Efficiency Improvement of Near-Stoichiometric CuInSe₂ Solar Cells for Application in Tandem Devices

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State of the art Cu(In,Ga)Se₂ (CIGS) solar cells are grown with considerably sub-stoichiometric Cu concentrations. The resulting defects, as well as potential improvements through increasing the Cu concentration, are known in the field for many years. However, so far cells with high Cu concentrations shown decreased photovoltaic parameters.

In this work, it is shown that RbF post deposition treatment of CuInSe₂ solar cells allows to capture the benefits from the improved absorber quality with increasing Cu content. A reduced defect density and an increased doping level for cells with high Cu concentrations close to stoichiometry is demonstrated. Implementing a high mobility front TCO, the improved absorbers with 1.00 eV bandgap yield a solar cell efficiency of 19.2 %, and combined with a perovskite top-cell a 4-terminal tandem efficiency of 25.0 % is demonstrated, competing with the record efficiency of both sub-cell technologies.
1. Introduction

Structural defects play an important role in semiconductor materials and devices. Point defects especially, such as vacancies, impurities, antisites, and interstitials, as well as the defect pairs of those, are known to influence the electronic properties of the materials. The effects can be beneficial, as for the doping of the semiconductor, or detrimental by providing centers of recombination and trapping.[1,2] For highly efficient CIGS solar cells, semi-empirical optimization of the elemental composition lead to an optimum Cu to group-III element ratio (CGI) in the range of 0.80 to 0.90.[3–6] As a result of this off-stoichiometric, Cu deficient composition, a high density of native defects exist within the absorber layer.[7,8] The remarkably low formation energies of some of these defects results in the formation of defect complexes and possibly even phases of ordered defect compounds.[9–12]

Increasing the Cu content towards stoichiometry can considerably reduce the presence of such defects and defect complexes. It has been shown that stoichiometric Cu concentrations can be beneficial for absorber crystallinity,[13] defect density,[7,13] mobility,[14,15] and doping density.[14–16] Despite this, solar cells based on Cu stoichiometric CuInSe2 (CIS) have never reached efficiencies above 13.5 %,[7,17–19] while Cu deficient CIS yielded efficiencies only up to 15.0 %.[20] CIS cells with high CGI are mainly limited by a low open circuit voltage (VOC), and to a lesser extent, by a reduced fill factor (FF) and current density. However, the implementation of a Cu deficient surface layer has shown to recover the VOC loss in those high CGI cells, while a decrease in current density remains, attributed to tunneling recombination.[17,21] Similar improvements of the absorber surface have been achieved with alkali treatments after etching of the secondary phases in Cu rich samples, [22,23] although most recent results indicate this treatment may passivates defects that were at least partly generated by the etching in the first place.[24] This suggests that the front absorber surface limits the efficiency of Cu stoichiometric devices. Therefore, it is important to reduce the front interface recombination, besides any other, in such devices.
In an earlier publication, we have shown that ungraded CIS solar cells are constrained by recombination at the back interface,[25] which limits the solar cell efficiency. This back surface recombination can be effectively suppressed by the implementation of a single bandgap grading achieved by adding Ga close to the Mo back contact, leading to improved efficiencies up to 16.1 % with a bandgap of 1.0 eV absorber[25] and later to 18.0 % with application of a RbF post deposition treatment (PDT).[26] Those solar cells were processed with Cu deficient absorbers (CGI 0.85-0.90). CIS solar cells processed with high Cu content show lower VOC, and therefore lower efficiency. Believing in recombination as the root cause, we hypothesize that the application of heavy alkali PDT, for example with RbF, may suppress the recombination observed for absorbers with stoichiometric Cu concentrations. To investigate this, we processed and analyzed CIS based solar cells with various Cu concentrations and amounts of RbF during PDT treatment.

