EPJ Photovoltaics **1**, 10601 (2010)
www.epj-pv.org
DOI: 10.1051/epjpv/2010002

Experimental verification of optically optimized $CuGaSe_2$ top cell for improving chalcopyrite tandems[⋆]

M. Schmid[1,a], R. Caballero[1], R. Klenk[1], J. Krč[2], T. Rissom[1], M. Topič[2], and M.Ch. Lux-Steiner[1]

[1] Helmholtz Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
[2] University of Ljubljana, Faculty of Electrical Engineering, Tržaška 25, 1000 Ljubljana, Slovenia

Received: 15 July 2010 / Accepted: 15 September 2010

Abstract An efficient tandem solar cell requires a top cell which is highly transparent below the energy gap of its absorber. Previously we had reported on a theoretically optimized $CuGaSe_2$ top cell stack based on realistic material properties. It promised a significant increase in optical transparency and, consequently, enhanced $CuGaSe_2$/Cu(In,Ga)Se_2 tandem efficiency. Here we present the first steps taken towards the experimental realization of this optimized tandem. We started with a mechanically stacked device which achieved 8.5% efficiency. Optical measurements of the improved top cells and corresponding photo current densities of the filtered bottom cell are reported. The experimental findings are in agreement with the optical modeling. These data are used to assess the level of tandem performance that could be accomplished in the near future and to discuss the priorities of further research.

1 Introduction

Up to now, tandem and multi junction solar cells are the only concept exceeding the Shockley-Queisser efficiency limit of 30% under solar illumination without concentration [1]. High transparency of the top cell below its energy gap is – apart from efficient absorption above E_g – a crucial requirement for an efficient tandem cell. The chalcopyrites constitute a system of absorber materials with energy gaps suitable for tandem cells, e.g. $CuGaSe_2$ with $E_g = 1.68$ eV and Cu(In,Ga)Se_2 with $E_g = 1.1$ eV. However, the best $CuGaSe_2$/Cu(In,Ga)Se_2 tandem efficiency published so far is 7.4% [2]. This relatively low value is fundamentally related to the low efficiency of the top cell together with a top cell transparency of only 60% in its sub-gap range.

Previously we had developed an optical model of the n-ZnO/i-ZnO/CdS/$CuGaSe_2$/SnO_2:F/glass solar cell that allowed for the description of the optical properties of this top cell [3]. Based on this model in [4] an optimized top cell stack had been derived that showed significant improvement in transparency. In this paper we will give the experimental proof of enhanced top cell transmission and resulting gain in bottom cell performance in the tandem. An improved efficiency of the mechanically stacked $CuGaSe_2$/Cu(In,Ga)Se_2 tandem will be reported which is however still far from surpassing the Cu(In,Ga)Se_2 single cell efficiency. Our discussion will point out options and requirements for building an efficient chalcopyrite tandem.

2 Experimental and results

Chalcopyrite absorbers were prepared by physical vapor deposition in a three stage process [5]. For the bottom cell the approx. 2 μm thick Cu(In,Ga)Se_2 was deposited onto a molybdenum back contact, whereas for the $CuGaSe_2$ top cell a transparent back contact is required. SnO_2:F with a thickness of approximately 850 nm was used in the initial configuration. The junction of each cell was formed by chemical bath deposition of CdS and sputtering of intrinsic and Al-doped ZnO. The standard configuration of a Cu(In,Ga)Se_2 bottom cell is ZnO:Al(200 nm)/ i-ZnO(125 nm)/CdS(50 nm)/Cu(In,Ga)Se_2(2000 nm)/ Mo(800 nm)/glass substrate.

The starting structure and the layer thicknesses of the $CuGaSe_2$ top cell are indicated as initial stack (J) in Table 1. The theoretically optimized top cell stack derived in [4] is set beside. It is characterized by 1) reduced layer thicknesses; 2) careful adaptation of layer thicknesses to anti-reflection behavior; 3) reduced reflection by an anti-reflection coating on top and 4) a substrate simulating monolithic integration. Furthermore, the experimentally realized stacks are given: first the absorber was grown with a thickness approaching 1 μm (opt. stack exp. (A) in Table 1), then the thicknesses of the front ZnO layers were reduced (stack (B)). Note; for the thinner transparent back contact, the SnO_2:F was replaced by ZnO:Al,

---

[⋆] This article has been previously published in PV Direct, the former name of EPJ Photovoltaics.

