<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):

Englund, S., Kubart, T., Keller, J., Moro, M V., Primetzhofer, D. et al. (2019)
Antimony-Doped Tin Oxide as Transparent Back Contact in $\text{Cu}_2\text{ZnSnS}_4$ Thin-Film Solar Cells
Physica Status Solidi (a) applications and materials science, 216(22): 1900542
<https://doi.org/10.1002/pssa.201900542>

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-402260>

This is the accepted version of the following article:

Englund, S., Kubart, T., Keller, J., Moro M. V., Primetzhofer, D., Suvanam, S. S., Scragg, J. J. S., Platzer-Björkman, C. (2019) Antimony-doped Tin Oxide as Transparent Back Contacts in CZTS Thin Film Solar Cells, *Physica Status Solidi a*, 2019, 1900542, which has been published in final form at <https://onlinelibrary.wiley.com/doi/full/10.1002/pssa.201900542>

Original paper

Antimony-Doped Tin Oxide as Transparent Back Contact in CZTS Thin Film Solar Cells

Sven Englund, Tomas Kubart, Jan Keller, Marcos V. Moro, Daniel Primetzhofner, Sethu Saveda Suvanam, Jonathan J. S. Scragg, Charlotte Platzer-Björkman**

S. Englund, Dr. T. Kubart, Dr. J. Keller, Dr. S. Saveda Suvanam, Dr. J. J. S. Scragg, Prof. C. Platzer-Björkman

Uppsala University, Department of Engineering Sciences, Division of Solid State Electronics, Ångströmlaboratoriet, Lagerhyddsvägen 1, 752 37 Uppsala, Sweden

sven.englund@angstrom.uu.se

charlotte.platzer@angstrom.uu.se

Dr. M. V. Moro, Dr. D. Primetzhofner

Uppsala University, Department of Physics and Astronomy, Applied Nuclear Physics, Ångströmlaboratoriet, Lagerhyddsvägen 1, 752 37 Uppsala, Sweden

Keywords: CZTS, thin film solar cells, transparent back contact, antimony-doped tin oxide, sulfurization

Abstract

Antimony-doped tin oxide ($\text{Sn}_2\text{O}_3\text{:Sb}$, ATO) is investigated as a transparent back contact for $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin film solar cells. The stability of the ATO under different anneal conditions, and the effect from ATO on CZTS absorber growth is studied. It is found that ATO directly exposed to sulfurizing anneal atmosphere reacts with S, but when covered by CZTS, it does not deteriorate when annealed at $T < 550$ °C. Electrical properties of ATO are even found to improve when CZTS is annealed at $T = 534$ °C. At $T = 580$ °C, it is found that ATO reacts

with S and degrades. Analysis shows repeatedly that ATO affects the absorber growth as large amounts of Sn-S secondary compounds are found on the absorber surfaces. Time-resolved anneal series show that these compounds form early during anneal and evaporate with time to leave pinholes behind. Device performance can be improved by addition of Na prior to anneal. The best CZTS device on ATO back contact in this study has an efficiency of 2.6%. As compared to a reference on a Mo back contact, a similar open circuit voltage and short circuit current density are achieved, but lower fill factor is measured.

1. Introduction

During recent decades, the risk of a forthcoming climate crisis due to CO₂ emissions in combination with a continuous cost-reduction has caused the demand for renewable energy sources to rise. The International Energy Agency concludes that photovoltaics have “the potential to become a major source of electricity at an extremely rapid pace”.^[1] The photovoltaic absorber material Cu₂ZnSn(S,Se)₄ (CZTS(e)) has gained interest due to its composition of non-toxic, inexpensive and earth-abundant materials, making it a promising candidate for the next generation solar cells.^[2] So far, all high-efficiency CZTS(e) solar cells have been produced in various two-step processes, i.e. deposition of a CZTS(e) precursor onto a back contact followed by a heat treatment (anneal) in S (and/or Se) atmosphere. The anneal is a major challenge as it may cause chemical reactions between the precursor and the back contact and decompose both the absorber and back contact.^[3,4] Finding alternative, inert back contact materials has been identified as one key to improve CZTS(e) performance.^[5,6] At the same time, one strategy that has potential to increase the efficiency of thin film solar cells is the use of transparent conductive oxides (TCO) as back contacts. Transparent back contacts would make it possible to produce (i) bifacial solar cells, thereby increasing the amount of light reaching the solar cell, or (ii) tandem solar cells with CZTS as the top cell, to more efficiently capture light from the whole spectrum of visible light. Pure CZTS is more suitable in tandem

configuration due to its larger band gap of around 1.45 eV compared to 1.0 eV for CZTSe.^[7] Despite all the aforementioned reasons and references, few studies have been published on pure CZTS on transparent back contacts. Mali et al. deposited CZTS on fluorine-doped tin oxide (FTO) by a solution based process, reaching an efficiency (η) of 1.9%.^[8] Mahajan et al. used the Successive Ionic Layer Adsorption and Reaction (SILAR) method to deposit CZTS on indium-doped tin oxide (ITO) and FTO, reaching η of 1.7% and 2.1% respectively.^[9] Ge et al. deposited CZTS by co-electroplating on ITO, and found that In diffused into the absorber when using anneal temperatures above 500 °C.^[10] However, they still reached $\eta = 2.7\%$, with front illumination (and 3.1% with bifacial illumination) after anneal in H₂S at 520 °C. In a following publication, they instead annealed at 540 °C in less reactive “S vapour atmosphere” and could reach a front illumination η of 5.8%.^[11]

ATO is a well-known TCO and was initially commonly used in liquid crystal displays (LCD).^[12] Moreover, it has been suggested for high temperature applications and for solar cells.^[13-15] In this publication, ATO is, for the first time to our knowledge, investigated as back contact for CZTS thin film solar cells.

2. Experimental Section

For optimization of the ATO deposition, films with thickness $t \approx 300$ nm were deposited on soda-lime glass (SLG) by reactive radio frequency (RF) sputtering in a Lesker CMS-18 sputter system from a compound target manufactured with nominal composition of 97% SnO₂ and 3% SbO₃, giving an Sb to metal ratio ($\text{Sb}/(\text{Sb}+\text{Sn})$) of $\approx 3.6\%$. The composition was chosen in order to optimize the conductivity of the ATO as described in literature.^[16] The size of the target was 101 mm in diameter and a discharge power of 280 W (1.14 W cm⁻²) was used. Base pressure of the deposition system was below 3×10^{-5} Pa and process pressure was set to 0.67 Pa. The depositions were made in an atmosphere of Ar/O₂, at a constant Ar flow, and the effect of the varied O₂ flow was investigated in terms of conductivity, transparency and in some cases also

residual stress. In addition, different ways to apply heating to the process were investigated, e.g. post anneal at 500 °C in vacuum, or heating during deposition at 500 °C in order to optimize the deposition conditions for ATO. For anneal (sulfurization) experiments, the ATO thickness was $t \approx 850$ nm. Details are summarized in **Table S1** in the Supporting info.

