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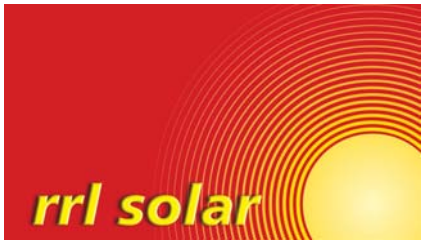

Properties of Cu(In,Ga)Se_2 solar cells with new record efficiencies up to 21.7%

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We report on a new thin-film Cu(In,Ga)Se_2 (CIGS) solar cell record efficiency of 21.7%. In order to better understand this newest development, we describe the specific solar cell data as obtained from *I–V* measurement and diode analysis, quantum efficiency and secondary neutral mass spectrometry measurements. We hope that such a description will help to exploit the potential of this promising thin-film solar technology even further.

1 Introduction As we had predicted in our last contribution to this journal [1], the thin-film solar cell record efficiency of 20.8% did not last for very long due to the fact that with the most recent introduction of the alkali post deposition treatment (PDT) in its current form [2, 3] a whole new realm of experimental possibilities has been opened. This new impetus since has produced one new record efficiency after the other in various laboratories so that within only a few months the thin-film solar cell record efficiency has increased from 20.4% to 21.0% (EMPA: 20.4% [3], ZSW: 20.8% [1], Solar Frontier: 20.9% [4], Solibro 21.0% [5], see also Table 1). However, instead of now slowly moving into a saturation of the record value development, an optimised PDT procedure has once more helped to further increase the value for the best polycrystalline thin-film solar cell to 21.7%. In order to trace this dynamic development, it is our goal in this Letter, to describe the changes in the properties of such high efficiency Cu(In,Ga)Se_2 (CIGS) solar cells. This characterisation and analysis will lead to a better understanding of CIGS solar cells and aid to exploit the still untouched experimental potential for even higher solar cell conversion efficiencies.

2 Experimental methods

2.1 Processing of CIGS cells For the production of CIGS solar cells, we begin with washing a standard soda-lime glass (3 mm) or thinner (2 mm) alkali-aluminosilicate glass. This cleaned substrate is covered with a thin film of sputtered molybdenum (500–900 nm/electrical back contact). Then we co-evaporate Cu, In, Ga, and Se to grow the CIGS semiconductor layer in a multi-stage process (2.5–3.0 μm/p-doped absorber layer). This resulting layer is p-doped by defects in the crystal structure. Further doping occurs by diffusion of alkali elements from the substrate during the high temperature growth phase and by subsequent alkali treatment. After the CIGS process, we perform a PDT procedure. In a next step, the samples are dipped into a chemical bath to form a thin layer of CdS (30–50 nm/n-doped buffer layer). Then we sputter intrinsic ZnO (50–100 nm/buffer layer) and Al-doped ZnO (150–200 nm/conductive window material). Finally, we evaporate a nickel/aluminium/nickel grid (electrical contact at the front), and the cell size is defined by mechanical scribing. The resulting cell area is about 0.5 cm^2. For high-efficiency cells we also evaporate an anti-reflective coating (ARC) on top of the whole cell stack (MgF_2/105–115 nm).

2.2 Characterisation methods For the analytical description of the CIGS solar cells, current–voltage (*I–V*) analysis was performed under a simulated AM 1.5 G spectrum at 25 °C with a four-point measurement setup. The obtained data was further analysed by diode analysis ac-

Table 1 Current–voltage (*I–V*) and diode analysis data (light *I–V*) of the new 21.6% and 21.7% record cells compared to former record cell as measured and certified by Fraunhofer ISE (all with ARC).

lab.	date of public.	η (%)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	CGI	GGI	R_s (Ω cm^2)	R_p (kΩ cm^2)	J_0 (A/cm^2)	A	J_{ph} (mA/cm^2)
ZSW	**09/2014**	**21.7***	**746**	**36.6**	**79.3**	**0.91**	**0.32**	**0.32**	**1.76**	**2.4×10^{-11}**	**1.38**	**36.6**
ZSW	**09/2014**	**21.7***	**748**	**36.5**	**79.4**	**0.90**	**0.32**	**0.30**	**1.54**	**2.2×10^{-11}**	**1.38**	**36.5**
ZSW	**09/2014**	**21.6***	**748**	**36.3**	**79.4**	**0.90**	**0.32**	**0.36**	**1.58**	**1.6×10^{-11}**	**1.35**	**36.4**
Solibro	06/2014 [5]	21.0*	757	35.7	77.6							
Sol. Front	04/2014 [4]	20.9*	686	39.9	76.4							
ZSW	**02/2014 [1]**	**20.8***	**757**	**34.8**	**79.1**	**0.91**	**0.32**	**0.24**	**0.95**	**1.6×10^{-11}**	**1.37**	**34.8**
EMPA	11/2013 [3]	20.4*	736	35.1	78.9	0.78–0.82	0.33–0.38					
ZSW	**01/2011 [7]**	**20.3***	**740**	**35.4**	**77.5**	**0.88**	**0.34**	**0.07**	**0,76**	**3.8×10^{-10}**	**1.57**	**35.6**

