

Closing the gap with silicon-wafer-based technologies: Alkali post-deposition treatment improves the efficiency of $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells

Oliver Kiowski, Theresa M. Friedlmeier, Roland Würz, Philip Jackson & Dimitrios Hariskos, Centre for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW), Stuttgart, Germany

ABSTRACT

With the introduction of the alkali post-deposition treatment (PDT) for the absorber layer in $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS)-based solar cells, new efficiency records approaching 22% have become feasible. After gallium incorporation, sodium doping and the three-stage process, this is the next milestone on the CIGS roadmap. In this paper the current understanding of how PDT alters the CIGS surface and affects device parameters is illustrated. A comparative study of cell device parameters from ZSW and the evolution of efficiencies from other institutes and companies with and without PDT is presented.

Introduction

Every once in a while there is a leap forward in technology with the introduction of a new technological development. For CIGS thin-film photovoltaics, the incorporation of Ga to increase the band gap [1], the discovery of Na doping [2], and the three-stage process [3], among others, should be mentioned. The efficiency 'learning curve' in Fig. 1 historically groups these and other advances in CIGS process technology.

The latest of such efficiency-boosting milestones is a further development of the NaF post-deposition treatment (PDT), which was originally designed to provide CIGS layers on Na-free substrates with Na after the growth of the CIGS has finished [4]. The PDT process was then extended to KF to dope alkali-free CIGS layers with potassium [5]. The application of this KF-PDT to already Na-doped CIGS layers has subsequently led to a significant boost in efficiency [6].

Further optimization of the CIGS devices including the alkali PDT has led to new record efficiencies in CIGS laboratories all around the world [7–9], the latest being 21.7% from the group at ZSW [10]. The certified solar cell characteristic (current vs. voltage, I - V), device parameters (efficiency, open-circuit voltage (V_{oc}), fill factor (FF), short-circuit current density (J_{sc})) and quantum efficiency (QE) of this cell with a total area of 0.5cm^2 are shown in Fig. 2(a) and (b). The same efficiency for three neighbouring cells [10] has been certified, and since then,

more than 100 cells exceeding 21% have been made, demonstrating the potential scalability and reproducibility of the PDT process. Fig. 2 also compares the data to the previous 20.3% ZSW record cell without PDT [11].

It should be noted, however, that several improvements, including the alkali PDT, led to the new record efficiency of 21.7%. (For a comparative study of cells differing only in ZSW's alkali PDT, see Fig. 4(a) and (b); for an evolution of record efficiencies from ZSW and others, see Fig. 5.) Only mini-module results have so far been published [12], but ZSW believes that there are no basic or technical

obstacles to PDT entering into production.

“Several improvements, including the alkali PDT, led to the new record efficiency of 21.7%.”

The next section gives a brief overview of the PDT process and how it affects the device parameters of CIGS solar cells. A direct comparison of an ensemble of CIGS cells prepared with and without the alkali PDT at ZSW is then presented, followed by a discussion of the influence of the alkali

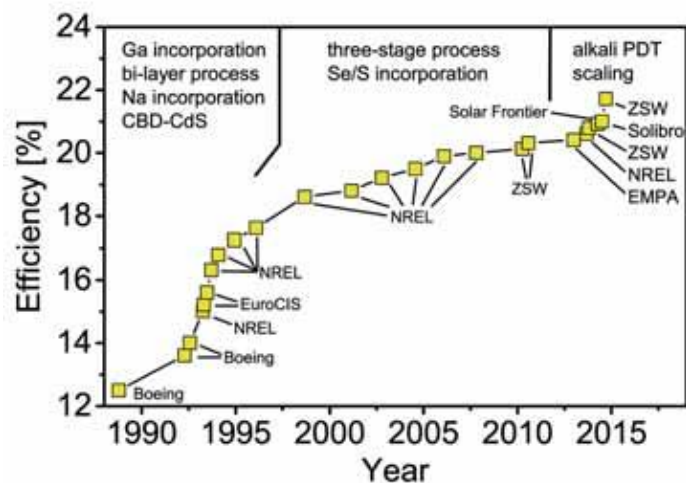


Figure 1. CIGS efficiency 'learning curve', attributing the advances in efficiency to developments in CIGS processing technology.