CZTS precursors ($t \approx 1$ μm) were deposited by binary compound (i.e. CuS, SnS and ZnS) target co-sputtering in another Lesker CMS-18 sputter system. The experiments were designed to give a direct comparison between the behaviour and performance of solar cells with ATO- and Mo back contacts used in the in-house baseline process. The compositions of the precursors were determined by X-ray Fluorescence (XRF) using a reference with composition determined by Rutherford Backscattering Spectrometry (RBS) (see Ericson et al.^[17] for further details).

The samples were annealed under different conditions in a tube furnace, with samples loaded in a pyrolytic carbon (PyC) coated graphite box with a volume of 15 cm³. The furnace had a preheated hot zone, and an outer, water-cooled zone and loading area. The graphite boxes were introduced to the hot zone using a rod and the time of anneal was measured from the moment when the temperature reached around 30 °C below the target temperature, typically within 90 s from insertion. The background Ar pressure was set to 47 kPa. 80 mg of solid S was added in the box prior to the anneal.

Details of the different anneal experiments are given in **Table S2** in the Supporting info. In short they consisted of: 1) anneal of bare ATO films (“ATO anneals” in Table S2), 2) anneal of CZTS precursors on ATO (“Temp. series”) at different temperatures, 3) a time-resolved study (“Time series 534”) of CZTS precursors on ATO, 4) testing of Mo interlayers between ATO and CZTS (“Mo interlayers”), 5) testing addition of Na, either by depositing NaF (evaporation, Balzer UMS) or adding an SLG piece on top of the precursor (“Na addition”) and 6) two time-resolved anneal series with a higher Cu/Sn ratio (“High Cu/Sn”) and lower Cu/Sn ratio (“Low Cu/Sn” in), respectively.

Parts of the samples were saved for material characterization, and the rest of the samples were used for further device processing and current-voltage analysis. Device processing included etching in KCN, chemical bath deposition (CBD) of 60 nm CdS, sputtering a window layer of 80 nm intrinsic ZnO and 210 nm Al-doped ZnO (sheet resistance (R_{sheet}) $\sim 40 \Omega \square^{-1}$). Some samples were finished by evaporation of Ni/Al/Ni front contact grids, and finally mechanical scribing was used to define the solar cells in desirable sizes. See Table S2 for the details of all samples used in the different series.

Characterization of the ATO was made using the following equipment; R_{sheet} was measured by four-point-probe in CMT-SR2000N from AIT. Film thickness was measured by profilometer Dektak 150 from Bruker/Veeco. Residual stress was calculated by measuring the curvature of a thin ($t \approx 180 \mu\text{m}$) microscope cover glass before and after film deposition in the same profilometer and using Stoney's formula.^[18] Absorption was determined from transmittance- and reflectance measurements (absorption = 100% – transmittance – reflectance) on ATO on SLG (absorption in SLG was $\sim$ negligible) by using a Perkin Elmer Lambda 900 spectrometer with an integrating sphere. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) was done in a Merlin microscope from Zeiss equipped with Schottky FEG detector for SEM and X-Max SDD detector for EDS. X-ray Diffraction (XRD) was measured in θ -2 θ mode in a D5000 from Siemens, using Cu K_α radiation.

Scanning Transmission Electron Microscopy (STEM) lamellae were prepared using a Focused Ion Beam (FIB) (FEI Strata DB235 FIB-SEM), following the in situ lift-out method.^[19] A probe corrected FEI Titan Themis 200 equipped with SuperEDS detection system was used for STEM-EDS analysis.

Depth profiles were measured by Glow Discharge Optical Emission Spectroscopy (GDOES) in GDA 750 HR from Spectrums, and by a combined analysis of RBS and Particle Induced X-ray Emission (PIXE). RBS and PIXE were performed using the 15SDH-2 pelletron tandem

accelerator located at the tandem laboratory at Uppsala University.^[20] RBS was performed using 2 and 5 MeV He⁺ primary ions, and the latter was simultaneously used with the PIXE measurements.

Finally current-voltage (*JV*) of solar cell devices was measured in one-sun solar simulator (Newport, ABA class) with an Xe lamp, sweeping from negative to positive bias. The lamp intensity (AM1.5) was calibrated using the current measured from quantum efficiency (QE). Since the baseline thickness of 1 μm was used, the presented results are limited to front illumination. Meaningful measurements of back- and bifacial illumination would require an optimization of absorber thickness, which is outside the scope of this article.

3. Results and discussion

3.1. Optimization of ATO

Resistivity and optical absorption in ATO are determined by both Sb- and O content. Sb content was fixed and determined by the target composition. The content of O on the other hand, can be modified by changing the O₂ flow during the sputtering. As seen in **Figure 1**, an optimal O₂ flow was found around 0.4-0.6 sccm (and Ar flow fixed to 60 sccm). The optical absorption and resistivity had their optima around the same O₂ flow. The resistivity of the as-deposited ATO films could be reduced significantly by post-anneal in vacuum. Heating to the same temperature during the deposition in a one-step process did not result in as low resistivity as the post-anneal, as seen in Figure 1, but affected the stress significantly (see Table S1). The two-step process (sputtering+post-anneal) was chosen for further experiments. Exact determination of the Sn/Sb ratio is challenging due to the very similar atomic properties in size and weight and overlapping of their L and K X-ray lines. However, using PIXE and RBS in a combined experiment, the composition of the as-deposited and vacuum annealed ATO films could be determined as $\approx 66.5/31.3/2.2$ at.% of O/Sn/Sb, respectively (see **Figure 2**). This composition is similar to the target composition of 66.5/32.3/1.2 at.%, except for the increase in the Sb

content, which is not fully understood. In Figure 2, the RBS and PIXE spectra (black solid-dotted line and black solid line, respectively) of the ATO sample measured simultaneously and analysed self-consistently,^[21] is shown (red solid line represents the final fit obtained with SIMNRA software.^[22] However, the achieved minimum resistivity (ρ) of 3.6 m Ω ·cm is within the range typically reported in literature (~1-7 m Ω ·cm) for sputtered ATO.^[16,23]

3.2. Anneal and integrity of ATO films.

As-deposited ATO films were annealed in S atmosphere at 3 different temperatures, 534 °C, 547 °C and 580 °C. It was, however, found that the films degraded severely as they turned opaque and the resistivity increased significantly. Analysis of the XRD spectra, see **Figure 3** (a), showed that the films had reacted with S and formed preferentially SnS₂ at the lower temperatures, and Sn₂S₃ at the higher temperatures. This observation is consistent with previous findings related to the behaviour of Sn and S content in the present anneal setup.^[24] It follows from the fact that the partial pressure of S (P_s) in the initial phase of the anneal increases rapidly initially as the elemental S evaporates, and then decays during the rest of the anneal time as the system (graphite box) is not fully tight (see e.g. ^[25]). Therefore, the ATO film initially reacts with S and forms SnS₂ which then starts to lose S as P_s decays and ends up as Sn₂S₃. In this series, as the duration is the same, the same observations can be explained by the fact that at lower temperatures, the P_s required to stabilize a given sulfide will be lower, so it takes longer time for the critical P_s to be reached and a phase change to occur (see e.g. Scragg et al. ^[26]).

