, 2) the cap should not evaporate at 550 °C, 3) the cap should continuously cover the surface throughout the annealing, 4) the cap should be easily removable after annealing. The idea to apply a protective cap before annealing has previously been examined by Redinger et al. for CZTSe [3]. They found that a thin SnSe_2 eliminated the Sn losses due to SnSe evaporation. In this work the potential of CuS as a cap material for CZTS will be investigated. Unlike SnSe_2 it is not expected that CuS evaporates at the annealing temperature. Furthermore CuS is known to be rapidly and selectively

Copyright line will be provided by the publisher

etched by KCN, and could therefore be a good candidate as a cap material.

2 Experimental A set of experiments were designed to test the potential of the CuS as a cap material to prevent surface decomposition. The surface of a sputtered Cu-Zn-Sn-S precursor is capped with an around 100 nm thick CuS layer prior to annealing. After the annealing in a sulfur containing graphite box the cap is removed by

KCN etching before devices are completed. In order to test the viability of this approach to prevent surface decomposition, the experiment is repeated in an open box without sulfur, since one expects the most severe decomposition under these conditions. Samples discussed in this paper were all prepared with a baseline process described in the following. Soda-lime glass coated with 300 nm Mo by direct current (DC) sputtering was used as substrates. Cu-Zn-Sn-S precursor films were deposited onto the substrates by pulsed DC reactive co-sputtering from 4 inch CuS, Zn, and Sn targets. Constant sputtering powers of 175W, 430W and 100W were used for the respective targets. The atmosphere during sputtering consisted of H₂S and Ar both supplied with a flow rate of 15 sccm to yield a constant pressure of 0.7 Pa. A deposition time of 65 minutes yielded a precursor thickness of approximately 1.5µm. After precursor deposition the samples were unloaded and exposed to air before half of the samples are loaded in the same system. The precursors were allowed air exposure before cap deposition in order to verify the composition of the precursor material and enable us to directly compare capped and uncapped material from the same sputtering run. A CuS cap was deposited in the same system with all parameters kept the same as during precursor deposition, but only sputtering from the CuS target for 10 minutes yielding a CuS cap with a thickness of around 100 nm. For one set of samples an approximately 15 nm thick TiN layer was deposited onto the Mo back contact by sputtering before CZTS precursor deposition. A detailed description of the TiN deposition is available in reference [4]. The precursors were stored in a dry nitrogen cabinet before annealing in a tube furnace. The precursors were loaded in a graphite box containing about 90 mg sulfur. The graphite box was placed in the cold zone on a titanium transfer plate with an embedded thermocouple. In the furnace a block of graphite designed to fit the graphite box is preheated to 565 °C. The background pressure of the furnace was adjusted to 350 mbar by introduction of argon, and the graphite box is then introduced into the preheated graphite block leading to rapid ramp up of the sample temperature to a temperature of 555 °C in 150s. During a 600 s dwell time the temperature slowly rise to 560 °C. Upon pulling the samples out of the hot zone the temperature drops to 200 °C in 170 s. After unloading the absorbers, devices were immediately prepared. The device fabrication follows our baseline procedure, the first step of which is an etching

step in a 5 wt% potassium cyanide solution for 2 min. Cadmium sulphide buffer layer was then deposited by chemical bath deposition followed by deposition of an intrinsic and aluminium doped zinc oxide window layer by sputtering. Contact Ni/Al/Ni grids were deposited by e-beam evaporation before eight individual 0.5 cm² cells were defined on each sample by mechanical scribing.

SEM studies are performed using 15kV acceleration voltage and an in-lens detector. Energy dispersive x-ray spectroscopy (EDX) measurements, also using 15kV acceleration voltage, were calibrated with XRF measurements.

Grazing incidence X-Ray diffraction (GIXRD) is performed with an incidence angle of 1 degree to enhance the diffracted intensity from the CZTS film.

