RbF post deposition treatment for narrow bandgap Cu(In,Ga)Se₂ solar cells

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Abstract

Multi-junction solar cells are known to have a considerably increased efficiency potential over their typical single junction counterparts. In order to produce low cost and lightweight multi-junction devices, the availability of suitable narrow (<1.1 eV) bandgap bottom cells is paramount. A possible absorber for such a bottom cell is the Cu(In,Ga)Se₂ (CIGS) compound semiconductor, one of the most efficient thin film materials to date.

In this contribution we report on the RbF post deposition treatment of narrow bandgap CIGS absorbers grown with a single bandgap grading approach. We discuss the necessary deposition conditions and the observed improvements on solar cells performance. A certified record efficiency of 18.0 % for an absorber with 1.00 eV

optoelectronic bandgap is presented and its suitability for perovskite/CIGS tandem devices is shown.

Highlights

- RbF post deposition conditions for low bandgap CIGS are investigated.
- A maximal efficiency of 18.0 % is achieved for an optoelectronic bandgap of 1.00 eV.
- Projections for 23.5 % tandem with a NIR transparent perovskite top cell are given.

Keywords

photovoltaics; Copper indium gallium selenide; Narrow bandgap; Thin film solar cells; Tandem solar cells; Rubidium fluoride; Post deposition treatment

1. Introduction

One of the most promising approaches to increase solar cell efficiency beyond the Shockley-Queisser (SQ) single junction limit [1] is the implementation of tandem device concepts. Calculations show that for double junction devices, the bandgap of the top-cell should be in the range of 1.5 to 1.7 eV, while the bottom-cell should have a bandgap close to 1.0 eV [2]. One of the promising technologies for such a bottom cell is Cu(In,Ga)Se₂ (CIGS) which has a tunable bandgap range down to 1.0 eV for CuInSe₂ and has shown very high efficiency up to 22.9 % for band gaps around 1.14 eV [3,4]. Recent important improvements in CIGS solar cells are due to the introduced post deposition treatment with heavy alkali fluorides in addition to sodium (from the substrate or externally supplied) [5–7].

Recently we have shown that the efficiency of solar cells with narrow bandgap absorbers can be improved significantly by implementing a single grading with increased bandgap towards the back contact [8]. While those cells already displayed significantly increased open circuit voltage (V_{OC}), the efficiencies are still lower than expected. Here in this paper we show further improvements with RbF post deposition treatments (PDT) on narrow bandgap CIGS and the resulting enhancements of photovoltaic properties.

2. Experimental details

CIGS absorber layers were deposited on Mo coated soda lime glass by multistage co-evaporation. The Ga back-grading was introduced during the first stage at a substrate temperature of approximately 390 °C, followed by a normal multistage CIS process with a maximal substrate temperature of 500 °C. The deposition was finished by evaporation of a short In capping layer at a substrate temperature of 380 °C and immediately underwent PDT treatment without any break of vacuum. The absorbers were treated with NaF first at a substrate temperature of 380 °C, followed by RbF with substrate temperatures as described below, 20 minutes each under a reduced Se flow. For the reference sample without RbF treatment the absorbers were post-annealed in Se only atmosphere for 20 min at 380 °C. A detailed schematic of the metal fluxes and temperatures during growth can be found in Figure 1.

All solar cells were finished with CdS buffer layer by chemical bath deposition (~60 nm for the untreated samples and ~35 nm for samples with RbF PDT) and a window layer using non-intentionally doped zinc oxide (~70 nm) and Aluminum doped zinc oxide (~200 nm) by radio frequency magnetron sputtering. Ni/Al grids and MgF_2 anti

reflection coatings were deposited by electron beam evaporation. For more details on the window layers see [9]. Cell size was defined by mechanical scribing and is approximately 0.57 cm^2 .

Current-Voltage (IV) characteristics were measured using a Keithley 2400 source meter in 4-contact sensing at standard test conditions (1000 Wm^{-2} , 25°C). A simulated AM1.5G spectrum from a class ABA solar simulator was used and the intensity was calibrated with a Fraunhofer certified silicon reference cell.

For external quantum efficiency (EQE) measurements we used a chopped halogen light source. The signal beam was monochromatized using a triple grating monochromator and a halogen light bias of around 0.2 sun intensity was applied during the measurement. Certified Si and Ge cells were used for calibration.

For temperature dependent IV (T-IV) and admittance measurements a vacuum stage with liquid nitrogen and heating elements for temperature control was used. All measurements were done in 4-terminal sensing, using a Keithley 2400 source meter and an Agilent E4980A LCR meter respectively. For the measurement of doping concentrations, the frequency was chosen in a region of flat capacity-frequency behavior over all temperatures investigated, in the presented measurements at 1kHz. Illumination for T-IV was supplied using a halogen light source and adjusted to yield the same short circuit current density as obtained by the solar simulator.

