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Efficient Cu(In,Ga)(Se,S)$_2$ modules with sputtered Zn(O,S) buffer layer

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ABSTRACT

We demonstrate that a simple and low-cost industrial sputter process can be used to substitute the In$_x$S$_y$:Na buffer and intrinsic ZnO layer with a single film of Zn(O,S). Cu(In,Ga)(Se,S)$_2$ (CIGS) modules with an aperture area of 667 cm^2 and efficiencies up to 15.6% were prepared using a sputtered Zn(O,S) buffer layer. In comparison with our In$_x$S$_y$:Na reference, Zn(O,S) modules exhibit a superior short-circuit current which is overcompensated by a loss in the open-circuit voltage. The quality of the Zn(O,S)/CIGS interface, as judged from saturation current density and ideality factor, is close to that of the In$_x$S$_y$:Na reference. Electroluminescence images demonstrate a low and uniform recombination across the active module area. In first experiments, damp heat tests reveal a degradation in conversion efficiency of 4–6% relative. Hence, if the interface properties can be improved by further process optimization, the sputtered Zn(O,S) buffer is a promising candidate to increase the efficiency and reduce the costs of CIGS modules.

1. Introduction

Chalcopyrite-based (CIS) thin film technology attracts increasing interest in the photovoltaic community due to new record conversion efficiencies on laboratory (22.6%) [1,2] and module scale (17.9%) [3–5]. Accompanied by the increase in efficiency, the $/watt ratio is reduced by upscaling the production capacity and using more efficient and simple process steps. For the latter, a significant potential is exploitable in the buffer layer between the transparent ZnO:Al front electrode and the CIS absorber. The AVANCIS Cd-free buffer layer is based on In$_x$S$_y$:Na, deposited with a soft but more complex thermal evaporation process. Additionally, an undoped ZnO layer (i-ZnO) is sputtered on top. With the present results, we want to demonstrate that a simple and low-cost industrial sputter process can be used to substitute the conventional buffer and i-layer with a single film of Zn(O,S). Replacing the buffer/i-layer by Zn(O,S) was already investigated in an earlier work by AVANCIS in collaboration with the Helmholtz-Zentrum Berlin (HZB), using reactive radio frequency (RF) sputtering from a ZnS target [6–8]. Since then, the HZB further developed the Zn(O,S) deposition process, applying a non-reactive RF-sputter process using a ZnO/ZnS mixed target, leading to highly efficient Zn(O,S)-buffered CIS solar cells with conversion efficiencies exceeding 18% [9,10].

In this work, we investigate the RF-sputtered Zn(O,S) buffer layer developed at the HZB in AVANCIS R&D modules on a 10 × 10 cm^2 and 30 × 30 cm^2 scale. Furthermore, the influence of an additional i-ZnO film between the Zn(O,S) buffer and the ZnO:Al front electrode layer will be evaluated. Finally, we compare the results obtained with the simplified Zn(O,S) buffer stack and the In$_x$S$_y$:Na reference buffer in terms of electrical performance and damp heat stability.

2. Experimental details

The Cu(In,Ga)(Se,S)$_2$ (CIGS) absorbers used in the present study were fabricated according to the AVANCIS SEL-RTP process (stacked elemental layer – rapid thermal processing) [11]. The Zn(O,S) deposition was carried out at the HZB using a mixed target with a nominal composition of [ZnS] / ([ZnS] + [ZnO]) = 0.25. The process parameters are described elsewhere [10]. For shipping of the AVANCIS absorbers to the HZB labs, the 10 × 10 cm^2 and 30 × 30 cm^2 substrates were sealed in nitrogen atmosphere. Some absorbers were rinsed with deionized water and dried with nitrogen prior to shipping. After the Zn(O,S) deposition of typically 60 nm, the modules were transferred to the AVANCIS pilot line for further processing. Without any surface treatment, the i-ZnO film was deposited onto the Zn(O,S) buffer layer using RF-sputtering. Zn(O,S) modules which did not receive an additional i-ZnO film were transferred directly to P2-patterning and, subsequently, to the ZnO:Al deposition. After P3-patterning, edge-deletion and contacting, current-voltage (IV) characteristics were recorded under illumination and in dark conditions. Further IV-measurements were performed after encapsulation and light-soaking for approximately 48 h. All solar cell parameters presented in this paper were extracted from IV-curves measured after light-soaking.