Capacitance-voltage (CV) and Drive level capacitance profiling (DLPC) characterisation was performed with four-point probes and a Agilent 4284A Precision LCR Meter. The frequency of the probing AC signal was 40 kHz for all measurements.

A series of samples all prepared in the same precursor run is compared in order to limit variation between samples. Sample A is a reference sample that is prepared with the baseline process, i.e. without cap and annealed in a sulfur containing box. Sample B is similar to A, but annealed in a box without lid and sulfur. The purpose of this sample is to demonstrate the effect of the decomposition reaction on the unprotected surface. Sample C is CuS capped and annealed with sample A in a sulfur containing box. This sample is included to investigate the effect of the cap under baseline annealing conditions. Sample D is capped with CuS and annealed with sample B in an open box without added sulfur. This sample serves as the ultimate test of the CuS cap since it is expected that the decomposition reaction which proceed with a maximum rate under these conditions. A set of samples with a barrier TiN layer that prevents reactions between Mo and the CZTS layer[4] are prepared in with the same procedures (samples AT-DT). The annealing conditions for the samples are summarized in Table 1.

Table 1 Annealing conditions for samples. Samples AT-DT are processed under the same conditions as A-D, but contain a TiN barrier layer between CZTS and Mo.

A(T)	B(T)	C(T)	D(T)
No cap	No cap	Cap	Cap
Sulfur in box	No sulfur	Sulfur in box	No sulfur

3 Results and discussion

3.1 Absorber morphology and composition Before discussing the absorber and resulting devices, it is worthwhile to investigate the CuS cap. Figure 1 shows the GIXRD patterns measured at 1° of incidence for a CuS capped precursor. In order to help identification of the peaks this is compared to a scan of the same sample performed after 2 minute etching in 5wt% KCN. It is

assumed that peaks, which disappear in this etch can be related to the Cu_xS_y phase [5]. The peak positions marked with squares match the expected peak positions of hexagonal CuS [6] (card no. 04-004-8687 in Joint Committee on Powder Diffraction Standards (JCPDS)). This assignment is in agreement with a previous study that found that the layer deposited from a Cu_2S target in a $\text{H}_2\text{S}/\text{Ar}$ atmosphere without sample heating yields hexagonal CuS [7]. After annealing, two of the characteristic peaks of CZTS appear in the spectrum (16.4° and 18.2°). We can therefore conclude that the presence of the cap does not prevent formation of CZTS. The other interesting observation is that the CuS cap appears to partly transform into a sulfur poor phase. The peaks appearing in Figure 1, labelled by Δ agree well with the peaks expected in cubic $\text{Cu}_{1.8}\text{S}$ (04-003-4437) [8]. A small peak shift corresponding to a 0.4% smaller lattice parameter relative to the database values for $\text{Cu}_{1.8}\text{S}$ is observed. This could be explained by a slightly different composition of the phase, i.e. Cu_{2-x}S . A few peaks (most noteworthy 31.8° and 32.9°) related to CuS remain present in the annealed sample. This could be an indication that only the surface of CuS is Cu_{2-x}S during annealing. The conversion of CuS to Cu_{2-x}S following the reaction $(2-x)\text{CuS} \rightarrow \text{Cu}_{2-x}\text{S} + (1-x)\text{S}(\text{g})$ is expected at high temperature and should yield a high activity of sulfur near the surface.

Figure 1 GIXRD pattern at 1° incidence of a CuS capped precursor compared to the same precursor after KCN etching. This is compared to a similar CuS capped precursor that has been annealed at 560°C . Peaks are assigned according to the following labelling: $\square$ is hexagonal CuS (04-004-8687), $*$ is CZTS, Δ is cubic $\text{Cu}_{1.8}\text{S}$ (04-003-4437), and ∇ is Mo.

In order to understand the effect of the cap during annealing, precursors and annealed absorbers were studied by SEM and EDX. Figure 2 shows SEM top view images of the sample surfaces. The morphology of the uncapped precursor is typical for the reactive sputtering baseline process. The grains seen in the topview image are columnar in shape, extending through the thickness of the film as shown in previous work [9]. After cap deposition, the grain structure of the absorber remains visible, but

features with smaller dimensions related to the CuS cap are visible on the grains.