PDT on different CIGS deposition technologies. Finally, potential future improvements of the CIGS process are examined.

PDT process

The current understanding of the alkali PDT is still incomplete and is steadily evolving as more and more groups implement the process in their CIGS processing lines. In standard cells a molybdenum-coated glass substrate supports the CIGS absorber layer grown either by co-evaporation of the elements Cu, Ga, In and Se at elevated temperatures or by a

sequential process, where precursors are deposited at a low temperature in a first step and heated in the presence of Se in a second. Typical precursors are, for example, sputtered layers of Cu, In and Ga or nanoparticle inks.

Both deposition techniques form intrinsically p-type absorbers. If the substrate is soda-lime glass, the absorber already contains a certain amount of ‘intrinsic’ sodium and potassium which diffuse from the glass during the high-temperature growth phase [7,13]. Some groups employ flexible substrates, such as polyimide, steel foils or glass with a diffusion barrier, all of which need an ‘extrinsic’

sodium doping, for example via a NaF-PDT [4]. Both kinds of sodium doping lead to high efficiencies and have been known for many years.

The importance of other alkali elements like potassium came into focus when CIGS solar cells on K-rich enamelled steel substrates performed better than the reference samples on soda-lime glass substrates [13]. However, a PDT turned out to be a more effective and versatile technique for introducing alkali elements [5,6] than relying on out-diffusion from a given substrate. A PDT with additional alkali elements clearly improves the efficiency of CIGS solar cells,

