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Copper variation in $Cu(In,Ga)Se_2$ solar cells with indium sulphide buffer layer

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ABSTRACT

In the manufacturing of $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells the application of a buffer layer on top of the absorber is essential to obtain high efficiency devices. Regarding the roll-to-roll production of CIGS cells and modules a vacuum deposition process for the buffer is preferable to the conventional cadmium sulphide buffer deposited in a chemical bath. Promising results have already been achieved for the deposition of indium sulphide buffer by different vacuum techniques. The solar device performance is very sensitive to the conditions at the absorber-buffer heterojunction. In view of optimization we investigated the influence of the Cu content in the absorber on the current–voltage characteristics. In this work the integral copper content was varied between 19 and 23 at.% in CIGS on glass substrates. An improvement of the cell performance by enhanced open circuit voltage was observed for a reduction to ~21 at.% when thermally evaporated indium sulphide was applied as the buffer layer. The influence of stoichiometry deviations on the transport mechanism and secondary barriers in the device was studied using detailed dark and light current–voltage analysis and admittance spectroscopy and compared to the reference CdS-buffered cells. We conclude that the composition of the absorber in the interface region affects current transport in In_xS_y-buffered and CdS-buffered cells in different ways hence optimal Cu content in those two types of devices is different.

1. Introduction

$Cu(In,Ga)Se_2$ (CIGS) thin-film technology shows a fast growth in the solar market. Module efficiencies on glass >14% in production were demonstrated [1,2], and recently cell record efficiencies up to 20.9% exceeding the Poly-Si world record were announced [3,4]. Besides optimizing the CIGS technology on glass, the Zentrum für Sonnennergie- und Wasserstoff-Forschung (ZSW) is investigating alternative substrates. A complete roll-to-roll vacuum-deposition system was established for the cell processing on polyimide web. The standard non-vacuum deposited CdS buffer by chemical bath deposition (CBD) cannot be applied in this system. Therefore alternative buffer materials like sputtered ZnOS [5] or thermally evaporated In_xS_y [6] are investigated. In this work we present results on indium sulphide buffer layer by physical vapour deposition (PVD) in an in-line evaporation system on glass substrates. Efficiencies >16% were already demonstrated [6]. In former works on indium sulphide buffer layers the electrical behaviour of the solar devices was shown to be very sensitive to diffusion processes between absorber and buffer by temperature impact [7–9]. In the following, the influence of various copper contents in the CIGS absorber on the cell performance and further electrical characteristics is presented. A comparison to CdS references is included. For CIGS solar devices with CBD-CdS usually a Cu content of <24 at.% is applied. In this work we investigated Cu contents of 19–23 at.% as previous studies indicated that a lower copper content could be favourable for the In_xS_y buffer.

2. Experimental details

2.1. Cell processing

The CIGS absorber was deposited on molybdenum coated soda-lime glass substrates by co-evaporation in an in-line multi-stage deposition system. In this paper the results of several experiment series are shown. Altogether the integral copper content was varied in the range of about 19–23 at.% Cu. After CIGS deposition the samples were stored in vacuum and some were etched with KCN solution immediately prior to buffer deposition.

The indium sulphide buffer layer was evaporated from commercial In_2S_3 powder at ~750 °C in an in-line evaporation system. The powder was pressed to pellets prior to evaporation. The thickness was controlled by the substrate carrier velocity and was varied in the range of 8 to 20 nm. The substrate temperature was about 100 °C due to the radiated heat of the powder source. CdS references were processed for some of the experiments.

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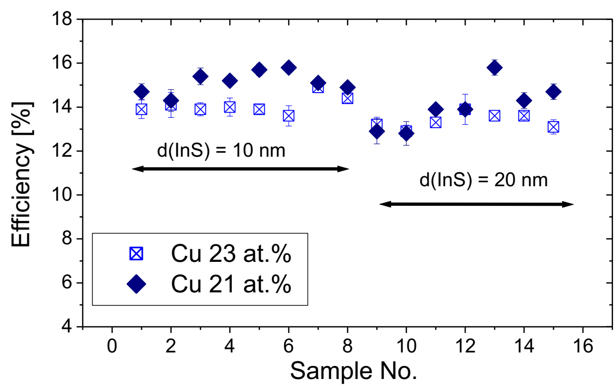

Fig. 1. Cell efficiencies for sample series A with indium sulphide buffer on CIGS with 21 at.% and 23 at.% Cu (average values of 10 cells). The buffer layer of the samples starting at no. 9 is twice as thick (20 nm) as for samples 1 to 8.

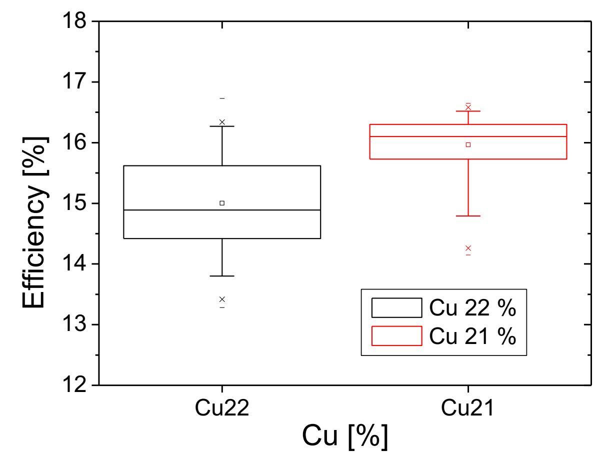

Fig. 2. Box-plot of cell efficiencies of series B for 21 and 22 at.% Cu.