Figure 2 SEM micrographs of the precursors (left) and the annealed absorbers before KCN etching. The scale bar shown on the baseline precursor is valid for all samples. The sample names A, B, C, D are described in the text.

The baseline anneal of the uncapped precursor (sample A) leads to recrystallization and grains with sizes ranging from a few hundred nanometres to more than a micrometer. Annealing of the same precursor without sulfur (sample B) results in significantly different microstructure with grain sizes smaller than 200 nm . It has previously been observed that annealing in an open box results in small grains [4], which could be related to a temperature difference in the absence of the lid of the box or the fact that the absence of a high sulfur partial pressure does not favour the formation of CZTS. The small bright particles seen on the uncapped samples are most likely ZnS as seen in e.g. reference [4]. Similar bright particles were seen in SEM on capped absorbers after KCN etching (see Figure 3). Raman spectroscopy measured with a 325 nm laser (not shown) confirms the presence of ZnS on all samples studied here. Sample C, i.e. the capped precursor annealed in a sulfur-containing atmosphere, did not experience significant grain growth like the comparable uncapped reference (A). The film is instead composed of a film with relatively small grains ($\sim 200\text{ nm}$) on top of which larger grains ($500\text{ nm} - 1000\text{ nm}$) can be seen. Point EDX measurement on one of the large grains shows that these consist of a Cu-rich phase (less than 1 percent Zn and Sn detected), while point EDX in the smaller grains yields $\text{Cu}/(\text{Zn}+\text{Sn}) = 1.3$. The small grains are therefore interpreted as a CZTS phase. The observation that the CuS cap appears to dewet the surface during the annealing could be problematic, since most of the surface will be unprotected under these circumstances. Annealing of the capped sample in an open box (sample D) leads to a microstructure that is similar to the uncapped layer annealed in the same process (B) with small grains. The CuS layer does not dewet to form large Cu-rich grains in this case, but does not cover the surface uniformly. Figure 3 demonstrates this with an EDX line scan across the surface of sample D. It has to be kept in mind that the large interaction volume relative to the grain smears out the elemental distribution obtained in this measurement. It

is, however, seen that the Cu-content varies indicating that the CuS cap has partially opened up in regions of the sample. In order to further illustrate this point, the sample was etched in KCN to remove the Cu_{2-x}S cap and re-examined by SEM. The result shown in Figure 3(b) reveals a surface where bright ZnS particles are visible, like the surfaces of the uncapped samples. One also clearly observes small voids with diameters in the range of 200 nm in the surface. One interpretation of these voids is that they occur where Cu_{2-x}S particles were removed during KCN etching. This indicates that the CuS cap dewets the surface also when annealed without sulfur.

Figure 3 (a) EDX line scan on surface of CuS capped CZTS layer after annealing without S (sample D). (b) Shows the surface of sample D after KCN etching.

Comparing all four samples in Figure 2, it is observed that grain growth is limited for samples annealed without sulfur (B,D) as well as the CuS capped sample annealed in sulfur (C). One possible reason for this could be that recrystallization requires a sufficiently high sulfur pressure. For sample C this would imply that the CuS cap prevents sulfur in the atmosphere from reaching the CZTS surface, while the sulfur loss from the CuS cap decomposing to Cu_{2-x}S provides an insufficient amount of sulfur to promote grain growth.

Table 2 Composition of samples after KCN etching determined by EDX.