Thin Film

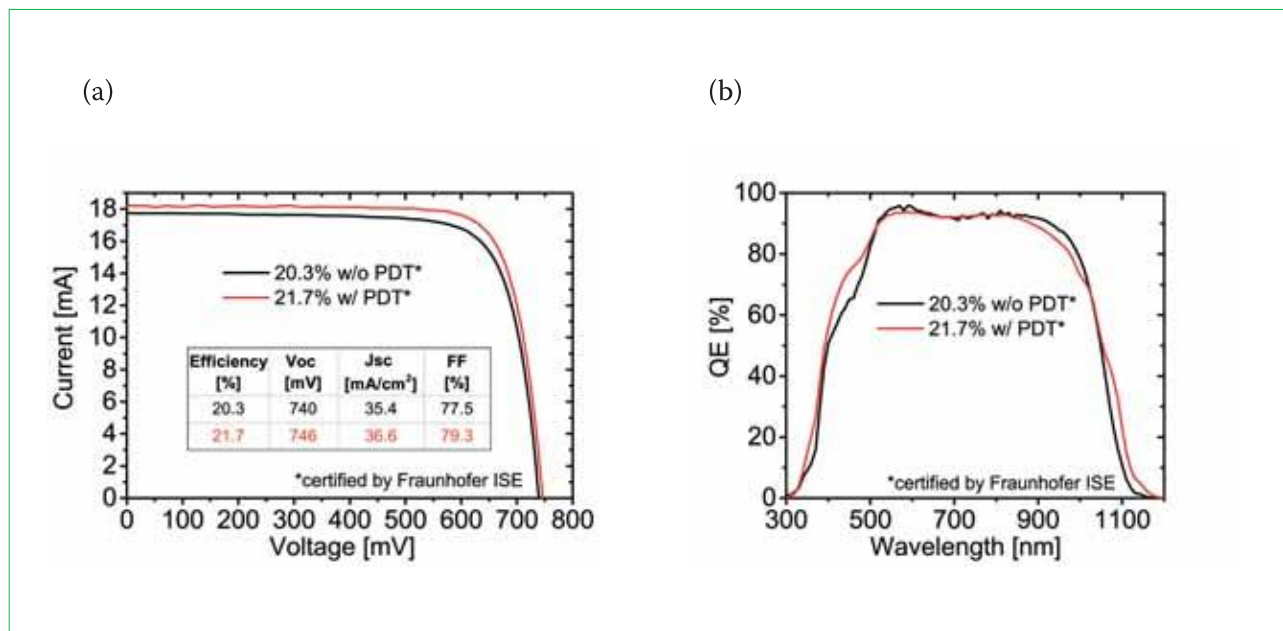


Figure 2. (a) Certified $I-V$ curve for the 21.7% ZSW CIGS record cell employing ZSW's alkali PDT (w/PDT) and other improvements (red). The inset table shows the device parameters [10]. (b) QE curve of the same cell (red). The data are compared with the 20.3% ZSW record cell without (w/o) PDT from 2011 (black) [11].

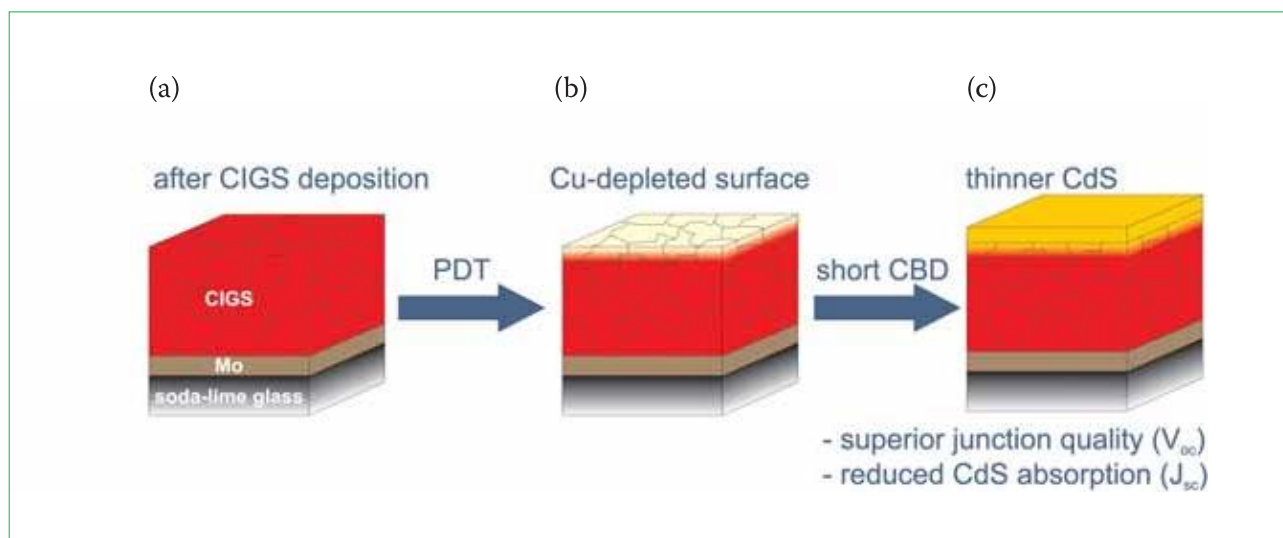


Figure 3. Effect of the alkali PDT on the CIGS/CdS heterojunction: (a) The CIGS layer has an initial alkali content through the diffusion of alkali elements from the glass substrate. (b) After the PDT process the alkali content has been modified and the surface is Cu depleted. (c) The improved diffusion of Cd or Zn during CBD buffer deposition enables better junction formation, improved coverage during initial growth, and higher efficiencies with thinner CdS layers.