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Table 1
Solar cell parameters of 10 × 10 cm² (aperture area of 48 cm²) and 30 × 30 cm² (aperture area of 667 cm²) modules with a Zn(O,S) buffer layer, with (w/) and without (w/o) an additional i-ZnO layer.

Module size	Eta_mean (%)		Jsc_mean (mA/cm²)		Voc/cell_mean (mV)		FF_mean (%)	
	w/	w/o	w/	w/o	w/	w/o	w/	w/o
10 × 10 cm²	14.1	14.2	37.4	37.6	569	580	66.1	65.3
30 × 30 cm²	15.6	15.4	38.7	38.9	586	585	68.7	67.8

3. Results and discussion

3.1. Scale-up to 30 × 30 cm²

In the first experiment, 10 × 10 cm² modules were prepared using a sputtered Zn(O,S) buffer layer deposited directly onto the CIGS absorber, without any surface treatment prior to deposition. Before encapsulation and light-soaking, the IV-curves showed kinks, resulting in low fill factors (FF) and, thus, poor efficiencies. After encapsulation and light-soaking, however, these kinks disappeared and efficiencies around 14% were reached. Table 1 summarizes the mean value of solar cell parameters for all 10 × 10 cm² modules, with (w/) and without (w/o) an additional i-ZnO layer, extracted from IV-characteristics recorded after light-soaking.

There is a small difference (0.2 mA/cm²) in the short-circuit current (Jsc) of the 10 × 10 cm² modules, which can be attributed to parasitic absorption in the i-ZnO film. In contrast, the additional i-layer shows a strong influence on the open-circuit voltage (Voc), resulting in a loss of ~2% in average. The loss in Voc is compensated by a slightly higher FF for modules with i-ZnO. In total, the efficiency with and without an additional i-layer is on the same level. The overall low fill factor is driven mainly by an elevated series resistance in both Zn(O,S) modules. A possible reason is a (photo-activated) potential barrier at the buffer/absorber interface which disturbs the carrier transport across the pn-junction, resulting in a distortion of the IV-curve under forward bias. This effect has been seen in earlier work but only at higher S/(S + O) ratios in the buffer [12,13].

In the follow-up experiment, modules with a size of 30 × 30 cm² were prepared. Here, the absorber was rinsed with deionized water and dried with nitrogen prior to Zn(O,S) deposition. As can be seen in Table 1, efficiencies of around 15.5% were reached. It should be noted that in this series there was only a small difference in efficiency before and after light-soaking. All modules revealed kink-free IV-curves with improved parameters as compared to the 10 × 10 cm² modules. Fig. 1 depicts the IV-characteristics of the best 30 × 30 cm² module, prepared with a Zn(O,S)/ZnO:Al stack (w/ i-ZnO). In average, the solar cell parameters exhibit the same dependency on the i-layer as observed for the 10 × 10 cm² modules, except for the Voc, which is similar for modules with and without an i-layer.

A possible reason for the strong improvement from 10 × 10 cm² to 30 × 30 cm² modules could be the surface pre-treatment. Sodium has been washed away during the surface cleaning, resulting in a dipole-free buffer/absorber interface [14] as well as higher effective doping in the absorber [15].

3.2. Comparison with a reference In_xS_y:Na buffer

We have shown that 30 × 30 cm² CIGS modules with a simplified Zn(O,S)/ZnO:Al stack can reach efficiencies in the mid 15%-range, independent of an additional i-layer. In the following, we compare the results obtained on 30 × 30 cm² Zn(O,S) modules with our reference process, using a thermally evaporated In_xS_y:Na buffer layer. The In_xS_y:Na layers are several tens of nm thick. Fig. 2 exhibits relative solar cell parameters of Zn(O,S) modules, with and without an additional i-layer, referenced to the averaged parameters of the In_xS_y:Na modules (dashed lines). The Zn(O,S) modules show a superior short-circuit current by 1.5–2.0% relative, which is overcompensated by a loss in the open-circuit voltage in the range of 6% relative, compared to the In_xS_y:Na reference. This trend is typical for the Zn(O,S) modules in comparison with In_xS_y:Na references. The elevated FF up to 2% relative, however, could not generally be observed for all Zn(O,S) modules.