	Precursor	A	B	C	D
Cu/(Zn+Sn)	0.94	0.94	0.96	1.01	1.04
Zn/Sn	1.02	1.08	1.15	1.01	1.15
Cu/Zn	1.86	1.81	1.79	2.00	1.95

The composition of the samples after KCN etching determined by EDS is shown in Table 1. The precursor has a slightly Cu poor and Sn rich composition. When annealing the uncapped material in presence of S (sample A) the Zn/Sn ratio increases slightly. This indicates that the Sn content in the layer is reduced due decomposition of the CZTS layer and evaporation of the volatile SnS . Annealing

of the uncapped precursor without lid on the box (sample B) leads to an even higher Zn/Sn ratio, showing that the decomposition reaction and SnS evaporation is more severe for this sample. This observation is expected due to the lower S partial pressure in the atmosphere above the sample surface, which favours decomposition of the CZTS surface. Annealing of the capped piece of the precursor in the S containing box (sample C) gives an absorber layer with an almost unchanged Zn/Sn ratio, showing that the cap successfully prevented decomposition and SnS evaporation. At the same time, it is, however, noticed that the Cu content is increased leading to a close to stoichiometric Cu content. This indicates Cu from the CuS cap diffused into the initially Cu poor precursor during annealing, thereby changing the composition of the bulk. Since the properties of the CZTS layer are dependent on the Cu-deficiency in the bulk[10], this observation has important implications for the device performance, as discussed later. The capped precursor annealed in the open box (sample D) ends up with a close to stoichiometric Cu content after annealing. The increase in Cu is again interpreted to be a result of Cu diffusion from the cap into the CZTS bulk. The increase of Zn/Sn shows that the cap does not efficiently limit the decomposition when the sulfur partial pressure is low, which was the initial aim with the experiment. These changes in the layer composition are expected to affect the device performance, as discussed in the following.

3.2 Device characteristics

Figure 4 Current-voltage characteristics of devices A-D. Dotted lines are measured in the dark, while solid lines are measured with 1 sun illumination.

Figure 4 shows the JV characteristics of the best device from each sample and Table 2 contains the corresponding device parameters. It is noticed that the reference device made without cap and annealed in the baseline process with sulfur in the box (sample A), is significantly better than the other devices. An efficiency of 7.4 % is obtained, which can be considered decent given that the world record for a pure sulfur CZTS is 9.2% [11]. It is not unexpected that annealing of the uncapped sample in an atmosphere

without sulfur (sample B) results in a poor device. Under these conditions the surface decomposition is expected to be the most severe. The JV curve of the device measured with 1 sun illumination is, unusual with a breakdown for a very low negative bias of -0.1V. This could be associated with Zener tunnelling breakdown, that can be observed in p-n junctions with high levels of doping [12], as discussed later. This non-ideal behaviour coupled with very low V_{OC} , J_{SC} and FF are all signs of a very poor device, and demonstrates the importance of sulfur during the annealing. A similar result has previously been seen for a similar sample annealed under identical conditions [4].

It should also be noted that the presence of sulfur is not only important for the decomposition reaction at the sample surface. Presence of sulfur plays an important role to prevent back contact decomposition by formation of a MoS_2 interlayer. In absence of sufficient sulfur back surface reactions result in significantly reduced J_{SC} [4]. This issue can be a part of the explanation for the low current for sample B and D annealed without sulfur as well as sample B, if the cap prevents sulfur from reaching the

back contact. Both capped samples (C,D) show very poor performance. It is, however, interesting to note that the sulfur free anneal yields better devices for the capped samples (comparing C to D), while the sulfur containing anneal resulted in a very significant degradation for the uncapped devices (comparing A to B). It can be suggested that this is related to the chemical changes in the Cu_xS_y cap. During annealing CuS losses sulfur to the atmosphere, while Cu diffuses into CZTS as mentioned earlier. In the sulfur free anneal it is expected that the cap becomes $Cu_{2-x}S$ faster than in the presence of sulfur. Since the compound $Cu_{2-x}S$ contains a high density of Cu vacancies [13], it is less likely to act as Cu supply for the Cu-poor CZTS. This is supported by the observation that the Cu/Zn ratio increases more for sample C than sample D. Another possible explanation could be that the presence of sulfur assists the cap dewetting process. As seen in the SEM images in Figure 2, the cap coverage of sample C annealed in sulfur is poor compared to sample D annealed without sulfur. The decomposition reaction is therefore reduced for the capped sample under sulfur free annealing conditions.