In a next series of experiments, CZTS was deposited on top of the ATO and the samples annealed under the identical conditions as described above. In this case, upon removal of the CZTS films, the ATO films were found still transparent and, as seen in the XRD patterns in **Figure 4**, structurally unaffected at $T = 534$ °C. Some minor changes were observed in the sample annealed at the higher temperatures, which showed a shoulder around 32.9° and a more significant peak at 54.4° for the sample annealed at 580 °C. These peaks could not be confirmed,

but could be a result of changes in preferred orientation. However, STEM-EDX was measured for the sample annealed at 580 °C, where a small amount of S (≈ 3.5 at.%) was detected in the ATO near the CZTS interface, **Figure 5**. As seen in **Table 1**, the same sample had increased R_{sheet} after sulfurization, while after anneal at 534 °C and 547 °C, the R_{sheet} of the ATO decreased. The absorption spectra in **Figure 6** show that the absorption of ATO is mostly unaffected after anneal below CZTS. The negative values of the fringes in the visible region are due to a small systematic error arising from the instrumentation. It can be concluded that the anneal steps did not deteriorate the optical properties of the ATO films. For all annealed samples the free charge carrier absorption peak in the infrared region is shifted to slightly lower wavelengths as compared to the as grown sample (i.e. plasma wavelength λ_p is reduced to about 2300 nm, according to Drude theory, see further e.g.^[30]). This indicates that the free electron concentration increases during anneal and explains the decreased resistivity of the ATO films after anneal below CZTS.

3.3. Anneal and analysis of CZTS absorbers

For the samples annealed at 580 °C, SEM images of the top surfaces revealed crack-like features (**Figure 7** (a)) in the absorber on ATO. The features were, in higher magnification, found to be formations of pinhole trenches in the absorber, along with an apparent phase segregation as seen in Figure 7 (b). The inset in Figure 7 (b) shows STEM-EDS maps, showing that the segregating phase is ZnS secondary phase. No cracks/pinholes were seen on the Mo reference (Figure 7 (c)), and the amount of secondary phases at the surface was significantly lower than for the corresponding ATO sample.

When the temperature was reduced, the cracks disappeared; the CZTS surface of the ATO sample was uniformly covered by flake-shaped features (see Figure 7 (d) and **Figure 8**), however. EDS mapping showed that these contained Sn and S, as seen in the inset of Figure 7 (d). At these lower temperatures, the grain size of the CZTS on the ATO decreased significantly

(Figure 7 (e)), while the CZTS on Mo was less affected (Figure 7 (f)), corresponding cross-sections shows in **Figure S1**. This could possibly be related to the (reduced) supply of Na during the anneal, as grain sizes increased when external addition of Na was supplied for anneal at 534 °C , as seen in **Figure S2**. Another observed aspect was the adhesion between the back contact and the absorber layer, which was found to be better for the higher temperatures. In some studies on CZTS_{Se} and other TCO back contacts, an optimal anneal temperature has been found around 500 °C, e.g.^[30], whereas in the present study, the adhesion for the sample annealed at 505 °C was so poor that CZTS delaminated by any mechanical contact.

In order to investigate the development of the surface features formed at the absorber surface of the ATO samples, a series of anneals with different durations, 13 min, 30 min, 2h and 10h was performed at 534 °C. The SEM images of the corresponding surfaces of the CZTS absorbers are shown in Figure 8. After 13 min (Figure 8 (a)), the absorber surface was again found to be covered by Sn-S rich features. After 30 min (Figure 8 (b)), the sticks had turned into flakes, and also a low density of trench shaped pinholes were observed (marked by red rings in Figure 8). After 2 hours of anneal (Figure 8 (c)), the absorber surface had a high number of the trench shaped pinholes, while the size of the remaining Sn-S features had increased. After 10 hours (Figure 8 (d)), the absorber surface resembled the one annealed at 580 °C with a clear phase segregation (similar as in Figure 7 (b)). The experiment provides a possible time-resolved explanation for the observation after the anneal at 580 °C. Absorbers on ATO have a tendency to quickly form large amounts of Sn-S secondary phases at the surface. These phases start to evaporate as the P_s decays and leave pinholes in the absorber surface. One discrepancy between the samples annealed for 13 min at 580 °C compared to 10 hours at 534 °C, is that the pinholes are uniformly distributed at lower temperature, while they appear more localized and continuous at the higher temperature. A comparison of a larger area of the ATO annealed for 13 minutes (ATO_13/534_2) and the corresponding Mo reference (Mo_13/534_2) is shown in

Figure S3 (a) and Figure S3 (b), respectively. Formation of SnS surface features has previously been observed also when Mo has been used as back contact, see e.g. Ren et al.^[31] the difference here is that they form in much larger amounts on ATO.

At lower temperature, poor adhesion was a recurring problem for ATO samples. In previous studies on CZTSSe with TCO back contacts, a solution has been to introduce an interlayer of Mo between the TCO and CZTSSe absorber to improve adhesion and overall device performance.^[30,32] Therefore, two series of samples with varied Mo interlayer thickness, sputtered with different power in order to investigate whether sputtering power could affect the orientation of the MoS₂ (as suggested by Gao et al.^[33]), were annealed for 13 min at 534 °C. The orientation of the MoS₂ was not affected by the varied sputtering power. The adhesion was significantly improved, however, but the Mo interlayers did not affect or reduce the formation of Sn-S features at the absorber surface as they again appeared on ATO samples. A comparison of the ATO reference (ATO_13/534_3) and the corresponding Mo reference (Mo_13/534_3) is shown in Figure S1 (c) and Figure S1 (d), respectively.