Thus, by improving the Voc, while maintaining a high Jsc, an enhanced efficiency compared to the reference buffer seems to be possible. In order to get a better understanding of the origin of the gain in Jsc and loss in Voc, compared to the In_xS_y:Na reference, we will discuss both parameters in more detail in the following.

3.2.1. Short-circuit current

Fig. 3 depicts the external quantum efficiency (EQE) of cells (effective area of 1.34 cm²) prepared with a Zn(O,S) buffer layer (blue and red curves), in comparison with the In_xS_y:Na reference (black curve). In the blue spectral range, for wavelengths below 600 nm, a significantly higher quantum efficiency can be observed for the Zn(O,S) cells. The elevated EQE corresponds well with a higher transparency in this wavelength regime due to a slightly larger optical band gap of Zn(O,S) (~3.15 eV) compared to In_xS_y:Na (~3.10 eV), as observed in optical measurements of single films on glass. In addition, a slightly higher EQE for the Zn(O,S) cell w/o i-ZnO is observed for wavelengths below 400 nm, which correlates well with the absorption edge of i-ZnO

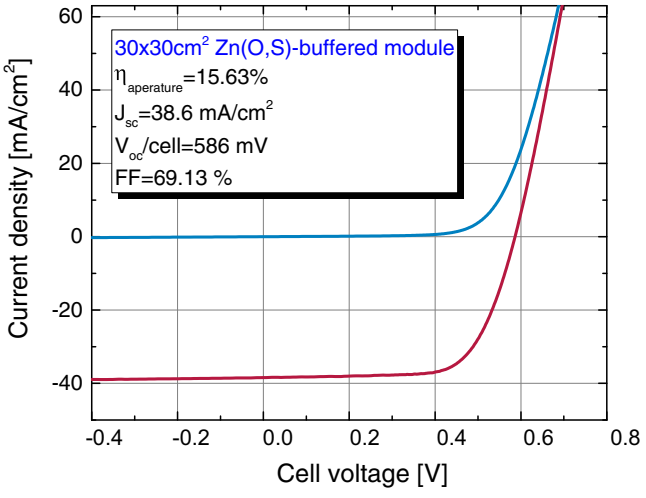

Fig. 1. IV-characteristics of the best 30 × 30 cm² module with a Zn(O,S) buffer layer w/ i-ZnO (in-house measurement).

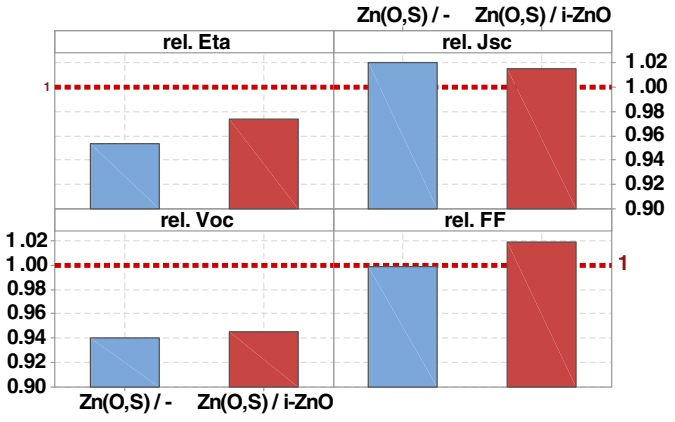

Fig. 2. Relative solar cell parameters of 30 × 30 cm² Zn(O,S) modules, referenced to averaged parameters of the In_xS_y:Na modules (dashed lines).

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