Table 3 Device parameters for the best device from each sample measured with 1 sun illumination. Net doping densities N are determined by DLCP and CV at 0V.

	Description	V_{OC} [mV]	J_{SC} [mA/cm ²]	FF [%]	Efficiency [%]	N_{DLCP} [cm ⁻³]	N_{CV} [cm ⁻³]
A	No cap + S	652	18.6	60.9	7.4	6E+16	4E+16
B	No cap - S	186	5.4	43.5	0.4	7E+18	4E+18
C	CuS cap + S	149	4.4	40.4	0.3	4E+18	1E+18
D	CuS cap - S	381	8.5	52.4	1.7	7E+17	6E+17
AT	TiN + S	629	18.4	54.9	6.4	9E+16	3E+16
BT	TiN -S	431	10.4	54.2	2.4	1E+18	2E+18
CT	TiN,CuS +S	133	3.9	41.0	0.2	3E+18	8E+17
DT	TiN,CuS -S	326	8.8	50.0	1.4	1E+18	7E+17

Figure 5 Current-voltage characteristics of devices AT-DT. Dotted lines are measured in the dark, while solid lines are measured with 1 sun illumination.

When comparing the sample set on Mo back contacts (A-D) to the similar set of samples with TiN back contacts

(AT-DT) in Figure 4, it is clear that they show the same general trends. The conversion efficiency of the uncapped precursor annealed in sulfur (AT) is slightly worse than the equivalent sample with Mo back contact (A). This difference can mainly be ascribed to a reduced FF caused by a higher series resistance in the sample on TiN (AT). The reason for this increased series resistance could be a barrier for majority carriers at the CZTS/TiN interface [4]. Except for sample BT, similar voltages and currents are obtained for Mo and TiN back contacts. The benefit of the chemically stable TiN back contact is in other words only noticeable when annealing in an open box without sulfur. Sample BT with a TiN back contact, is significantly better on all parameters, than the comparable sample on Mo (B). The reason for the very poor performance of sample B is therefore not only decomposition of the absorber surface. A part of the explanation for the poor performance must also relate to degradation at the back contact. To evaluate the effect of the cap without the influence of chemical instability of the back contact it is therefore relevant to

compare the samples on TiN back contacts. The conclusion is, however, the same since the capped devices are poorer than the uncapped devices both with and without sulfur supply during annealing. It can therefore be concluded that CuS does not act as a protective cap.

3.3 Effect of high doping density In order to understand the reason for the poor device performance DLCP and CV measurements [14] were performed on all devices. Table 2 shows the extracted net doping densities (N) for all devices. It is noticed that the measured doping density is very high for all devices, except for the baseline devices A and AT. Doping densities reported for high efficiency CZTS devices are around $1 \times 10^{16} \text{ cm}^{-3}$ [15, 16], not unlike the values measured for the reference devices here. Due to the non-ideal behaviour of the B-D devices, the very high N values obtained for the samples should be considered as an indication of a very high doping density rather than an exact measure of the doping. Also, one cannot completely rule out that this could be influenced by Cu_{2-x}S remaining in the film if it was not accessible to the KCN etchant. Even keeping this in mind, samples B-D all show an increased doping density of 1-2 orders of magnitude compared to the reference A. The large increase is very significant, and would, if it accurately reflects the doping in the absorber layer, be expected to have a significant effect on the device behaviour. The light activated reverse breakdown observed for sample B and C, may in fact be another indicator of a high doping density in these samples, since the breakdown voltage is inversely proportional to the doping density $V_{\text{BR}} \propto 1/N$ for Zener breakdown [17, 18]. These high doping levels could be related to the sample composition. It has been previously observed that the net doping in CZTS increases with increasing $\text{Cu}/(\text{Zn}+\text{Sn})$ [19, 20]. Very high net doping densities were obtained for material with close to stoichiometric Cu content ($1 \times 10^{19} \text{ cm}^{-3}$ for $\text{Cu}/(\text{Zn}+\text{Sn}) = 0.95$ [19] and $6 \times 10^{18} \text{ cm}^{-3}$ for $\text{Cu}/(\text{Zn}+\text{Sn}) = 0.98$ [20]). These values are similar to the ones measured here. For CuInSe_2 (CIS) it has similarly been observed that CIS grown under Cu-rich conditions result in material with at least one order of magnitude higher doping than comparable material grown under Cu-poor conditions [21]. This could explain the high doping density of the devices capped with CuS (C,D), since it was observed that Cu diffused into the initially Cu-poor precursor.

