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Optimization of buffer-window layer system for CIGS thin film devices with indium sulphide buffer by in-line evaporation

S. Spiering [a,*], A. Nowitzki [a], F. Kessler [a], M. Igalson [b,1], H. Abdel Maksoud [b]

[a] Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) Baden-Württemberg Industriestrasse 6, 70565 Stuttgart, Germany
[b] Warsaw University of Technology (WUT), Faculty of Physics, Koszykowa 75, 00-662 Warszawa, Poland

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Compound In_2S_3 powder was evaporated on $Cu(In,Ga)Se_2$ substrates from the ZSW inline multi-stage co-evaporation process. Laboratory devices with the complete layer structure Mo/CIGS/In_2S_x/i-ZnO/ZnO:Al/Ni–Al grid on 0.5 cm^2 total cell area were prepared and analysed for their *J–V* characteristics. A post-annealing step in air after completing the device is essential to enhance the cell performance. In this work the influence of window process conditions like process temperature, layer thickness and sputtering gas composition on the cell characteristics was investigated. Electrical characterisation by temperature-dependent current voltage and admittance spectroscopy were performed to better understand the impact of buffer parameters on electrical transport. By optimization of the buffer layer thickness in combination with window layer variations, cell efficiencies $>16\%$ could be achieved. A record cell efficiency of 18.2% with anti-reflective coating was obtained.

1. Introduction

Indium sulphide is one of the most promising candidates for substituting the conventional chemical bath deposited (CBD) CdS buffer layer in $Cu(In,Ga)Se_2$ (CIGS) thin-film solar cells. The material is investigated in Europe by several groups with different deposition methods [1]. In terms of easy up-scalability and process implementation for roll-to-roll production, physical vapor deposition (PVD) processes like sputtering and thermal evaporation are the preferred deposition techniques.

In the last years, thermal evaporation of compound indium sulphide was studied for stationary processing with promising results [2,3]. Recently, we could demonstrate efficiencies up to 16.6% for a CIGS device with in-line deposited indium sulphide buffer [4].

In this work we investigated different process parameters for the buffer-window layer system for further optimization of cell performance. The thicknesses of the buffer layer and the following intrinsic ZnO-layer (i-ZnO) were varied. The interaction of these layers and their influence on the *J–V* performance was explored. Besides the thickness we also varied the oxygen flow during i-ZnO process. In former works it was shown that i-ZnO process conditions influence the layer properties and the resulting cell performance of CdS-containing devices [5].

A set of selected samples was characterized in more detail: current–voltage–temperature characteristics were measured and analysed, and admittance spectroscopy was employed as a tool for providing information on the potential distribution in a junction. The work aimed to explain the observed dependencies of the cell photovoltaic performance on the buffer-window process parameters.

2. Experimental

2.1. Cell preparation

In Section 3.1–3.4 the cell results of individual experiment series processed at different times are presented. Efficiency differences result from various absorber preparation in the experiments.

The complete cell processing was performed at the ZSW CIGS module technical pilot line. Multi-stage CIGS absorber was deposited on molybdenum-coated soda-lime glass for the buffer experiments. These substrates were stored in vacuum until cell processing.

Wet chemical treatment with KCN or other solutions prior to the buffer deposition did not show any beneficial effects for fresh substrates or when samples were processed within a few weeks. Only for long-term substrate storage, e.g. for one year, a clear enhancement of the performance could be achieved by etching.

Indium sulphide buffer layer was deposited by thermal evaporation of commercially available compound In_2S_3 powder which was pressed to pellets. The evaporation was performed at a source temperature of $\sim 750\,°C$. At the beginning of evaporation preferential

* Corresponding author. Tel.: +49 711 7870253.
E-mail addresses: stefanie.spiering@zsw-bw.de (S. Spiering), igalson@if.pw.edu.pl (M. Igalson).
[1] Tel.: +48 22 234 8214.

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sulphur loss is observed which leads to a sulphur deficient source material In_2S_x (x ~ 2.3). Prior to the buffer deposition we held the source at the deposition temperature for about two hours until the material composition stabilized. The thickness of the buffer layer was varied between 5 and 60 nm.

A double window layer of i-ZnO and ZAO is deposited by sputtering afterwards. The oxygen content in the sputter gas as well as the thickness of the i-ZnO layer was varied between 0.3% and 4.5% and 40–120 nm, respectively.

The cells are completed with a Ni–Al contact grid and the area is defined by a mechanical scribe to 0.5 cm^2. The devices are post-annealed in air for ~30 min at 200°.

2.2. Analysis and characterization

Current–voltage characteristics of the cell devices were measured at ZSW before and after post-annealing with an ORIEL sun-simulator at 25 °C and under AM1.5 illumination (1000 W/m^2).