Here we report a large improvement in efficiency of solar cells processed with Cu composition close to stoichiometry. In addition to a large gain in VOC due to increased Cu content and RbF PDT, a higher current density is obtained by substitution of conventional aluminum doped zinc oxide (AZO) front contact with high mobility indium zinc oxide (IZO) to improve the near-infrared response. A maximum solar cell efficiency of 19.2 % is achieved. Due to the low bandgap (1.0 eV), such cells are highly suitable for tandem devices in conjunction with perovskite top cells. Such tandems represent one of the most promising technologies to overcome the thermodynamic limitations for single junction solar cells, the so-called Shockley Queisser limit. The combination of CIGS and perovskite is especially interesting in this field due to its all thin-film nature and the tunability of the bandgap of top- and bottom cells. This allows to carefully match the absorption of both partners, which is advantageous for 2- and 4-terminal devices. Here we show the efficiency gains when perovskite and CIS cells are used in 4-terminal tandem configuration.
2. Results

All solar cells in this study are processed with single graded absorbers with 1.00 eV front CIS layer while a small amount of Ga is present in a part of the layer close to the interface with Mo.[19] Fabrication details are reported in the experimental details. Figure 1 shows a combined picture of the changes in \( V_{OC} \) for samples with different amount of RbF and different concentrations of Cu in the absorber. The largest effect is seen in \( V_{OC} \), making it the best metric to compare the different experiments. Device efficiencies follow the \( V_{OC} \), as \( J_{SC} \) and FF vary to a lesser extent, following the same tendencies (see Figure S1). The Cu contents in this comparison are 0.87, 0.88 and 0.87 for the low CGI samples (no-, low-, and high RbF) and 0.93, 0.96 and 0.96 in the high CGI case. The respective error of measurement is 0.03 absolute. Concentrations above 0.96 lead to decreased \( V_{OC} \) (see Figure S2). The notation of low- and high- RbF refer to source temperatures of around 500 and 530 °C, respectively, corresponding to an expected doubling of the amount of evaporated RbF.

For samples without RbF, the \( V_{OC} \) is reduced when going to high CGI (\( \Delta V_{OC} \approx 20 \) mV), as described in the introduction. The external quantum efficiency (EQE) curve of those samples displays a decreased in maximum EQE value (Figure S3), consistent with the interface recombination described in literature.[17] Upon RbF treatment \( V_{OC} \) improves for cells with low Cu content, but the gain is considerably larger for cells with increased Cu content. For low CGI samples, a gain of about 25 mV is achieved with RbF PDT, similar to that observed with double-graded absorbers.[27,28] We have previously shown that this improvement is led by a substantial increase in carrier lifetime from about 100 to 400 ns.[26] The high Cu content samples show a remarkably higher improvement of ~80 mV with RbF treatment, yielding a \( V_{OC} \) of 611 mV (best cell value, \( 606\pm4 \) mV on 18 cells).

Figure 2 (a) shows the apparent doping density extracted from capacitance-voltage measurements on samples with a high amount of RbF during PDT. The apparent doping
increases by about half an order of magnitude. This increase in doping density is expected to reduce the width of the space charge region (SCR). In the investigated solar cells, the collection of charge carriers generated deep within the absorber appears unaffected by the reduced SCR width, EQE measurements even show a small increase in the near infrared region (Figure S4). This is believed to be caused by increased absorption for high CGI, similar to what has been previously shown.\[^{29}\] Improved mobility of charge carriers, as reported for stoichiometric absorbers in literature,\[^{14,15}\] could also contribute to their efficient collection.