Figure 6 Quantum efficiency of sample A-D.

For the devices with highly doped absorbers a very shallow space charge region (SCR) is observed. Due to the limited extension of the SCR and a short diffusion length typically seen in CZTS [16], the current collection is very poor for sample B and C. The quantum efficiency of the devices shown in Figure 6, confirms that the poor collection dominates in these devices. The slope towards high wavelengths indicates poor collection of light absorbed deepest in the layer, outside the SCR.

While the high doping density can explain the low current for the capped devices, it does not implicitly explain the low voltage unless other effects are considered. There are several possible effects occurring at high doping levels that causes increase recombination and therefore reduces performance. Increasing importance of tunnelling enhanced recombination in bulk and at the interface are both effects that become increasingly important at high doping levels [22]. Alternatively the low voltage could be related to intrinsic defects forming in CZTS with low Cu deficiency. It has been suggested that Cu-poor, Zn-rich conditions yield better devices due to a lower probability for formation of $\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$ and $2\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$ defect clusters [23]. $\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$ forms deep defect level while $2\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$ causes band gap lowering. Both defect cluster types are predicted to be present at high concentrations for material with almost stoichiometric composition $\text{Cu}/(\text{Zn} + \text{Sn}) = 1$ and $\text{Zn}/\text{Sn} = 1$. Since these are expected to be detrimental to device performance, Cu deficiency is required to obtain high efficiency devices.

Finally, we will reflect on the similarity of the capped samples (C,D) and the sample annealed in an open box without sulfur (B). One could speculate that the origin of the very similar device behavior is fundamentally the same in both cases. When annealing without sulfur it is expected that the precursor decomposes into Cu_2S , ZnS and SnS . While the SnS tends to evaporate the ZnS and Cu_2S would be left on the surface. It can therefore be proposed that the Cu_2S acts as a source of Cu for the CZTS layer and causes a reduction of the Cu-deficiency. This would also explain the high doping level of the sample annealed without sulfur (B). The fact that CuS capping and the sulfur free annealing

result in similar devices could also have an alternative explanation. If the cap prevents sulfur from reaching the absorber, one could argue that the devices have similar poor performance due to a lack of sulfur in both cases.

4 Summary The potential of CuS as a cap layer to protect CZTS from decomposition during annealing was examined. It was concluded that the cap layer dewets the CZTS surface during annealing, and does not prevent SnS evaporation. It was furthermore found that Cu from the cap diffuses into the initially Cu-poor CZTS. Devices made from capped CZTS show very poor performance. This could be caused by the very high doping levels measured in these samples. It can therefore be concluded that CuS is a poor cap material for CZTS. Alternative materials could instead be investigated.

Acknowledgements The authors acknowledge funding from the Swedish Research Council, the Wallenberg Academy Fellows program and the People Program (Marie Curie Actions) of the European Union's seventh Framework Program FP7/2007-2013/ under REA Grant Agreement No. 316488 (KESTCELLS). Tomas Kubart is gratefully acknowledged for deposition of TiN layers.