The thicknesses of the buffer layers were partly analysed with a high-resolution scanning electron microscope (HRSEM) from FEI on cross-sections of indium sulphide on CIGS. As thickness determination from microscope images is difficult for very thin layers, reflectivity measurements were additionally performed on indium sulphide layers on glass with a PANanalytical EMPYREAN x-ray diffractometer and evaluated with X'PERT reflectivity software.

Detailed current–voltage–temperature (*J–V–T*) characterization was conducted for selected cells at the Warsaw University of Technology (WUT) in the temperature range 100–330 K. Two light sources were used in this case: white and red LED (λ=620 nm). The intensity of illumination was adjusted to give similar values of short circuit current as under the sun-simulator for a given device. The values of photovoltaic parameters obtained in these measurements as a function of temperature thus represent the trends.

Admittance spectroscopy was performed at the same temperatures using a HP 4285A LCR meter in the ac frequency range 200 Hz–500 kHz. Since metastable changes of the electrical characteristics due to prolonged illumination typical for the CIGS cells were observed, we have chosen to measure admittance spectra in the relaxed state of the device (after annealing in darkness at 330 K for 1 h). The *J–V–T* characteristics were measured after white light soaking for 1 h in order to operate at conditions typical for working cells.

3. Results and discussion

3.1. In_2S_x buffer thickness

Fig. 1 shows the *J–V* data for an experimental series of cell devices with different buffer thicknesses between 10 and 60 nm In_2S_x. The process conditions for the window layers were kept constant for all devices. The given data are average values of ten cells. The efficiency clearly decreases with increasing thickness. This is due to a decrease of all other *J–V* parameters.

Concluding from the performance of various deposition series, best results were obtained for cell devices with 10–15 nm indium sulphide buffer layer.

3.2. i-ZnO thickness and oxygen content

The oxygen content in the i-ZnO process was varied between 0.3 and 4.5%. In parallel, different ZnO thicknesses were deposited. Fig. 2(a and b) shows the *J–V* parameters for three different i-ZnO thicknesses between 40 nm and 120 nm in dependence of the oxygen content for non-annealed cells and the post-annealed cells, respectively. The thickness of the In_2S_x buffer layer was kept constant at ~10 nm.

The data show a clear difference between non-annealed and post-annealed devices. For the non-annealed devices a significantly lower FF is observed which is more pronounced with increasing thickness of the i-ZnO layer.

After annealing all devices show an improved cell performance with an efficiency level of ~15–16%. A higher V_{OC} is obtained for all devices, but the FF drastically increases especially for the cells with low performance before heat treatment. A possible explanation for this behavior is the passivation of defects and intermixing in the interface region [6]. Shimakawa et al. observed a recovery of defects at the interface by annealing for sputtered ZnMgO layers on CIGS [7]. Buffiére et al. stated a positive effect of lightsoaking for devices with chemical bath deposited Zn(O,OH,S) buffer and different iZnO layers [8].

The *J–V* data of the post-annealed cells show a slight tendency for improved performance with thicker i-ZnO up to an oxygen flow of 3%. Overall the differences in the results for the variations of ZnO oxygen flow and thickness are quite less significant as for the buffer thickness variation. As post-annealing is generally necessary for our

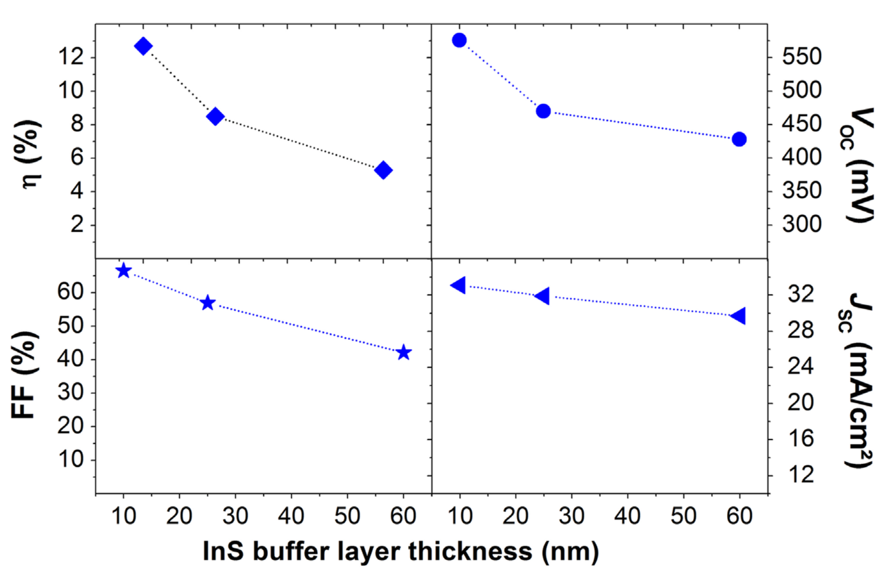

Fig. 1. *J–V* parameters of post-annealed CIGS cell devices with different In_2S_x buffer thickness (av. values of 10 cells, error bars are located within the scatters).