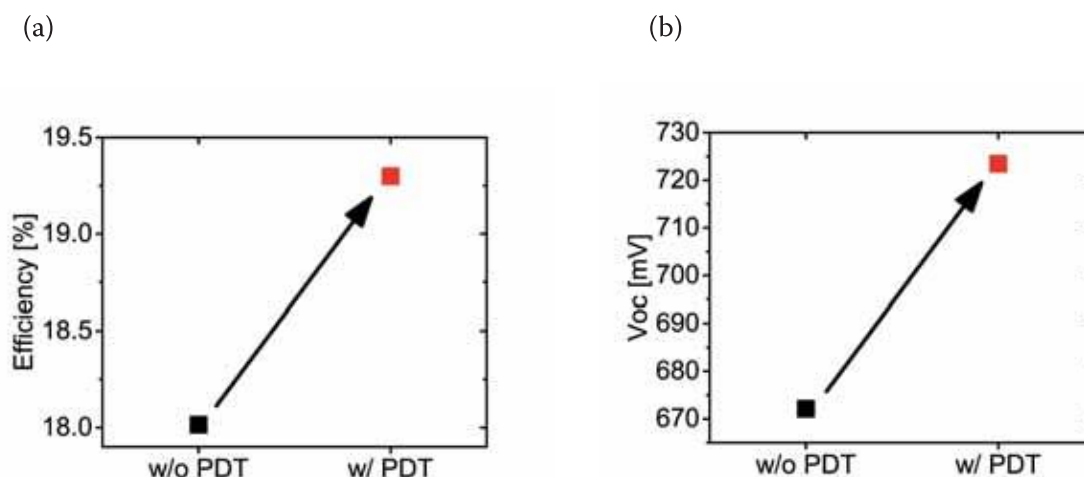


Figure 4. (a) Average efficiencies and (b) average V_{oc} values for an ensemble of about 50 cells. The ensemble was split into two groups after the CIGS process: approximately one-half received an alkali PDT (w/ PDT, red symbols), and the other half did not (w/o PDT, black symbols). Subsequent processes for buffer and window layers were essentially the same for all samples.

regardless of the choice of substrate.

The process in the case of CIGS grown on soda-lime glass is illustrated in Fig. 3. Alkali elements diffuse into the CIGS layer from the substrate during film growth. After CIGS deposition, the post-deposition adjusts the alkali content from the CIGS surface. PDT involves the evaporation of alkali-containing species in the presence of Se and heating to drive the diffusion processes. The alkali elements are found to displace Cu and thus induce a Cu-depleted surface with a depth of a few nanometres [6]. The residual compounds are water-soluble and are therefore washed off in the subsequent chemical bath deposition (CBD) process of a buffer layer, typically CdS. This step forms the heterojunction of the cell, and here the positive impact of a PDT unfolds: Cd ions can more easily diffuse into the Cu-depleted surface and form a junction of superior quality (better V_{oc}) compared with the CBD on CIGS without PDT. This is implied by the continuous transition as marked from red to yellow in Fig. 3(c). It has been suggested that the position of the p-n junction (the location where $n = p$, n and p being the electron and hole densities, respectively) is located within the absorber layer, thereby forming a buried junction with less interface recombination [14].

For CIGS-based solar cells with PDT, the coverage of the CdS layer appears to improve in the nucleation phase, as indicated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements [15]. It has been shown