3.4. Na addition

It has been repeatedly shown that Na plays a crucial role for the performance of CZTS solar cells.^[34,35] In the present study, the samples were deposited on SLG substrates, which usually act as a source of Na supplied through the back contact to the absorber. Previous studies suggest that the nature of the back contact may affect the diffusion of Na.^[36-38] Therefore, Na profiles of the different samples were measured by GDOES. When annealed at 580 °C, the Na content in the absorber was comparable to the Na content in the corresponding sample on Mo. The measured Na content is shown in **Figure 9** for samples annealed at 534 °C. It shows that the Na content in the absorber is significantly lower in the ATO sample compared to Mo sample after anneal at 534 °C. Therefore, two different routes were investigated to increase the Na content in the absorbers, either deposition of NaF on top of the CZTS precursor prior to the

anneal, or supply of Na from an SLG piece placed on top of the sample during the anneal (see Yang et al.^[39]). As seen in Figure 9, the Na content in the stack could be increased both by NaF and the additional SLG. However, while the NaF gave significantly higher Na content in the absorber, the Na from the SLG apparently ended up mainly in the ATO back contact. The NaF improved the adhesion between the ATO and the CZTS absorber significantly, which was not the case for the SLG method, where around 50 % of the sample had peeled off after CBD of the CdS buffer layer. In both cases, Sn-S secondary compounds were present at the surface.

3.5. Varied CZTS composition

A second time-resolved series of anneals was performed to investigate how the composition of the precursor affected the formation of the Sn-S surface compounds. The best performing CZTS devices typically have a Zn-rich and Cu-poor composition.^[40,41] As the Sn-content (here measured in terms of Cu/Sn-ratio, with fixed Zn/(Cu+Sn)-ratio) may directly affect the access of Sn to form Sn-S compounds, two series of precursors were prepared with Cu/Sn-ratios of 1.85 and 1.96. The samples from the respective series were deposited with NaF and annealed in the same box at 580 °C for 2 min, 13 min and 30 min respectively. The precursor composition was found to influence the amount of Sn-S compounds on ATO samples. Top view SEM images are shown in **Figure 10**, illustrating the larger area coverage of Sn-S with a higher Sn content. The coverage was the largest after two minutes, and did then reduce as the anneal time increased, as in the previous time series. For samples on Mo, an opposite trend was found; Sn-S compounds were not initially seen on the surface, but arose on some occasions after 30 minutes (not shown here). The observations clearly indicate that the precursor (absorber) composition plays a crucial role for the formation and number of Sn-S compounds, in addition to the back contact material.

Samples annealed with NaF all exhibited an excellent adhesion. GDOES was measured on all samples in the series and profiles of selected elements are shown in **Figure 11**. As seen in Figure 5, the sample annealed for 13 minutes at 580 °C showed some S incorporation into the top part of the ATO film. In the profiles in **Figure 12**, it is obvious that the sample morphology and/or chemistry changes when the anneal time is extended further, as the profiles for the samples annealed for 30 minutes differ as compared to those from the shorter anneals. One possible explanation is that the ATO has further reacted to form AT(O,S) with a particularly large interface region, making both the absorber and ATO appear much thicker than the other samples. Furthermore, it can be seen that both the O- and Sb content decreases in the ATO as the anneal time is increased, the latter species is also seen to diffuse towards the surface of the absorber. This migration seems to happen in a sequence where almost no Sb is detected in the absorber after 2 min, contains most Sb after 13 min, and subsequently reduces again after 30 min, while the amount of Sb in the ATO continuously decreased. The increased S content is expected to degrade the electrical properties of the ATO, consistent with the results shown and discussed above. On the other hand, it has previously been shown that Sb has positive effect on CZTS solar cell performance.^[42-44] Also the profiles of Cu and to some extent Zn changed in the absorber for the samples annealed on ATO (not shown here), while the depth profiles of the absorbers annealed on Mo typically did not exhibit any significant change during the anneal.

3.6. Device analysis

The device performance of selected samples is shown in **Table 2**. The full table can be found in Table S2. Electrical parameters of the devices were extracted by fitting the one-diode model to both dark and light *JV* measurement using the procedure described by Hegedus and Shafarman.^[45] Of the samples with ATO back contact, only samples with NaF or SLG on top of the precursor during anneal reached efficiencies over 2%. This behaviour could follow both from the improved adhesion (for NaF) and the increased level of Na throughout the

samples (as seen in Figure 9). Figure 12 (a), shows the *JV*-curves of ATO samples annealed with (ATO_13/534_NaF) and without (ATO_13/534_2) NaF, illustrating the overall improvement when using NaF. The sample annealed with the additional SLG (ATO_13/534_SLG) turned out to give the cell with the best solar cell performance of the ATO samples in this study, its *JV*-curve shown in Figure 12 (b) together with the corresponding Mo reference (Mo_13/534_2). The V_{oc} of ATO_13/534_SLG is among the best in the whole study and is even fairly good for CZTS in general. This observation, however, may not only be a result from the additional Na. It has been shown previously for Mo samples, that this configuration can also affect the surface dynamics and e.g. reduce the loss of S from the precursor in a S poor environment.^[3] Also the J_{sc} is close to Mo reference, but the fill factor (*FF*) is worse. Although the additional SLG gave the best individual cell, NaF was chosen for post-addition of Na in the following experiments because of the improved adhesion. Mo interlayers did also improve the adhesion, but the devices were very poor, following from very low J_{sc} .

In the three anneal series where different anneal times were compared, the best solar cells on ATO were those with an intermediate (13 min) anneal time. This observation could possibly be explained by the initial high amount of Sn-S compounds on the surface which is expected to cause losses for several reasons. With Sn-S sticks and flakes on the absorber surface, it is hard to keep the integrity of the top layers of the solar cell device, and it may also lead to shadowing of incident light and dead areas. For longer anneal times on the other hand, these surface features evaporate and leave pinholes behind, potentially shunting the devices, in addition to the decomposition of the ATO as it was found that it reacts with S at higher temperatures as shown in e.g. Figure 5.

When two series with a comparable Zn/(Cu+Sn)-ratio, but different Cu/Sn-ratio were annealed, the one with the higher Cu/Sn-ratio had lower coverage of Sn-S phases and had higher

efficiency. Figure 12 (c) shows the JV -curves of two ATO samples with high (ATO_13/580H_NaF) and low (ATO_13/580H_NaF) Cu/Sn-ratio, respectively, annealed in the same anneal. It can be seen that the J_{sc} is higher for the sample with the higher Cu/Sn ratio, consistent with the lower coverage of Sn-S secondary phases. The V_{oc} is still only slightly higher and the FF , despite the lower series resistance, is even smaller for this sample. The corresponding QE-curves are presented in **Figure S4**.