References

- [1] W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, *et al.*, *Advanced Energy Materials*, **4**, (2014).
- [2] A. Redinger, D. M. Berg, P. J. Dale, and S. Siebentritt, *Journal of the American Chemical Society*, **133**, 3320, (2011).
- [3] A. Redinger, M. Mousel, R. Djemour, L. Gütay, N. Valle, and S. Siebentritt, *Progress in Photovoltaics: Research and Applications*, **22**, 51, (2014).
- [4] J. J. Scragg, T. Kubart, J. T. Wätjen, T. Ericson, M. K. Linnarsson, and C. Platzer-Björkman, *Chemistry of Materials*, **25**, 3162, (2013).
- [5] B.-A. Schubert, B. Marsen, S. Cinque, T. Unold, R. Klenk, S. Schorr, *et al.*, *Progress in Photovoltaics: Research and Applications*, **19**, 93, (2011).
- [6] H. Fjellvåg, F. Grønvold, S. Stølen, A. F. Andresen, R. Müller-Käfer, and A. Simon, *Zeitschrift für Kristallographie-Crystalline Materials*, **184**, 111, (1988).
- [7] Y. Ren, J. J. Scragg, T. Ericson, T. Kubart, and C. Platzer-Björkman, *Thin Solid Films*, (2014).
- [8] K. Yamamoto and S. Kashida, *Journal of Solid State Chemistry*, **93**, 202, (1991).
- [9] T. Ericson, T. Kubart, J. J. Scragg, and C. Platzer-Björkman, *Thin Solid Films*, **520**, 7093, (2012).
- [10] T. Prabhakar and N. Jampana, *Solar Energy Materials and Solar Cells*, **95**, 1001, (2011).
- [11] H. Hiroi, N. Sakai, T. Kato, and H. Sugimoto, "High voltage Cu₂ZnSnS₄ submodules by hybrid buffer layer," in *Proceedings of the IEEE Photovoltaic Specialists Conference 39th: 16–21 June 2013*, 2013.
- [12] B. G. Streetman and S. Banerjee, *Solid state electronic devices vol. 4: Prentice Hall Upper Saddle River, NJ*, 2000.
- [13] S. Sanchez, S. Cassaignon, J. Vedel, and H. G. Meier, *Electrochimica Acta*, **41**, 1331, (1996).
- [14] J. T. Heath, J. D. Cohen, and W. N. Shafarman, *Journal of Applied Physics*, **95**, 1000, (2004).
- [15] I. L. Repins, H. Moutinho, S. G. Choi, A. Kanevce, D. Kuciauskas, P. Dippo, *et al.*, *Journal of Applied Physics*, **114**, 084507, (2013).
- [16] B. Shin, O. Gunawan, Y. Zhu, N. A. Bojarczuk, S. J. Chey, and S. Guha, *Progress in Photovoltaics: Research and Applications*, **21**, 72, (2013).
- [17] S. Puttnins, S. Jander, A. Wehrmann, G. Benndorf, M. Stölzel, A. Müller, *et al.*, *Solar Energy Materials and Solar Cells*, **120**, Part B, 506, (2014).
- [18] S. Mahadevan, S. M. Hardas, and G. Suryan, *physica status solidi (a)*, **8**, 335, (1971).
- [19] D. M. Bishop, B. E. McCandless, R. Haight, D. B. Mitzi, and R. W. Birkmire, *Photovoltaics, IEEE Journal of*, **5**, 390, (2015).
- [20] A. Nagaoka, H. Miyake, T. Taniyama, K. Kakimoto, and K. Yoshino, *Applied Physics Letters*, **103**, 112107, (2013).
- [21] V. Deprédurand, D. Tanaka, Y. Aida, M. Carlberg, N. Fèvre, and S. Siebentritt, *Journal of Applied Physics*, **115**, 044503, (2014).
- [22] R. Scheer and H.-W. Schock, *Chalcogenide Photovoltaics: Physics, Technologies, and*

Thin Film Devices. Germany: John Wiley & Sons, 2011.

- [23] S. Chen, L.-W. Wang, A. Walsh, X. G. Gong, and S.-H. Wei, *Applied Physics Letters*, **101**, 223901, (2012).