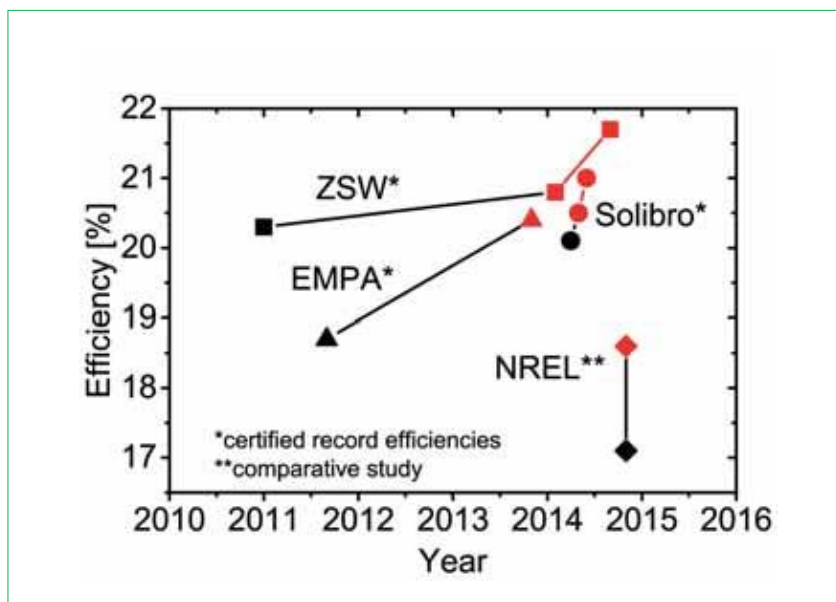


Figure 5. Evolutions of record cell efficiencies from ZSW (squares) [7,10,11], Solibro (circles) [8,9,16] and EMPA (triangles) [6,17]. Red symbols indicate the use of an alkali PDT. The data from NREL (diamonds) are from a comparative study about the effectiveness of an alkali PDT on sequential CIGS absorber layers [18].

experimentally that high V_{oc} s can be maintained with a thinner buffer layer (20–30nm) than with standard CBD-CdS layers (40–50nm) [6,10]. A thinner CdS layer improves J_{sc} , since parasitic absorption is reduced. The surface adjustment induced by PDT also increases V_{oc} for Cd-free buffer layers, such as CBD-Zn(O,S) [15].

Comparison of ZSW device parameters

Fig. 4 shows average device parameters (efficiency and V_{oc}) for an ensemble

of about 50 CIGS cells which were deposited by a multistage process under very similar conditions, except that approximately one-half received ZSW's alkali PDT, whereas the other half did not. The complete layer sequence was soda-lime glass/Mo/CIGS/CdS/i-ZnO/ZnO:Al/grid. The cell size was $\sim 0.5\text{cm}^2$, as defined by mechanical scribing. No anti-reflection coating was applied.

As expected, with PDT the efficiency and V_{oc} increased by $\sim 1.3\%$ abs. and $\sim 50\text{mV}$ respectively; the gain in V_{oc} can be clearly attributed to the alkali

PDT. No significant changes in FF as a result of PDT were observed and the corresponding plot is omitted. J_{sc} was also similar for all samples, since the thickness of the CdS layer was kept constant in this comparative study, as mentioned above.

Impact on other CIGS deposition technologies

The evolutions of certified record efficiencies from ZSW, EMPA and Solibro are shown in Fig. 5. Red and black symbols indicate respectively the implementation of alkali PDT or no implementation. ZSW [7,10,11] and Solibro [8,9,16] both use a high-temperature co-evaporation process on glass substrates, whereas EMPA employs a low-temperature co-evaporation process on flexible substrates [6,17].

The results from a comparative study by NREL for a sequential selenization process on glass substrates are also included in Fig. 5 [18]. Remarkably, an efficiency improvement due to PDT was observed even when the CIGS layer was stored in dry nitrogen for two months after deposition (not shown). It is evident that all mentioned CIGS

deposition technologies benefit from the alkali PDT.

No data of the effect of alkali PDT upon sulphur-containing, sequentially processed $Cu(In,Ga)(S,Se)_2$ (CIGS_{Se}) absorbers have so far been published. Many commercially available modules from, for example, Avancis, Solar Frontier and TSMC possess a gallium-poor and sulphur-rich surface by using a combination of selenization and sulphurization step. It is not clear how an alkali PDT affects this surface and whether or not it is beneficial.

Future potentials

At the laboratory level, the 21.7% CIGS cell efficiency already exceeds the record of 20.4% for polycrystalline Si wafer-based cells [19]. The high V_{oc} s of 740–750mV are even on a par with the currently best monocrystalline-Si-based cells from Panasonic (heterojunction with intrinsic thin layer – HIT) [20]. Thus, a similar low V_{oc} temperature coefficient is also expected, since the band gaps of Si and CIGS are comparable. Two potential directions to take to further close the efficiency gap with Si technology are pointed out in the following

sections. Since Si solar cells have had a ‘head start’ compared with the much younger CIGS technology, the authors are confident that it is only a matter of time before CIGS catches up.