[a] e-mail: `martina.schmid@helmholtz-berlin.de`

Table 1. Layer structure and thicknesses of the $CuGaSe_2$ top cells: standard structure of the initial stack (J) compared to theoretically optimized structure and stepwise adaptation of the latter one in the experiment by stacks (A) to (C).

layer thickness (nm)	initial stack (J)	optim. stack theory	optim. stack exp. (A)	optim. stack exp. (B)	optim. stack exp. (C)
MgF_2	0	120	0	0	0
ZnO:Al	455	90	455	105	105
i-ZnO	95	50	95	50	50
CdS	50	65	50	50	50
$CuGaSe_2$	1600	1050	1190	1190	1190
SnO_2:F or	835	90	835	835	
ZnO:Al					105
substrate	glass	CdS	glass	glass	glass

which has comparable optical properties but was in contrast to SnO_2:F available with arbitrary thickness (stack (C)). Hence, stack (C) implements the theoretically derived modifications 1) and 2). Steps 3) and 4) were not implemented because monolithic integration is not yet feasible and the MgF_2 anti-reflection coating lacks long-term stability. In addition, the exact tuning of the layers to the optimal (anti-reflective) thicknesses is difficult to achieve in the experiment.

Figure 1 shows the transmission spectra measured for the various $CuGaSe_2$ top cell stacks. The lowest curve gives the measurement of the initial stack (J) which reaches a maximum transparency of 60%. A reduction of the absorber layer thickness for approx. 1/3 leads to an increase in top cell transparency of 8% in the wavelength range from 700 to 1200 nm (stack (A)). Further overall enchancement of the top cell transparency (including the long wavelengths) is obtained by reduction of the thicknesses of the front ZnO layers (stack (B)). The optimized structure (C) finally features an average transparency of 80% and stays at a constant level in the wavelength region defined by the energy gaps of the top $CuGaSe_2$ ($\lambda_g \approx 700$ nm) and the bottom $Cu(In,Ga)Se_2$ ($\lambda_g \approx 1200$ nm) absorber. The 80% transmission of the optimized stack means an increase of 20% absolute compared to the initial stack. The observed improved transparency fitted well to the optical model established in Diplot [6], see the dashed curve in Figure 1. The parameters were derived from the modeling of the initial stack (compare [3]) but corrected to include reduced layer thicknesses and related small changes in material properties. The increase in transparency in the long-wavelength regime is due to reduced free charge carrier absorption in the front and back transparent conducting oxide of the top cell. Close to the energy gap, additional reduced defect absorption of the thinner $CuGaSe_2$ absorber contributes to the enhanced transmission.

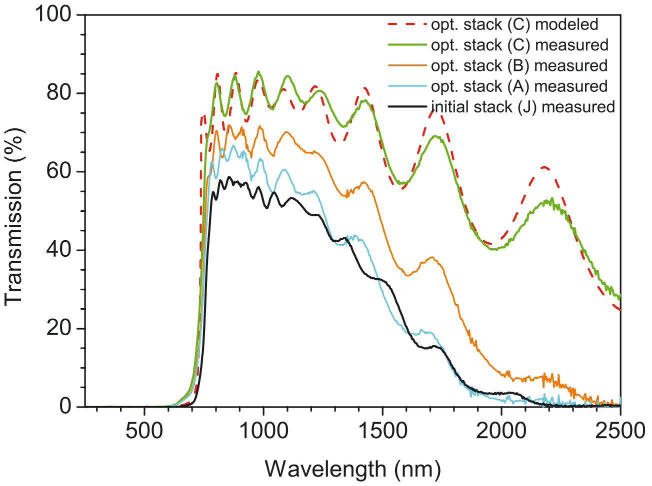

Fig. 1. Measured transparency of the $CuGaSe_2$ top cell in the initial configuration (J) and of the experimentally optimized structures (A), (B) and (C) (see Table 1); comparison to modeling results for the optimized stack.