The best ATO samples still had a high amount of the secondary Sn-S phases, which is believed to contribute to the overall low performance. Figure S1, with large area SEM images of CZTS absorbers on ATO (Figure S1 (a) and Figure S1 (c)) and Mo (Figure S1 (b) and Figure S1 (d)) shows the typical difference in amount of Sn-S secondary phases between the two different back contacts. Of the 30 samples summarized in Table S2, the 7 best performing cells had Mo back contacts. All ATO samples exhibited a rather low fill factor (FF), dominated by the high series resistance (and to a more various extent with contribution from low shunt resistance (R_{shunt})). This fact could partly be explained by high R_{sheet} of the ATO, e.g. it was observed that JV -characteristics of the cells on ATO were affected by the distance between probe contact and the cell. Also the J_{sc} was typically lower for the ATO samples compared to Mo samples. To achieve high performance CZTS solar cells on ATO, the ATO itself will need further optimization, and R_{sheet} must be reduced to minimize the R_{series} and increase FF . As thick films also increase stress, optimization of the temperature during deposition of ATO would required to simultaneously optimize the stress in the films. The best J_{sc} of the ATO samples were achieved for samples with less pronounced “Cu-por/Zn-rich” composition (ATO_13/580H_NaF), and it is not unlikely that a precursor composition with the “opposite” stoichiometric relationship would produce the best CZTS devices on ATO back contacts. As only one thickness of NaF was used in this study, it is also likely that the NaF thickness could be optimized.

For the devices with Mo back contacts in this study, long anneal times (at 580 °C) typically results in deteriorated devices due to loss of S and Sn according to literature.^[25,26] In this study, however, it was repeatedly found that long anneal times resulted in not only working devices, but also better devices compared to those processed with shorter anneal times. One hypothesis is that the formation of the Sn-S surface compounds and continuous degradation of the ATO results in a sufficient high P_s and P_{Sn} to stabilize the CZTS surface of the Mo samples. The exact mechanisms behind the formation of Sn-S secondary compounds is beyond the scope of this article, but is suggested to be addressed in future studies.

4. Conclusions

ATO films were deposited by reactive RF sputtering from a compound target, and optimized electronic and optical properties could be achieved by tuning the O₂ flow during deposition to reach a low resistivity for an ATO thin film. ATO films directly exposed to anneal in S atmosphere reacted with S and formed SnS₂ and Sn₂S₃. ATO films covered by CZTS precursors, on the other hand, were found to be stable up to 550 °C for the same anneal time, and the electrical properties were even found to improve. At the typical anneal temperature of 580 °C however, small amounts of S was detected in the ATO after 13 min, and further breakdown was seen after 30 min. The absorber growth differed significantly for samples on ATO compared to samples on Mo, with a strong preference to form Sn-S surface compounds on the absorber in the case of ATO. These compounds evaporate as the anneal time increased, leaving pinholes behind, making it challenging to produce higher efficiencies. With reduced anneal temperature, Na diffusion from the SLG substrate decreased as well. This can be addressed by external addition of Na, either by placing an SLG piece on top of the CZTS absorber during anneal, or deposition of NaF on the absorber prior to anneal. The latter strategy also improved the adhesion between the ATO and the CZTS. Despite all challenges, the best

CZTS device with ATO back contact had a competitive V_{oc} and J_{sc} comparable to its Mo reference.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Dr. Valentina Paneta is acknowledged for the initial work and discussion about RBS/PIXE analysis. Sigbjørn Grini is further acknowledged for valuable discussion about depth profiling and provision of literature. Dr. Jes K. Larsen is acknowledged for discussion, help with equipment and general support. Dr. Lars Riekehr is acknowledged for the STEM images and the related work. The Swedish Foundation for Strategic Research (FFL13-0178 and RMA15-0030) is acknowledged for the financial support of this work. Support by VR-RFI (contracts#821-2012-5144 & #2017-00646 9) and the Swedish Foundation for Strategic Research (SSF, contract RIF13-0053) supporting accelerator operation is gratefully acknowledged.

Conflict of interest

The authors declare no conflict of interest.

References

- [1] International Energy Agency Photovoltaic Power Systems Programme (IEA PVPS), *Press Release: International Energy Agency Photovoltaic Power System Programme (IEA PVPS) publishes its new "Snapshot of Global Photovoltaic Markets 2018"*, Paris **2019**
- [2] K. Ito, *Copper Zinc Tin Sulfide-Based Thin-Film Solar Cells*, John Wiley & Sons, Chichester, West Sussex, United Kingdom, **2015**, <https://doi.org/10.1002/9781118437865>
- [3] J. J. Scragg, T. Kubart, J. T. Wätjen, T. Ericson, M. K. Linnarsson, C. Platzer-Björkman, *Chem. Mater.* **2013**, 25, 3162, <https://doi.org/10.1021/cm4015223>
- [4] J. T. Wätjen, J. J. Scragg, T. Ericson, M. Edoff, C. Platzer-Björkman, *Thin Solid Films* **2013**, 535, 31, <https://doi.org/10.1016/j.tsf.2012.11.079>
- [5] A. Polman, M. Knight, E. C. Garnett, B. Ehrler, W. C. Sinke, *Science* **2016**, 352, aad4424, <https://doi.org/10.1126/science.aad4424>