The buffer layer

As regards the photocurrent of CIGS solar cells, the potential for improvement still exists. The reduced QE below 500nm for the 21.7% cell in Fig. 6 is due to absorption inside the thin CdS buffer layer. To minimize the loss, the goal of many research efforts has been to replace this layer by a Cd-free alternative with a higher band gap. Up until now, efficiencies for different kinds of alternative buffer layer (Zn(O,S), In_2S_3 , etc.) have not been able to keep up with record devices employing CdS from a CBD process.

When ZSW’s PDT-optimized CIGS was combined with a solution-grown Zn(O,S) buffer layer, a certified cell efficiency of 21% was achieved [15]. This result is the current world record for Cd-free buffer layers and reduces the gap towards CIGS with CBD-CdS to just 0.7% abs. The certified QE curve of this cell is shown in Fig. 6 and compared with the QE of the 21.7%

Thin Film

VON ARDENNE

www.vonardenne.biz

Our experts are looking forward to meeting you at the **EU PVSEC** at booth **F5b**.

EASY AND PRECISE
**SIMULTANEOUS
DOUBLE-SIDED**
VACUUM COATING

With our horizontal wafer coating system XEA|nova, even very thin substrates can be coated on both sides without breaking the vacuum or flipping the substrates. The system enables both sequenced and simultaneous treatment.

XEA|nova

cell. The gain in photocurrent below 500nm is evident but is partly offset by losses in the visible region. The authors are confident that these losses can be further minimized (for example by adjustments in the anti-reflection coating), and thus the efficiencies will come to match, or even exceed, CdS-buffer-based record efficiencies.

Grain boundaries

Another potential source of improvement may be to minimize the polycrystalline structure and the resultant grain boundaries of the CIGS absorber. The SEM cross-section in Fig. 7 shows a remarkable density of grain boundaries perpendicular to the current flow and many different grain sizes ($\sim 0.5\text{--}2\mu\text{m}$). However, they cannot be critical, as this image was taken from the 21.7% record cell. Further passivation of these grain boundaries or the growth of larger grains together with back surface passivation layers could lead to an improved diffusion length and corresponding current collection, especially in the long wavelength region; this would generate a more rectangular shape of the QE curve around 1000nm (see Fig. 6).

“All CIGS deposition technologies benefit from the alkali PDT.”

Summary

In this paper the technological advances that led to the current CIGS solar cell world record of 21.7% efficiency have been summarized. The direct beneficial effect of PDT on V_{oc} , and also the indirect improvement of J_{sc} , have been explained. The former was demonstrated by a comparative study of ZSW cells from the same CIGS run, either with or without

PDT. Except for sulphur-containing absorbers, where no data are available, all CIGS deposition technologies benefit from the alkali PDT. Current advances with Cd-free devices yielding almost the same efficiencies as CIGS cells with CdS buffer layers, as well as further passivating grain boundaries and the back surface, are potential routes to meeting ZSW's efficiency goal of 25% in the near future.

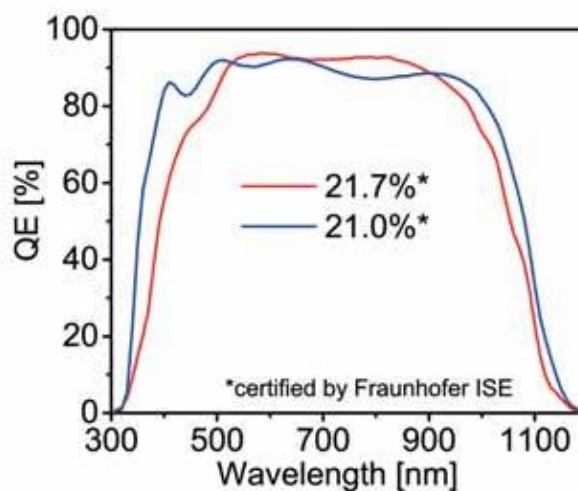


Figure 6. Certified QE curves of the 21% Cd-free world-record cell [15] compared with the 21.7% world-record cell with a CdS buffer layer [10]. Parasitic light absorption below 500nm has been reduced as a result of a CBD-Zn(O,S) buffer layer. In both cases, CIGS films had an alkali PDT.