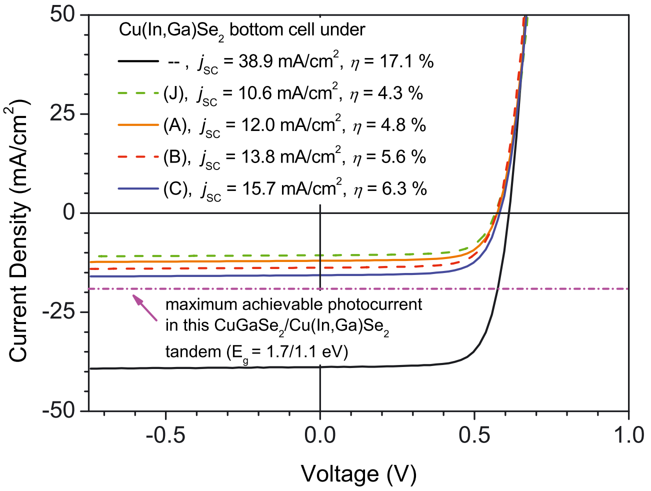

Fig. 2. Measured *j-V* characteristics of a $Cu(In,Ga)Se_2$ bottom cell filtered by the $CuGaSe_2$ top cell stacks as specified in Table 1. The curve of the unfiltered device is given as a reference. Current densities and efficiencies of the bottom cell are indicated.

The increased transparency of the top cell above its E_g is crucial for improving the short circuit current density of the bottom cell. The *j-V* characteristics of a $Cu(In,Ga)Se_2$ bottom cell filtered by the various $CuGaSe_2$ top cell stacks are shown in Figure 2. Corresponding short circuit current densities j_{SC} and efficiencies η of the bottom cell are indicated. The current density of 38.9 mA/cm^2 for the unfiltered bottom cell decreased to 10.6 mA/cm^2 under the initial stack (J). When filtering with the optimized top cell stack (C), however, the remaining current density increases to $j_{SC} = 15.7$ mA/cm^2. This corresponds to 82% of the maximum achievable value which is given by the split of the solar spectrum according to the 1.7 / 1.1 eV energy gap pair. Figure 2 shows how the current density improves in step with the top cell improvements and how it approaches the theoretical limit. The measured values are in agreement with theoretical

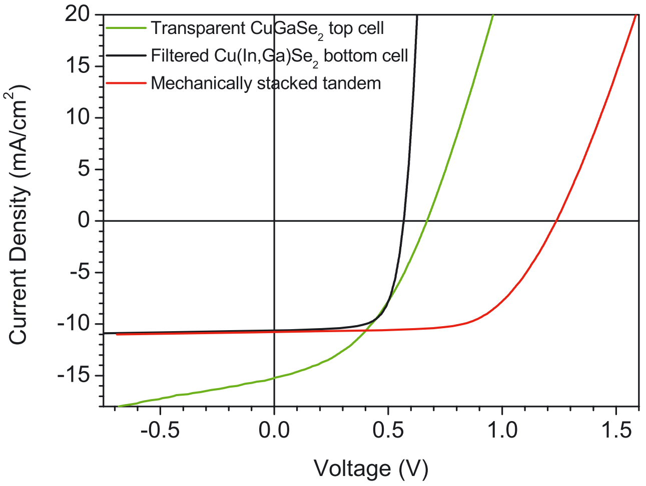

Fig. 3. Solar cell characteristics of a $CuGaSe_2/Cu(In,Ga)Se_2$ tandem solar cell and the related $CuGaSe_2$ top and filtered $Cu(In,Ga)Se_2$ bottom cell; for the electrical parameters see Table 2.