The Urbach energy has been extracted from exponential decay fits to the EQE below the bandgap. The Urbach energy is reduced from approximately 20 meV to 16 meV upon the increase in Cu concentration, as shown exemplary in Figure 2 (b) for the high RbF cells. The behaviour is similar for cells with and without PDT. Above a CGI of approximately 0.95 no further reduction in the value of the Urbach energy is obtained (Figure S5). The Urbach energy is a measurement for potential fluctuations due to potential non-uniformities and fluctuating charges at defects in the absorber. Hence our results indicate a significant reduction in defect concentration with increased Cu concentration, independent of RbF treatment. Similar improvements have also been reported for double-graded absorbers.\[^{30}\]

Narrow-bandgap CIS cells are more sensitive to free carrier absorption in the transparent conductive oxide (TCO) front contact than CIGS, due to the extended NIR response. By replacing aluminium doped zinc oxide (AZO) with indium zinc oxide (IZO), the absorption losses in the near infrared region can be significantly reduced while maintaining comparable sheet resistance in the TCO, as shown in Figure 3 (b).

At comparable majority carrier concentration (IZO $3.6 \times 10^{20}$ cm$^{-3}$, AZO $4.0 \times 10^{20}$ cm$^{-3}$), the increased mobility (IZO $47.3$ cm$^2$V$^{-1}$s$^{-1}$, AZO $14.7$ cm$^2$V$^{-1}$s$^{-1}$) enables a reduction of the TCO thickness and free carrier absorption while maintaining the same sheet resistance. The gains in the NIR response are partially compensated by losses below 400 nm due to the
reduced bandgap of the IZO, resulting in a total increase of 0.5 mAcm\(^{-2}\) in current density. Using IZO as front contact, a solar cell efficiency of 19.2\% is obtained, with photovoltaic parameters given in Table 1.

As their spectral response extends in the NIR wavelength up to 1300 nm, we investigated those cells in 4-terminal tandem configuration with a semi-transparent perovskite top-cell. We use a methylammonium-lead-iodide perovskite solar cells in substrate configuration (glass substrate/In\(_2\)O\(_3\):H/PTAA/CH\(_3\)NH\(_3\)PbI\(_3\)/PCBM/ZnO nanoparticles/ZnO:Al/Ni-Al grid) as described in Ref.[31] These cells show an optical bandgap of 1.60 eV and a very little sub bandgap absorption. Using the transmission from the top cell and the CIS EQE we calculated that the bottom cell delivers a current density of 18.6 mAcm\(^{-2}\) (Figure 3 (c)). Reproducing this illumination with neutral density- and long-pass filters, a bottom-cell efficiency of 8.0\% (Figure 3 (d) and Table 1) is measured, and a tandem efficiency of 24.1\% is achieved in 4-terminal configuration. This is well above the efficiency of both sub-cells (+4.9\% vs. CIS, +8.0\% vs. perovskite), and well in the range of the current record efficiencies of both sub-cell technologies.[32,33]

Recently, after manuscript submission, an actual 4-terminal tandem device using these bottom cells was measured. The device uses a semi-transparent perovskite top cell provided by Solliance (\(V_{OC}\) 1,034 V; \(J_{SC}\) 20.79 mAcm\(^{-2}\); FF 79.8 \%; MPP Efficiency 16.9 \%). A cell like the one described above (single cell efficiency 18.7 \%) was used as a bottom cell (\(V_{OC}\) 0.565 V; \(J_{SC}\) 19.4 mAcm\(^{-2}\); FF 74.2 \%; Efficiency 8.1 \%), yielding a 25.0 \% tandem device.

The efficiency improvement of perovskite/CIGS 4-terminal tandem devices over the years are displayed in Figure 4
3. Conclusions

In this work we show that heavy alkali (RbF) PDT is effective to overcome the recombination issues in CIS based solar cells with Cu concentration close to stoichiometry. The quality of the absorber is improved with high CGI compositions, as assessed by an increase in apparent doping concentration as well as a reduction of defect density evidenced by decreases in Urbach energy. Using the improved processes overcoming some of the key limitations, we demonstrate a solar cell with a \( V_{OC} \) of 609 mV and a power conversion efficiency of 19.2% for an EQE bandgap of 1.00 eV. The increases in \( V_{OC} \) and FF are attributed to a decrease of recombination in the bulk as well as at the interface. We propose that the presence of an alkali-indium-selenide phase between buffer and absorber layer, suggested by multiple laboratories,\(^{[28,40,41]}\) possibly reduces the front interface recombination.