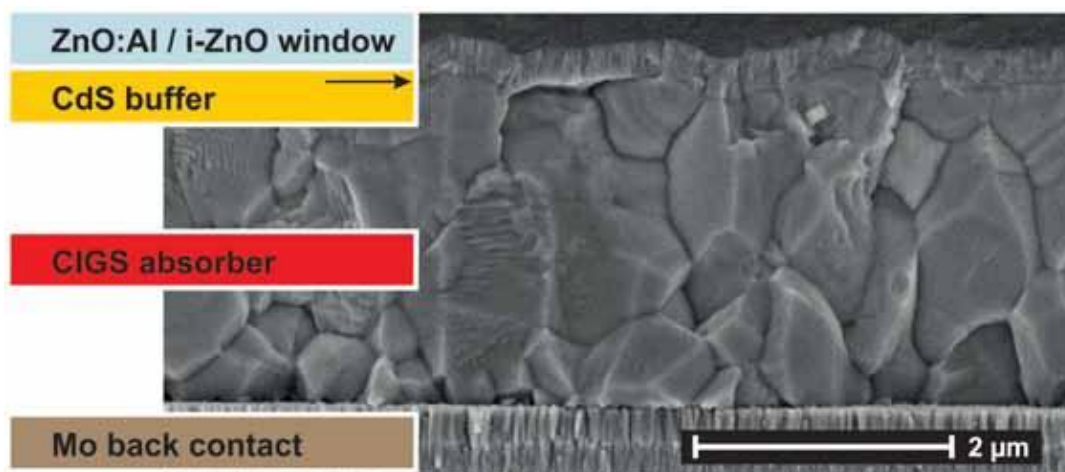


Figure 7. SEM cross-section image of the 21.7% CIGS record cell. The ZnO:Al / i-ZnO, CIGS and Mo layers (from top to bottom) are visible (the CdS buffer layer is too thin to be observed). The remarkable density of grain boundaries leaves room for improvement (CIGS grain boundaries perpendicular to the current flow, if not sufficiently passivated, are potentially detrimental to current collection).

References

- [1] Chen, W.S. et al. 1987, "Development of thin-film polycrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ solar cells", *Proc. 19th IEEE PVSC*, New Orleans, Louisiana, USA, pp. 1445–1447.
- [2] Hedström, J. et al. 1993, "ZnO/CdS/Cu(In,Ga)Se₂ thin film solar cells with improved performance", *Proc. 23rd IEEE PVSC*, Louisville, Kentucky, USA, pp. 364–371.
- [3] Gabor, A.M. et al. 1994, "High efficiency $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ solar cells made from $(\text{In}_x\text{Ga}_{1-x})_2\text{Se}_3$ precursor films", *Appl. Phys. Lett.*, Vol. 65, No. 2, pp. 198–200.
- [4] Rudmann, D. et al. 2004, "Efficiency enhancement of $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells due to post-deposition Na incorporation", *Appl. Phys. Lett.*, Vol. 84, pp. 1129–1131.
- [5] Laemmle, A., Wuerz, R. & Powalla, M. 2013, "Efficiency enhancement of $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin-film solar cells by a post-deposition treatment with potassium fluoride", *physica status solidi (RRL)*, Vol. 7, pp. 631–634.
- [6] Chirilă, A. et al. 2013, "Potassium-induced surface modification of $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films for high-efficiency solar cells", *Nature Mater.*, Vol. 12, pp. 1107–1111.
- [7] Jackson, P. et al. 2014, "Compositional investigation of potassium doped $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells with efficiencies up to 20.8%", *physica status solidi (RRL)*, Vol. 8, pp. 219–222.
- [8] Stolt, L. 2014, "Solibro CIGS to the next level", Int. Worksh. CIGS Sol. Cell Technol., Berlin, Germany.
- [9] Herrmann, D. et al. 2014, "CIGS module manufacturing with high deposition rates and efficiencies", *Proc. 40th IEEE PVSC*, Denver, Colorado, USA.
- [10] Jackson, P. et al. 2015, "Properties of $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells with new record efficiencies up to 21.7%", *physica status solidi (RRL)*, Vol. 9, pp. 28–31.
- [11] Jackson, P. et al. 2011, "New world record efficiency for $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin-film solar cells beyond 20%", *Prog. Photovoltaics Res. Appl.*, Vol. 19, pp. 894–897.
- [12] Reinhard, P. et al. 2015, "Cu(In,Ga)Se₂ thin-film solar cells and modules – A boost in efficiency due to

potassium", *IEEE J. Photovolt.*, Vol. 5, pp. 656–663.