- [6] V. Karade, A. Lokhande, P. Babar, M. G. Gang, M. Suryawanshi, P. Patil, J. H. Kim, *Sol. Ener. Mater. Sol. Cells* **2019**, 200, 109911, <https://doi.org/10.1016/j.solmat.2019.04.033>
- [7] S. Englund, N. Saini, C. Platzer-Björkman, *Sol. Energy* **2018**, 175, 84 <https://doi.org/10.1016/j.solener.2018.04.024>
- [8] S. S. Mali, B. M. Patil, C. A. Betty, P. N. Bhosale, Y. W. Oh, S. R. Jadkar, R. S. Devan, Y.-R. Ma, P. S. Patil, *Electrochim. Acta* **2012**, 66, 216, <https://doi.org/10.1016/j.electacta.2012.01.079>
- [9] S. Mahajan, E. Stathatos, N. Huse, R. Birajdar, A. Kalarakis, R. Sharma, *Mater. Lett.* **2018**, 210, 92, <https://doi.org/10.1016/j.matlet.2017.09.001>
- [10] J. Ge, J. Chu, Y. Yan, J. Jiang, P. Yang, *ACS Appl. Mater. Interfaces* **2015**, 7, 10414, <https://doi.org/10.1021/acsami.5b01641>
- [11] J. Ge, Y. Yu, W. Ke, J. Li, X. Tan, Z. Wang, J. Chu, Y. Yan, *ChemSusChem*. **2016**, 9, 2149, <https://doi.org/10.1002/cssc.201600440>
- [12] H. H. David Ginley, David C. Paine, *Handbook Transp. Conductors*, Springer, Boston, MA, **2010**, <https://doi.org/10.1007/978-1-4419-1638-9>
- [13] J. Spannhake, A. Helwig, G. Müller, G. Faglia, G. Sberveglieri, T. Doll, T. Wassner, M. Eickhoff, *Sens. Actuators, B: Chemical* **2007**, 124, 421, <https://doi.org/10.1016/j.snb.2007.01.004>
- [14] S. R. J. N. Srinivasa Murty, *Thin Solid Films* **1983**, 108, 277, [https://doi.org/10.1016/0040-6090\(83\)90075-5](https://doi.org/10.1016/0040-6090(83)90075-5)
- [15] J. Lee, N.-H. Kim, Y. S. Park, *J. Nanosci. Nanotechnol.* **2016**, 16, 4973, <https://doi.org/10.1166/jnn.2016.12173>
- [16] B. S. S. Jäger, J. Szcyrkowski, G. Bräuer, *Surf. Coat. Technol.* **1998**, 98, 1304, [https://doi.org/10.1016/S0257-8972\(97\)00145-X](https://doi.org/10.1016/S0257-8972(97)00145-X)
- [17] T. Ericson, Licentiate Thesis, Uppsala University, 2013
- [18] J. A. Thornton D. W. Hoffman, *Thin Solid Films* **1989**, 171, 5, [10.1016/0040-6090\(89\)90030-8](https://doi.org/10.1016/0040-6090(89)90030-8)
- [19] R. M. Langford M. Rogers, *Micron* **2008**, 38, 1325, <https://doi.org/10.1016/j.micron.2008.02.006>
- [20] S. M. M. Mayer, M. Rubel, A. Widdowson, S. Charisopoulos, T. Ahlgren, N. Alamanos, E. Alves, G. Apostolopoulos, N.P. Barradas, S. Donnelly, S. Fazinić, K. Heinola, O. Kakuee, H. Khodja, A. Kimura, A. Lagoyannis, M. Li, S. Markelj, M. Mudrinic, P. Petersson, I. Portnykh, D. Primetzhofer, P. Reichart, D. Ridikas, T. Silva, S. M. Gonzales de Vicente, W. Yongqiang, *Nucl. Fusion* **2019**, Submitted paper
- [21] M. V. Moro, , R. Holeňák, L. Zendejas Medina, U. Jansson, D. Primetzhofer, *Thin Solid Films* **2019**, 686, 137416, <https://doi.org/10.1016/j.tsf.2019.137416>
- [22] M. Mayer, W. Eckstein, H. Langhuth, F. Schiettekatte, U. von Toussaint, *Nucl. Instrum. Methods Phys. Res., Sect. B* **2011**, 269, 3006, <https://doi.org/10.1016/j.nimb.2011.04.066>
- [23] T. R. Giraldo, M. T. Escote, A. P. Maciel, E. Longo, E. R. Leite, J. A. Varela, *Thin Solid Films* **2006**, 515, 2678, <https://doi.org/10.1016/j.tsf.2006.06.025>
- [24] Y. Ren, N. Ross, J. K. Larsen, K. Rudisch, J. J. S. Scragg, C. Platzer-Björkman, *Chem. Mater.* **2017**, 29, 3713, <https://doi.org/10.1021/acs.chemmater.7b00671>
- [25] S. G. Nils Ross, Katharina Rudisch, Lasse Vines, Charlotte Platzer-Björkman, *IEEE J. Photovoltaic* **2018**, 8, 1132, <https://doi.org/10.1109/JPHOTOV.2018.2831452>
- [26] J. J. Scragg, T. Ericson, T. Kubart, M. Edoff, C. Platzer-Björkman, *Chem. Mater.* **2011**, 23, 4625, <https://doi.org/10.1021/cm202379s>

- [27] E. T. B. Gržeta, C. Goebbert, M. Takeda, M. Takahashi, K. Nomura, M. Jakšić, *J. Phys. Chem. Sol.* **2002**, 63, 765, [https://doi.org/10.1016/S0022-3697\(01\)00226-8](https://doi.org/10.1016/S0022-3697(01)00226-8)
- [28] H. F. M. Marlene C. Morris, Eloise H. Evans, Boris Paretskin, Johan H. de Groot, Camden R. Hubbard, Simon J. Carmel, *Standard X-ray Diffraction Powder Patterns Section 13 - Data for 58 Substances*, Institute for Materials Research, National Bureau of Standards, Washington D.C., **1976**
- [29] R. Kniep, D. Mootz, U. Severin, and H. Wunderlich, *Acta Crystallogr., Sect. B: Crystallogr. Cryst. Chem.* **1982**, 38, 2022, <https://doi.org/10.1107/S0567740882007808>
- [30] J.-S. Kim, D.-H. Kim, D.-K. Hwang, *J. Power Sources* **2018**, 400, 9, <https://doi.org/10.1016/j.jpowsour.2018.08.001>
- [31] Y. Ren, M. Richter, J. Keller, A. Redinger, T. Unold, O. Donzel-Gargand, J. J. S. Scragg, C. Platzer-Björkman, *ACS Ener. Lett.* **2017**, 5, 976, <https://doi.org/10.1021/acsenergylett.7b00151>
- [32] M. Espindola-Rodriguez, D. Sylla, Y. Sánchez, F. Oliva, S. Grini, M. Neuschitzer, L. Vines, V. Izquierdo-Roca, E. Saucedo, M. Placidi, *ACS Sustainable Chem. Eng.* **2017**, 5, 11516, <https://doi.org/10.1021/acssuschemeng.7b02797>
- [33] S. Gao, Y. Zhang, J. Ao, S. Lin, Z. Zhang, X. Li, D. Wang, Z. Zhou, G. Sun, F. Liu, Y. Sun, *Sol. Energy Mater. Sol. Cells* **2018**, 176, 302, <https://doi.org/10.1016/j.solmat.2017.10.011>
- [34] H. Ehira, K. Jimbo, H. Katagiri, *AIP Conf. Proc.* **2017**, 1865, 050004, <https://doi.org/10.1063/1.4993369>
- [35] X. Liu, Y. Feng, H. Cui, F. Liu, X. Hao, G. Conibeer, D. B. Mitzi, M. Green, *Progr. Photovoltaics* **2016**, 24, 879, <https://doi.org/10.1002/pip.2741>
- [36] S. Englund, S. Grini, O. Donzel-Gargand, V. Paneta, V. Kosyak, D. Primetzhofer, J. J. S. Scragg, C. Platzer-Björkman, *Phys. Status Solidi A* **2018**, 215, 1800491, <https://doi.org/10.1002/pssa.201800491>
- [37] S. Englund, V. Paneta, D. Primetzhofer, Y. Ren, O. Donzel-Gargand, J. K. Larsen, J. Scragg, C. Platzer Björkman, *Thin Solid Films* **2017**, 639, 91, <https://doi.org/10.1016/j.tsf.2017.08.030>
- [38] F. Liu, J. Huang, K. Sun, C. Yan, Y. Shen, J. Park, A. Pu, F. Zhou, X. Liu, J. A. Stride, M. A. Green, X. Hao, *NPG Asia Mater.* **2017**, 9, e401, <https://doi.org/10.1038/am.2017.103>
- [39] Y. Yang, X. Kang, L. Huang, S. Wei, D. Pan, *J. Phys. Chem. C* **2015**, 119, 22797, <https://doi.org/10.1021/acs.jpcc.5b06381>
- [40] M. Paris, L. Choubrac, A. Lafond, C. Guillot-Deudon, S. Jobic, *Inorg. Chem.* **2014**, 53, 8646, <https://doi.org/10.1021/ic5012346>
- [41] W. Wang, M. Winkler, O. Gunawan, T. Gokmen, T. Todorov, Y. Zhu, D. Mitzi, *Adv. Ener. Mater.* **2014**, 4, 1301465, <https://doi.org/10.1002/aenm.201301465>
- [42] M. A. A. Suzon, L. Grenet, F. Emieux, E. De Vito, F. Roux, H. Mariette, *Phys. Status Solidi A* **2019**, 216, 1900070, <https://doi.org/10.1002/pssa.201900070>
- [43] X. Zhang, M. Han, Z. Zeng, Y. Duan, *J. Mater. Chem. A* **2017**, 5, 6606, <https://doi.org/10.1039/c7ta01090g>
- [44] D. S. Dhawale, A. Ali, A. C. Lokhande, *Sustainable Energy Fuels* **2019**, 3, 1365, <https://doi.org/10.1039/c9se00040b>
- [45] S. S. Hegedus. Shafarman William N., *Progr. Photovoltaics* **2004**, 12, 155, <https://doi.org/10.1002/pip.518>