Combination of a 19.2 % CIS cell with a 16.1 % semi-transparent perovskite top cell enables a 4-terminal tandem device with an efficiency of 24.1 %.
4. Methods

*Solar cell fabrication:* CIGS absorbers were grown in a multistage evaporation process on soda lime glass with a sputtered Mo back electrical contact. The highest substrate temperature during growth was 500 °C and the deposition was finished with an in-situ post-deposition treatment with NaF followed by RbF. A detailed description of the growth conditions can be found in.[26]

After the absorber growth, all samples were etched in 5% KCN solution for 1 minute prior to deposition of about 35 nm CdS as a buffer layer using a chemical bath. Approximately 70 nm of non-intentionally doped zinc oxide was added by sputtering.

As a transparent electrical contact either aluminum doped zinc oxide (AZO) or indium zinc oxide (IZO) was applied. AZO was deposited by radio-frequency magnetron sputtering at room temperature, using a ZnO target containing 2 wt% Al₂O₃. Power density during sputtering was 2.5 Wcm⁻² and the sputtering gas was an argon-oxygen mixture with 1% oxygen. For the IZO a sputtering target with a composition of In₂O₃:ZnO, 89.3:10.7 wt% was used. Power density during pulsed DC sputter deposition was 0.81 Wcm⁻², substrate temperature 110 °C and the oxygen flow was 2.33 % of the total gas flow. Both TCOs were deposited in the thickness necessary to reach a sheet resistance of 60 Ω/sq, which corresponds to a thickness of ~200 nm for AZO and ~110 nm for IZO. A typical cross-section of the finished device is shown in Figure 4 (a). The CIS layer shows smaller grains in the graded part of the absorber, as previously reported.[25]

All solar cells were finished with Ni/Al grids and an MgF₂ anti reflection coating. Cells of approximately 0.57 cm² were separated by mechanical scribing and the exact area of each cell was determined by optical scanning at 4800 dpi.

All cells underwent 24 h heat light soaking at approximately 1 sun illumination at 80 °C under nitrogen atmosphere as described before.[26]
Absorber and device characterization: Absorber composition was analyzed by x-ray fluorescence (XRF) after the growth. Because of re-absorption of the secondary x-ray emission, it is important to compare only absorbers with similar composition grading. We used inductively coupled plasma optical emission spectrometry (ICP OES) to calibrate the emission for multiple samples within this series. An experimental error (2σ) of ±0.03 on the Cu / III ratio remains for the XRF, therefore we measured key concentrations by ICP OES confirming the results within ±0.01 (Table S1).

Current-Voltage (IV) characteristics were measured in a 4-contact mode at standard test conditions (1000 Wm⁻², 25 °C, in air) using a Keithley 2400 source meter. A class ABA solar simulator was used to simulate the AM1.5G spectrum and the light intensity was calibrated with a silicon reference cell certified by Fraunhofer ISE.

EQE measurements were performed using a Stanford Research SR830 DSP lock-in amplifier and a monochromator to filter the halogen light source. A halogen light bias with approximately 0.2 sun intensity was applied during the measurement. Certified Si and Ge cells were used for calibration.

To quantify the tandem performance, the perovskite top cell was measured as described above. No pronounced hysteresis was found and the reported efficiency is taken after MPP tracking for 60 min. To measure the bottom cell performance, the IV response under filtered (neutral density- and long pass (780 nm) filters) illumination was taken. In that case, the illumination intensity was adjusted to reproduce the integrated EQE current obtained by multiplication of the top cell transmission with the bottom cell quantum efficiency.