- [13] Wuerz, R. et al. 2012, "CIGS thin-film solar cells and modules on enameled steel substrates", *Sol. Energy Mater. Sol. Cells*, Vol. 100, pp. 132–137.
- [14] Pianezzi, F. et al. 2014, "Unveiling the effects of post-deposition treatment with different alkaline elements on the electronic properties of CIGS thin film solar cells", *Phys. Chem. Chem. Phys.*, Vol. 16, pp. 8843–8851.
- [15] Friedlmeier, T.M. et al. [forthcoming], "Improved photocurrent in $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells: From 20.8% to 21.7% efficiency with CdS buffer and 21.0% Cd-free", *IEEE J. Photovolt.*
- [16] Wallin, E. et al. 2014, "Very high efficiency $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based thin-film solar cells grown with a single-stage process", E-MRS Spring Meeting, Lille, France.
- [17] Chirilă, A. et al. 2011, "Highly efficient $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells grown on flexible polymer films", *Nature Mater.*, Vol. 10, pp. 857–861.
- [18] Mansfield, L.M. et al. 2014, "Enhanced performance in $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells fabricated by the two-step selenization process with a potassium fluoride postdeposition treatment", *IEEE J. Photovolt.*, Vol. 4, pp. 1650–1654.
- [19] Green, M.A. et al. 2004, "Solar cell efficiency tables (version 24)", *Prog. Photovoltaics Res. Appl.*, Vol. 12, pp. 365–372.
- [20] Masuko, K. et al. 2014, "Achievement of more than 25% conversion efficiency with crystalline silicon heterojunction solar cell", *IEEE J. Photovolt.*, Vol. 4, pp. 1433–1435.

About the Authors



Dr. Oliver Kiowski studied chemistry at the Karlsruhe Institute of Technology (KIT) and the University of Massachusetts, Amherst, and received his Ph.D. from KIT in 2008. He works at ZSW as a project manager for a government-funded project, investigating the reliability of CIGS solar cells and modules. He is also responsible for the optical and electrical metrology of CIGS record cells.



Dr. Theresa M. Friedlmeier began working with CIGS in 1991 as a student at the Institute for Physical Electronics at the University of Stuttgart, where she also received her diploma (physics) and Ph.D. (electrical engineering). She joined ZSW in 2002 and currently focuses on analytics and high-efficiency CIGS solar cells.



Dr. Roland Würz studied physics at the Justus Liebig University Giessen and received his Ph.D. from Philipps University Marburg. He first became involved in CIGS solar cell research in 2001, and since 2006 he has been working at ZSW on the development of CIGS thin-film solar cells and modules on flexible substrates.



Philip Jackson studied physics at the University of Tübingen. For the past 13 years he has worked as a research scientist on $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells, both at the Institute for Physical Electronics (IPE), University of Stuttgart, and at ZSW in Stuttgart.

Dr. Dimitrios Hariskos received his diploma in chemistry from RWTH Aachen University and his Ph.D. from the Technical University of Darmstadt. He has been a researcher at ZSW in Stuttgart since 1998, and has worked on the up-scaling of CIGS technology from small-area cells to full-size commercial modules. His research interests focus on the development of high-efficiency Cd-free CIGS devices.

Enquiries

ZSW
Industriestrasse 6
70565 Stuttgart
Germany

Tel: +49 711 7870-0
Email: oliver.kiowski@zsw-bw.de
Website: www.zsw-bw.de