The cells were completed with a i-ZnO/ZnO:Al window and a Ni–Al–Ni contact grid. The cell area is defined to 0.5 cm^2 by a mechanical scribe. A post-annealing step in air for 20 min at 200 °C was performed later to optimize the device performance of the In_xS_y-buffered cells.

2.2. Characterisation

The composition of the CIGS absorber layer was determined by energy dispersive X-ray fluorescence (XRF) analysis with an EAGLE XXL instrument from Roentgenanalytik/EDAX. For analysis a Rh X-ray source was used, operating at 50 keV, with an aperture of 1 mm diameter. For quantification of CIGS thin films the peak areas of the fitted K lines of Cu, In, Ga and Se were used.

Current–voltage (I–V) characteristics were measured at ZSW before and after post-annealing with a steady state sun-simulator from ORIEL at 25 °C and under standard test conditions of AM1.5 illumination (1000 W/m^2).

For thickness determination of the buffer reflectivity measurements were performed on indium sulphide layers on glass with a PANalytical EMPYREAN X-ray diffractometer and evaluated with X'PERT reflectivity software.

For deeper characterisation detailed current–voltage–temperature (J–V–T) measurements were conducted for selected cells at the Warsaw University of Technology (WUT) in the temperature range of 100–330 K. Two light sources were used in this case: white and red LED ($\lambda = 620$ nm). Admittance spectroscopy and capacitance voltage profiling were performed at the same temperatures using a HP 4285A LCR meter in the ac frequency range of 200 Hz–500 kHz.

3. Results

3.1. IV results

3.1.1. Series A: Cu variation series 21 at.% and 23 at.%

For experiment series A a combined parameter variation of the processes for the absorber–buffer–window system was performed: CIGS with two different Cu contents (21 at.% and 23 at.%) was deposited with indium sulphide buffer with two different thicknesses (10 and 20 nm) and with different window layers (conditions not explained here). The influence of the buffer thickness and the sputter conditions of the window layer will be discussed in another publication. Fig. 1 shows the efficiencies of the cells for both Cu contents, 21 at.% and 23 at.% Cu, respectively. The corresponding samples for the individual variations are shown for each number. For many of the samples a slightly or considerably higher efficiency was observed for the lower copper content.

3.1.2. Series B: Cu variation series 19 at.% to 22 at.%

Based on the results of process series A, a second Cu variation was performed with further reduction of the Cu content from 22 at.% down to 19 at.%. The CIGS substrates were stored in vacuum about four weeks until the next deposition step. Most of the samples were etched with KCN prior to buffer coating to provide well-defined conditions on the absorber surface. Some samples were kept untreated to evaluate the influence of etching. No significant difference was observed for the non-treated cells. The experiment was also repeated in other series, and no certain trend could be identified.

In Table 1 the XRF results for the different CIGS absorber processes are presented. The values are given in atomic percent. The Cu content was varied by changing the Cu-rate with fixed conditions for the other elements. It should be noted that this slightly modifies the process, which might influence the cell properties.

Table 2 presents the corresponding I–V data of the cell series with indium sulphide buffer processed on absorbers of Table 1. The values of 60 cells in average are shown. The efficiency (eta) is enhanced by a better open circuit voltage (V_{OC}) and fill-factor (FF) for a copper content of 21 at.%. A further reduction of copper led to a decrease of the efficiency which is mainly caused by a drop of the short circuit current density (J_{SC}). Additionally the efficiency of an average of ten cells with CdS is presented. It has to be mentioned that the references were processed directly after CIGS deposition. For the CdS references a decrease in the performance is observed for Cu contents below 22 at.%. The average values of the sample series with In_xS_y buffer layer are lower than for the reference cells with CdS, also for the optimized performance at

Table 1
XRF data of CIGS series B with various Cu contents [at.%].

Cu	In	Ga	Se	CGI
21.8%	17.1	9.6	51.5	0.82
21.2%	17.2	9.6	52.0	0.79
20.1%	17.9	9.8	52.2	0.73
19.2%	18.4	10.1	52.3	0.67

Table 2
Average I–V data of 60 cells (sample series B) with a 10 nm indium sulphide buffer layer on CIGS with different Cu contents, including efficiency data of CdS references (average of 10 cells).

Cu	Eta [%]	V_{OC} [mV]	FF [%]	J_{SC} [mA/cm^2]	Eta [%] CdS
21.8%	14.9	679	67.8	32.4	16.7
21.2%	16.0	691	71.9	32.2	15.9
20.1%	14.3	682	69.4	30.2	15.0
19.2%	10.1	634	57.3	27.9	14.0

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