Figure 1. R_{sheet} and ρ values from the optimization of the O_2 flow during ATO sputtering. Samples used for optimization had $t \approx 300$ nm, the best ρ was measured for sample with $t \approx 850$ nm. $T = 500$ °C for both post-anneal and the heated

Figure 2. RBS spectrum of as-deposited and vacuum annealed ATO film (ATO reference) with the simultaneously acquired PIXE spectrum in the inset.

Figure 3. Normalized XRD patterns of annealed ATO films and corresponding major peaks of $Sn_{0.938}Sb_{0.062}O_{1.99}$, SnS_2 and Sn_2S_3 .^[27-29]

Figure 4. Normalized XRD patterns of ATO films measured after anneal and lift-off of CZTS, and corresponding major peaks of $\text{Sn}_{0.938}\text{Sb}_{0.062}\text{O}_{1.99}$.^[27]

Figure 5. STEM image of the CZTS and ATO with overlay from STEM-EDS showing S content in ATO_580 below 5 at.%.

Figure 6. Comparison of absorption spectra of ATO films annealed below CZTS.

Figure 7. (a) and (b) Cracks in absorber surface of ATO samples annealed at 580 °C at two different magnifications, also with inset STEM-EDS maps showing ZnS secondary phase at the surface, (c) corresponding Mo reference annealed in 580 °C. (d) Absorber surface of ATO samples annealed at 534 °C with flakes uniformly distributed, inset: EDS maps of surface features showing Sn-S secondary phase. (e) and (f) comparison of absorber surfaces of ATO and Mo samples respectively annealed at 534 °C. Please note the different magnifications of (a) and (d).

Figure 8. Top view SEM images on the CZTS absorber surfaces annealed at different durations (a)-(d). White arrows point on Sn-S sticks and flakes. The red rings indicate spots where pinholes have formed.

Figure 9. GDOES profiles of Na for different ATO samples, compared to an Mo sample. All samples had the same nominal precursor composition and annealed at 534°C for 13 min.

Figure 10. SEM images of CZTS absorbers. On top, samples on ATO with the two different compositions, on bottom, the corresponding samples deposited on Mo. All annealed for 2 min.

Figure 11. GDOES profiles. (a)-(d) showing ATO samples, profiles of Sn, Sb, O and S annealed for 2 min, 13 min and 30 min respectively. (e)-(h) showing Mo samples, profiles of Sn, O and S annealed for 2, 13 and 30 min respectively.

Figure 12. *JV*-curves, (a) ATO samples with same composition annealed with and without NaF. (b) The best ATO sample (annealed with SLG on top) and Mo reference. (c) ATO with high and low Cu/Sn ratio, both annealed with NaF. Continuous and dashed lines represents dark- and light measurements, respectively.

Table 1. R_{sheet} of the ATO. The Mo reference had $R_{sheet} \approx 0.5 \Omega \square^{-1}$.

Sample	Anneal T [°C]	R_{sheet} as-deposited + post. anneal 500 °C [$\Omega \square^{-1}$]	R_{sheet} sulf. ATO [$\Omega \square^{-1}$]	R_{sheet} ATO below sulf. CZTS [$\Omega \square^{-1}$]
ATO_580	580	~80	70 000	130
ATO_547	547	~80	9 000	60
ATO_534	534	~80	240	50

Table 2, composition and device performance of selected devices.

Sample	[Cu]/[Sn], [Zn]/([Cu]+[Sn])	Cell area [cm^2] ^a	Anneal T [°C]	Anneal time [min]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	η [%]
ATO_13/534_2	1.97, 0.37	0.5	534	13	0.34	4.7	26.3	0.4
ATO_13/534_SLG	1.97, 0.37	0.5	534	13	0.64	11.6	34.2	2.6
ATO_13/534_NaF	1.97, 0.37	0.5	534	13	0.51	10.3	39.5	2.1
Mo_13/534_2	1.97, 0.37	0.5	534	13	0.64	12.9	44.4	3.6
Mo_600/534	1.97, 0.37	0.5	534	600	0.54	16.5	47.1	4.2
ATO_13/580H_NaF	1.96, 0.34	0.05	580	13	0.57	13.0	34.1	2.5
Mo_13/580H	1.96, 0.34	0.05	580	13	0.65	13.7	42.5	3.7
Mo_30/580H	1.96, 0.34	0.05	580	30	0.61	20.2	45.0	5.5
ATO_13/580L_NaF	1.85, 0.35	0.05	580	13	0.56	10.2	36.4	2.1
Mo_13/580L	1.85, 0.35	0.05	580	13	0.25	13.0	37.2	1.2
Mo_30/580L	1.85, 0.35	0.05	580	30	0.60	15.2	48.1	4.4

^aTotal cell area. Only cells of area 0.5 cm² had grids, covering ~2.5% of the cell area.

Antimony-doped tin oxide ($\text{Sn}_2\text{O}_3\text{:Sb}$, ATO) is investigated as a transparent back contact for $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin film solar cells. The best CZTS device on ATO back contact in this study has an efficiency of 2.6%. As compared to a reference on a Mo back contact, a similar open circuit voltage and short circuit current density are achieved, but lower fill factor is measured.