* Independently certified by Fraunhofer ISE.

cording to the one-diode model. In addition, we have performed quantum efficiency measurements (QE). CIGS composition was determined with an X-ray fluorescence spectroscopy (XRF) instrument from EDAX (Eagle XXL). The determined compositional ratio values as the Cu/(Ga + In) (CGI) and Ga/(Ga + In) (GGI) ratios represent average values that do not further specify the compositional grading in the depth of the CIGS absorber as shown in [6]. In order to obtain such compositional depth profiles, secondary neutral mass spectrometry (SNMS) was performed in a LEYBOLD LHS 10 system with a secondary ion and neutral mass spectrometer module (SSM 200) using a Balzers 511 quadrupole for mass separation.

3 Results and discussion The experimental procedure as briefly outlined above has resulted in a new world record efficiency for thin-film solar cells of 21.7% (with ARC). The area of this solar cell (line 1 in Table 1) is (0.4972 ± 0.0031) cm^2 as determined by an optical method. These values have been measured and certified independently by Fraunhofer ISE in Freiburg, Germany. The *I–V* parameters as depicted in Table 1, however, show that we have been able to reach this very high efficiency not only with one but with three solar cells. With these we see a pronounced increase in efficiency η (+0.9%$_{absol.}$) compared to our former record cell (η = 20.8%) [1]. The data in Table 1 reveals the following: Since the introduction of the PDT procedure at the ZSW (20.8% result), we can observe a significantly increased open-circuit voltage V_{oc} level around 750 mV and fill-factors FF above 79% in our own record cells. What sets apart the most recent results is their strongly increased short-circuit current density J_{sc}. In order to better qualify this gain in J_{sc}, we have performed external quantum efficiency measurements (EQE) to compare these cells (see Fig. 1).

Particularly the comparison of the 21.7% (red line) with the 20.8% cell's (blue line) external quantum efficiency shows a significant increase in the longer wavelength region beyond 1000 nm for the former. For the 21.7% cell, we can also detect an increase of the EQE in the short wavelength region between 400 nm and 520 nm (J_{sc} gain: 0.43 mA/cm^2), which is due to the possibility to reduce the CdS thickness in connection with the PDT procedure (better coverage by thin CdS for PDT-treated CIGS).

The gain in J_{sc} in the longer wavelength region between 980 nm and 1200 nm (J_{sc} gain: 1.08 mA/cm^2) can better be understood when we also compare the compositional grading (obtained by SNMS) of these cells (see Fig. 2). Obviously, the 21.7% cell has a more pronounced

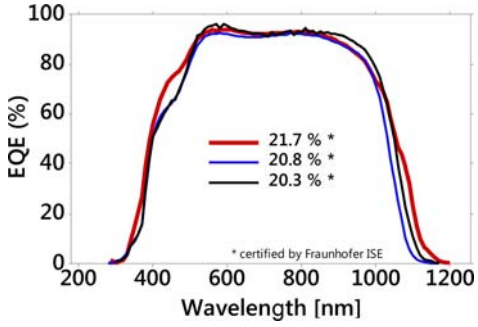

Figure 1 External quantum efficiency (EQE) as measured and certified by Fraunhofer ISE of former (black and blue line) and current record cell (red thick line) (all with ARC).

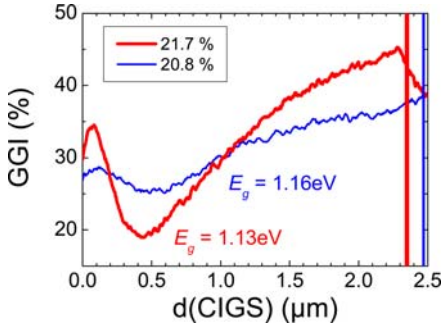

Figure 2 Comparison of the GGI grading of the 21.7% (red thick line) and the 20.8% cell (blue thin line) as obtained from SNMS analysis. The vertical red and blue lines represent the end of the CIGS absorber and the transition to the molybdenum back contact.