	j_{SC} (mA/cm^2)	V_{OC} (V)	*FF* (%)	η (%)
Top	15.2	0.67	41.8	4.3
Bottom	10.6	0.57	70.4	4.3
Tandem	10.7	1.24	64.1	8.5
Bottom single	38.9	0.61	72.8	17.1

Table 2. Solar cell parameters of a $CuGaSe_2/Cu(In,Ga)Se_2$ tandem solar cell and the related $CuGaSe_2$ top and filtered $Cu(In,Ga)Se_2$ bottom cell; for the *j*-*V* characteristics see Figure 3.

calculations for the cases (A), (B) and (C) within an error of 5% (not shown here). In the experiment, the efficiency of the $Cu(In,Ga)Se_2$ bottom cell shaded by the $CuGaSe_2$ top cell increases from 4.3 to 6.3%.

3 Discussion

Our latest results of a mechanically stacked $CuGaSe_2$/-$Cu(In,Ga)Se_2$ tandem in the initial configuration are presented in Figure 3. The *j*-*V* characteristics are shown for the $CuGaSe_2$ top cell (J), the $Cu(In,Ga)Se_2$ bottom cell filtered by it and the mechanical stack calculated from the top and bottom cell curves by considering series connection of the two single devices. A tandem efficiency of 8.5% was determined. This value surpasses previously reported efficiencies [2]. It is based on a top cell efficiency of 4.3% and a bottom cell efficiency of 4.3%, for detailed electrical data see Table 2. As these data show, the device is bottom cell limited regarding the photo current. The top cell photo current is still higher in the initial configuartion but will be lowered to better match when using the optimized top cell structures.

Under the improved transparency of the experimentally optimized $CuGaSe_2$ top cell stack (C), the $Cu(In,Ga)Se_2$ bottom cell efficiency reached 6.3%, see Figure 2. Assuming an unchanged top cell performance of 4.3%, the tandem device might reach over 10% efficiency, which is however still lower than the efficiency of the single bottom cell. From the optical point of view, the improvement of the top cell performance has been successfully performed. The improvement of the electrical properties of the $CuGaSe_2$ top cell presents the major task of tandem optimization in the future. The present record efficiency of a $CuGaSe_2$ solar cell is 9.7% on molybdenum [7] and 4.3% on transparent back contact [2]. If the electrical performance of the top cell becomes comparable to the one of the bottom cell – thus also reaching 20% as a single junction device – a tandem efficiency of 26% can be expected. This is the value predicted from our theoretical calculations, compare [4].

4 Summary

In conclusion, the optical model of the chalcopyrite tandem derived before [3, 4] has found experimental verification in this paper. The accuracy of the model as well as predicted design improvements have been shown. The data will be useful to guide further research concerning top cells with superiour optical and electrical properties, to quantify any progress made in the experiment, and to extrapolate feasible tandem efficiencies.

This work was supported by the EC-Project ATHLET, No. 019670. The authors thank C. Kelch, M. Kirsch, K. Kraft and T. Münchenberg for technical assistance and J. Hüpkes from the FZ Jülich for providing substrates.

References

1. W. Shockley, H.J. Queisser, J. Appl. Phys. **32**, 510 (1961)
2. S. Nishiwaki, S. Siebentritt, P. Walk, M.Ch. Lux-Steiner, Progr. Photovolt.: Res. Appl. **11**, 243 (2003)
3. M. Schmid, R. Klenk, M.Ch. Lux-Steiner, Sol. Energy Mater. Sol. Cells **93**, 874 (2009)
4. M. Schmid, J. Krč, R. Klenk, M. Topic, M.Ch. Lux-Steiner, Appl. Phys. Lett. **94**, 053507 (2009)
5. R. Caballero, S. Siebentritt, K. Sakurai, C.A. Kaufmann, H.W. Schock, M.Ch. Lux-Steiner, Thin Solid Films **515**, 5862 (2007)
6. E. Lotter, http://www.diplot.de
7. M. Saad, H. Riazi, E. Bucher, M.Ch. Lux-Steiner, Appl. Phys. A **62**, 181 (1996)