Alkali distribution in the samples was measured using time of flight secondary ion mass spectrometry (ToF-SIMS) on finished cells. The SIMS signals were normalized over the average Cu intensity in the region of flat Cu profile within the absorber, to prevent any influence from surface depletions. This allows comparing samples measured under different SIMS primary gun intensities (due to inevitable fluctuations).

Time resolved photoluminescence (TRPL) was measured using a 639 nm diode laser with a pulse duration of ~100 ps as excitation source. The spot size was adjusted to about 50 μm as determined with a beam profiler. An InGaAs photomultiplier in combination with time correlated single photon counting electronics was used for signal processing. Pulse repetition rate was approximately 1 MHz and the typically injected photon density per pulse was around $7 \times 10^{11} \text{ cm}^{-2}$ as estimated from total laser power measurements. For all TRPL measurements the front of the absorber was passivated with a thin layer of CdS.

Heat light soaking (HLS) was undertaken in a custom build oven using white light LED illumination of approximately 1 sun intensity and a temperature controlled measurement stage. In situ current-voltage measurements used 4-terminal measurement electronics. The atmosphere during the HLS was nitrogen at 500 mbar.

3. Results and discussion

3.1. PDT conditions

Starting from a back-graded CIGS as described before [8], we applied RbF PDT under different substrate temperatures (Figure 2) and evaporation rate conditions (Figure 3). While the substrate temperature shows a clear optimum close to 330 °C, the sublimation rate of RbF seems more forgiving, showing a wide region with high performance between 500 °C and 540 °C evaporation source temperature, corresponding roughly to a doubling of vapor pressure [10].

For all PDT conditions the main improvements can be seen in V_{OC} and short circuit current (J_{SC}). The current gain is partly explained by the reduced CdS thickness necessary for RbF treated samples as described before[5,11], but also contains a component of overall improvement of quantum efficiency response (see Figure 4 a). For high amounts of RbF (at 540 °C) efficiency of the solar cells is decreasing with a reduction in fill factor (FF) and current. Additional temperature dependent current-

voltage measurements indicate that a blocking of the photocurrent starts to appear for those cells (Figure 4 b+c).

3.2. Ageing behavior

In contrast to cells with a double Ga grading and wider bandgap [11], an improvement in cell properties over time is observed for all devices upon storage in dark (room temperature, in air) (Figure 5), an effect not seen for samples without RbF treatment. Improvements in V_{OC} lead to cell efficiency increase of about 5 % relative after 1 month. A similar effect is achieved by heat-light soaking (HLS) for about 2 hours at 80 °C, indicating the possibility of a kinetically hindered process. Comparing the apparent doping of the samples before and after ageing we notice a flattening of the doping profile, but no change in net doping concentration that could explain the improvements in V_{OC} as shown for HLS treatments by others [12]. Temperature depending V_{OC} measurements are indicating a change in recombination mechanism but further investigations are needed for a better understanding of this process. All data given outside of this section are stabilized values after ageing to ensure comparability.

3.3. Effects of RbF post treatment

We measured the alkali distribution within the absorbers and observed a substitution of Na and K by Rb within the front part of the absorber layer (Figure 6).

Similar behavior has been reported for state of the art CIGS absorbers [6,13], where a replacement throughout the absorber was observed. It has been shown that Rb tends to segregate at grain boundaries, replacing the lighter alkali elements[14]. We assume the difference between front and back stems from the particular morphology of the single graded cells, where the absorber changes strongly from a large grained surface area to smaller grains in the Ga graded part towards the back contact (see [8] for a comparison to ungraded samples). The supplied/diffused amount of RbF may not be enough to

saturate the high concentration of random grain boundaries towards the back of those samples, leaving room for the sodium to accumulate.

TRPL measurements show a significant increase in effective lifetime for absorber layers treated with RbF (Figure 7).

The effective lifetime extracted from the TRPL measurements increase from ~ 100 ns to over 400 ns in the case of RbF treated absorbers. This suggests that a reduction of non-radiative recombination is responsible for the enhancements. Admittance measurements show that the cells with RbF treatment have suppressed high temperature capacitance dispersion at low frequencies compared to the reference (Figure 7, b and c). This could be caused by a defect outside our measurement range or a reduction of tail states and inhomogeneities [15]. It is noted that a broad capacitance transition originates rather from the bulk (space charge region) of the absorber than from the interface [16], which hints to an improvement in the bulk of the absorber. For the main step, an activation energy around 125 meV is extracted (using the method described in [16]) for both cases, indicating that the underlying defect or barrier does not change with the RbF PDT.