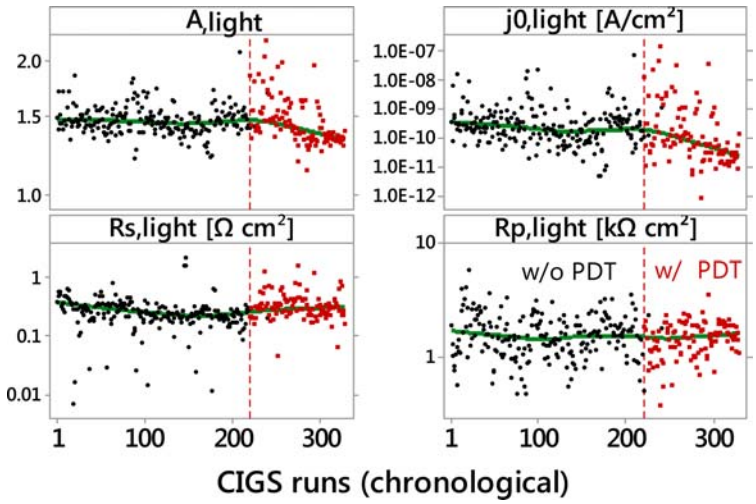

Figure 3 Diode analysis (light *I–V* curves) of chronological ZSW small area cell production over the past years (only best solar cell of each production run depicted). For CIGS solar cells with PDT (red squares) a trend towards smaller diode quality factors A and saturation current densities J_0 can be observed.

gallium grading, which includes a higher GGI at the front and at the back than for the 20.8% cell, but also a lower GGI minimum, which in turn explains the lower optical band-gap and higher J_{sc} in the IR range of the former cell.

However, it is remarkable that such a strong GGI gradient in the space charge region of the CIGS absorber as can be seen in the 21.7% cell does not lead to significant losses in V_{oc} or FF. Such losses have been discussed repeatedly over the years and have been attributed to an increase in structural defects in such strongly inhomogeneous crystals [8]. Thus, we are able to gain in J_{sc} by using a fairly strong GGI gradient without losing significantly in V_{oc} or FF. One could speculate that the PDT procedure helps to partially even passivate such structural defects.

If we compare our latest cell results with those of former record results obtained by other research laboratories (see Table 1), we can see that our latest 21.7% results relate to these results similarly as to our own former results: the J_{sc} values are significantly higher, V_{oc} show a general high level in all results since the introduction of the PDT procedure, and our FF are clearly higher. However, the results of Solar Frontier are an exception to the general trend, since they use Zn(O,S) buffer layers in combination with a sulfur rich CIGS surface. But this alternative approach together with our own approach may indicate how much more potential the CIGS technology still has.

Figure 3 shows a broader and at the same time statistically more relevant picture of the properties of our CIGS solar cells as derived from light *I–V* measurements (without ARC) and diode analysis according to the one-diode model. We have taken CIGS solar cells from our small-area cell production line, that has been produced from 2009 to 2014. From each production run only the best cell has been taken into account. The dashed vertical lines in the graphs mark the decisive separation line between CIGS without PDT treatment (left side of the graph) and CIGS with PDT treatment (right side). With the help of the calculated green moving average line it can be seen that the introduction of the PDT procedure and the subsequent optimisation of the same have lead to a reduction in the ideality factor A and saturation current density J_0. The series resistance R_s and parallel resistance R_p show no conclusive trend with regards to the named discrimination (with vs. w/o PDT). The specific values of the 21.7% cell are as follows (see also Table 1): $R_s = 0.32\ \Omega\ cm^2$, $R_p = 1.76\ k\Omega\ cm^2$, $J_0 = 2.4 \times 10^{-11}\ A/cm^2$, $A = 1.38$.

3 Conclusion The properties of the most recent CIGS solar cells with conversion efficiencies up to 21.7% show a remarkable increase in J_{sc}, a high V_{oc} level and improved FF when compared to former record results. The significant increase in J_{sc} can be explained by an optical gain through a thinner CdS buffer layer and a lower GGI minimum in the double-graded CIGS absorber. Seemingly, the very steep front grading does not harm the solar cell performance. The results may suggest that the PDT procedure has a passivating effect on (lattice-induced) defects. In addition, a general trend towards lower ideality factors and saturation current densities can be observed for PDT treated cells. The comparison of our results with the results of Solar Frontier (20.9%) permits the conclusion that a combination of PDT procedures and alternative buffer layers in one cell system has the potential for even higher efficiencies than reported here.

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