CZTS Thin Film Solar Cells

S. Englund*, T. Kubart, J. Keller, M. V. Moro, D. Primetzhofer, S. Saveda Suvanam, J. J. S. Scragg, C. Platzer-Björkman*

Antimony-Doped Tin Oxide as Transparent Back Contact in CZTS Thin Film Solar Cells

Supporting information

Antimony-Doped Tin Oxide as Transparent Back Contact in CZTS Thin Film Solar Cells

Sven Englund*, Tomas Kubart, Jan Keller, Marcos V. Moro, Daniel Primetzhofer, Sethu Saveda Suvanam, Jonathan J. S. Scragg, Charlotte Platzer-Björkman*

Table S1. Optimization of ATO.

Sample	Cu backing plate	O ₂ -flow [sccm]	Heating [500 °C]	R_{sheet} [k Ω $\square^{-1}$]	Thickness [nm]	ρ [m Ω ·cm]	Stress [MPa]
ATO1	No	0	Post	Very high	-	-	-
ATO2	No	0.1	Post	824	-	-	-
ATO3	No	0.2	Post	3.2	-	-	-
ATO4	No	0.4	Post	0.2	-	-	-
ATO4	No	0.6	Post	0.4	325	13	-
ATO5	No	0.8	Post	1.8	-	-	-
ATO6	No	2	Post	4.5	-	-	-
ATO7	Yes	0.4	Post	0.2	315	6.3	-340/250***
ATO8	Yes	0.6	Post	0.2	289	5.8	-70/250
ATO9	Yes	0.4	During dep.	0.5	315*	15.8	2600
ATO10	Yes	0.6	During dep.	0.4	289**	11.6	2500

Table S2. Experiments and devices. Before anneals ATO had $R_{sheet} \approx 80 \Omega \square^{-1}$, Mo $\approx 0.5 \Omega \square^{-1}$.

Experiment	Sample	[Cu]/[Sn], [Zn]/([Cu]+[Sn])	Anneal T [°C]	Anneal time [min]	Grid	Cell size [cm ²] ^a	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	η [%]
ATO anneals	ATO_580	-	580	13	-	-	-	-	-	-
	ATO_547	-	547	13	-	-	-	-	-	-
	ATO_534	-	534	13	-	-	-	-	-	-
Temp. series	ATO_13/580	1.94, 0.34	580	13	Yes	0.5	0.22	2.1	24.6	0.1
	ATO_13/547	1.94, 0.34	547	13	Yes	0.5	0.50	5.5	26.3	0.7
	ATO_13/534	1.94, 0.34	534	13	Yes	0.5	0.47	10.6	32.5	1.6
	Mo_13/580	1.94, 0.34	580	13	Yes	0.5	0.61	15.2	46.8	4.3
	Mo_13/534	1.94, 0.34	534	13	Yes	0.5	-	-	-	-
Time series 534	ATO_13/534_2	1.97, 0.37	534	13	Yes	0.5	0.34	4.7	26.3	0.4
	ATO_30/534	1.97, 0.37	534	30	Yes	0.5	0.47	9.0	35.9	1.5
	ATO_120/534	1.97, 0.37	534	120	Yes	0.5	0.51	7.7	27.5	1.1
	ATO_600/534	1.97, 0.37	534	600	Yes	0.5	0.48	7.4	30.7	1.1
	Mo_13/534_2	1.97, 0.37	534	13	Yes	0.5	0.64	12.9	44.4	3.6
	Mo_600/534	1.97, 0.37	534	600	Yes	0.5	0.54	16.5	47.1	4.2
	ATO_13/534_3	1.91, 0.37	534	13	Yes	0.5	0.46	3.3	30.5	0.5
	ATO+100W/10nm_Mo	1.91, 0.37	534	13	Yes	0.5	0.46	0.6	27.8	0.1
Mo interlayers	ATO+100W/20nm_Mo	1.91, 0.37	534	13	Yes	0.5	0.45	0.5	28.5	0.1
	ATO+100W/40nm_Mo	1.91, 0.37	534	13	Yes	0.5	0.48	0.6	28.3	0.1
	ATO+500W/10nm_Mo	1.91, 0.37	534	13	Yes	0.5	0.42	4.1	34.6	0.6
	ATO+500W/20nm_Mo	1.91, 0.37	534	13	Yes	0.5	0.42	1.9	30.3	0.2
	ATO+500W/40nm_Mo	1.91, 0.37	534	13	Yes	0.5	0.28	2.5	32.0	0.2
Na addition	Mo_13/534_3	1.91, 0.37	534	13	Yes	0.5	0.23	11.3	29.5	1.0
	ATO_13/534_SLG	1.97, 0.37	534	13	Yes	0.5	0.64	11.6	34.2	2.6
	ATO_13/534_NaF	1.97, 0.37	534	13	Yes	0.5	0.51	10.3	39.5	2.1
High Cu/Sn	Mo_2/580H	1.96, 0.34	580	2	No	0.05	-	-	-	-
	Mo_13/580H	1.96, 0.34	580	13	No	0.05	0.65	13.7	42.5	3.7
	Mo_30/580H	1.96, 0.34	580	30	No	0.05	0.61	20.2	45.0	5.5
	ATO_2/580H_NaF	1.96, 0.34	580	2	No	0.05	0.59	7.1	56.3	2.4
	ATO_13/580H_NaF	1.96, 0.34	580	13	No	0.05	0.57	13.0	34.1	2.5
Low Cu/Sn	ATO_30/580H_NaF	1.96, 0.34	580	30	No	0.05	0.28	6.3	27.2	0.5
	Mo_2/580L	1.85, 0.35	580	2	No	0.05	0.70	12.0	51.4	4.3
	Mo_13/580L	1.85, 0.35	580	13	No	0.05	0.25	13.0	37.2	1.2
	Mo_30/580L	1.85, 0.35	580	30	No	0.05	0.60	15.2	48.1	4.4
	ATO_2/580L_NaF	1.85, 0.35	580	2	No	0.05	0.52	6.3	50.2	1.7
	ATO_13/580L_NaF	1.85, 0.35	580	13	No	0.05	0.56	10.2	36.4	2.1
	ATO_30/580L_NaF	1.85, 0.35	580	30	No	0.05	0.39	8.7	25.7	0.9

^aTotal cell area. Only cells of area 0.5 cm² had grids, covering ~2.5% of the cell area.

Figure S1. SEM images of cross-sections of CZTS precursors annealed on ATO (a) and Mo (b) annealed for 13 minutes at 580 °C, and ATO (c) and Mo (d) annealed for 13 minutes at 534 °C.

Figure S2. SEM images of cross-sections of CZTS precursors annealed on ATO, (a) was annealed with an SLG on top, and (b) was annealed with NaF, both were annealed for 13 minutes at 534 °C.

Figure S3. SEM images of CZTS precursors annealed on ATO (a) and (c) compared to CZTS precursors annealed on Mo (b) and (d). All samples were annealed for 13 min at 534 °C.

Figure S4. External Quantum Efficiency (*EQE*) curves.