3.4. Cell performance and tandem investigation

Figure 8 and Table 1 show certified photovoltaic properties for a cell fabricated with single Ga back grading and RbF PDT at 330 °C substrate temperature and a RbF source temperature of 500°C.

Comparison of the V_{OC} with the EQE band gap and the SQ limits shows a very low V_{OC} deficiency of around 405 meV and SQ- V_{OC} difference of 155 meV, comparable to top level solar cells with wider bandgap [4,17].

Finally, we investigated the potential of these cells for tandem application with perovskite top cells. We used the transmission data measured from a full perovskite top cell similar to the one published in [18] multiplied with the EQE response measured here to calculate the EQE and current density of the bottom cell in a 4-terminal configuration tandem device. Using a combination of long-pass (to prevent excitation in the CdS) and neutral density filters (to regulate the total illumination level) we then measured the bottom cell (called CIGS sub cell) under conditions reproducing the perovskite filter to determine the other solar cell parameters. The resulting projections are shown in Figure 9 and Table 2.

4. Conclusion

In this contribution we have shown that the efficiency of narrow bandgap single graded CIGS solar cells can be improved by RbF PDT. Optimized post deposition treatment conditions have been identified, displaying a strong dependence on substrate temperature during PDT. We have shown that the efficiency of those cells increases with certain ageing and that the improvements compared to non-treated cells result from a reduction of recombination, leading to a very low V_{OC} deficit.

A certified efficiency of 18.0 % has been achieved for a cell with an optoelectronic bandgap of 1.00 eV. We have shown that these cells are potentially suitable for tandem devices with perovskite top cells by demonstrating efficiency of 23.5 % in 4 terminal tandem configuration.

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Figures

Figure 1: Exemplary deposition profile for the growth of narrow gap CIGS with RbF post deposition treatment

Figure 2: PV parameters for cells with RbF PDT at different substrate temperatures. All RbF depositions were made using evaporation source temperature of 500 °C. Each dataset contains 18 cells.

Figure 3: PV parameters for cells with RbF PDT at different source temperature, representing different RbF effusion rates. All depositions were carried out at a substrate temperature of 330 °C. Each dataset except the last contains 18 cells. For 540 °C only 9 cells are included as half of that sample has been separated for additional measurements.

Figure 4: a) Comparison of the external quantum efficiency of samples with and without RbF post deposition treatment. b) + c) Temperature dependent IV measurements of

cells with different RbF post treatment flux. An additional blocking of the Photocurrent starts to appear at lower temperatures for the cells with high RbF flux.

Figure 5: a) Ageing behaviour of narrow bandgap CIGS showing increased V_{OC} at room temperature shelf storage over the course of a month. b) + c) Apparent doping for narrow bandgap cells with RbF before and after ageing.

Figure 6: a) SIMS depth profile for Alkali elements in a sample with and without RbF PDT. b) SEM cross-section of the sample with RbF shown in a).

Figure 7: a) TRPL decays for back graded cells with and without RbF PDT. b) Capacitance-Frequency plot of samples with and c) without RbF PDT. A high capacitance spread is visible at lower frequencies for the untreated samples.

Figure 8: a) JV and b) EQE of a CIGS with a bandgap of 1.00 eV certified at Fraunhofer ISE. The inset shows bandgap extraction by tauc fit of the EQE measured in house.

Figure 9: a) Measured EQE of narrow bandgap (narrow bg) CIGS and Perovskite top cells. EQE's for the narrow bandgap CIGS as well as a regular bandgap CIGS solar cell

[5] in 4-terminal configuration based on perovskite transmission are included as dashed lines. b) JV curves of the sub cells in the projected 4-terminal tandem. The CIGS bottom cell is measured using long pass- and neutral density filters to reproduce a 4-terminal tandem configuration.

Tables

Table 1: Certified J-V parameters for the device shown above. Designated illumination area of the cell was measured at $0.553 \pm 0.0034 \text{ cm}^2$.

	$V_{OC} \text{ (mV)}$	$J_{SC} \text{ (mAcm}^{-2}\text{)}$	FF (%)	Eff. (%)
CI(G)S certified	595.2 ± 2.0	41.96 ± 0.80	71.93 ± 0.47	$17.97 \pm 0.36^*$

Table 2: Solar cell performance data for the projected 4 terminal CIGS/Perovskite tandem device.

	$V_{OC} \text{ (mV)}$	$J_{SC} \text{ (mAcm}^{-2}\text{)}$	FF (%)	Eff. (%)
CIGS standalone	587	41.4	73.2	17.8
Perovskite top cell	1'115	19.2	75.2	16.1
CIGS-sub cell	550	18.4	73.0	7.4
Efficiency in 4-terminal tandem configuration				23.5