Admittance was measured on a temperature-controlled vacuum stage in a 4-contact sensing mode. An Agilent E4980A LCR meter was used, measuring at 1 kHz and with a test signal of 30 mV.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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15516–15528.
Figure 1. Open circuit voltage of solar cells with low (~0.88) and high (~0.96) \([\text{Cu}] / ([\text{Ga}] + [\text{In}])\) composition and different amounts of RbF post treatment. For samples without RbF treatment a clear decrease in \(V_{\text{OC}}\) is visible, while samples with RbF show a clear improvement. The cell efficiencies follow the same trends (Figure S1).

Figure 2. (a) Apparent doping density from capacitance-voltage measurements at high RbF rates for samples with low (0.87) and high (0.96) Cu concentrations. (b) Urbach energy as extracted from EQE measurements of the same samples. The black lines show the exponential fits.
**Figure 3.** (a) SEM cross-section of the device with IZO as front contact. (b) Dashed line: Absorbance of AZO and IZO layers on soda lime glass, both with a sheet resistance of approximately 60 Ohm/square. Solid lines show the EQE curves of the resulting solar cells. Clear gains in the near infrared are partly compensated by losses in the blue region. (c) EQE and (d) J-V curves of the best CIS in this work under AM 1.5G illumination, as well as with filtered illumination representing a 4-terminal configuration with a semitransparent perovskite top cell. The EQE and J-V curve of the corresponding perovskite top-cell is shown in blue.

**Figure 4.** Development of record efficiency for 4-terminal CIGS/Perovskite tandem devices. The devices with contribution from our lab are marked with a star. Sources for the performance data are given in the references[31,34–39].
Table 1. IV-parameters of the best cell with 1.00 eV CIS absorber in standalone and 4-terminal tandem configuration with a NIR transparent perovskite top cell. For CIS bottom-cell measurements in the tandem device, illumination was realized using a combination of neutral density and longpass filters.

|                    | $V_{oc}$ (mV) | $J_{sc}$ (mA cm$^{-2}$) | FF (%) | Eff. (%) |
|--------------------|---------------|--------------------------|--------|----------|
| CIS standalone     | 609           | 42.3                     | 74.6   | 19.2     |
| Perovskite top-cell| 1'115         | 19.2                     | 75.2   | 16.1     |
| CIS bottom-cell    | 581           | 18.6                     | 74.2   | 8.0      |
| Efficiency in 4-terminal tandem configuration |               |                           |        | **24.1** |
CuInSe₂ thin film solar cells are grown with almost stoichiometric absorber compositions. The performance degradation commonly observed for such high copper contents is prevented by the implementation of a RbF post-deposition treatment. Improvements in carrier concentration and defect density results in cell performances up to 19.2% at a band gap of 1.00 eV and 24.1% in a 4-terminal tandem configuration with a perovskite top-cell.

Photovoltaic Devices

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Supporting Information

Efficiency Improvement of Near-Stoichiometric CuInSe₂ Solar Cells for Application in Tandem Devices

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**Figure S1.** Photovoltaic parameters for CIS solar cells with low (~0.88) and high (~0.96) [Cu]/([Cu]+[In]+[Ga]) compositions and different amounts of RbF post treatment. The main effect is seen in the open circuit voltage, although the other parameters follow the same trends of improvement/decrease.
Figure S2. Photovoltaic parameters of CIS solar cells with increasing [Cu]/([Cu]+[In]+[Ga]) (CGI) composition and low amounts of RbF post treatment. The decrease seen for cells without RbF is not visible anymore, and an increase in the PV parameters is observed up to a CGI of approximately 0.96.
Figure S3. EQE curves of cells without RbF treatment and different Cu concentrations. A decrease in the short wavelength region is consistent with possible recombination at the front interface. The absorbers with near stoichiometric composition exhibit an increase in the near infrared region, attributed to increased optical absorption and possibly to improved charge carrier collection due to reduced defect concentration and increased carrier mobility.

Figure S4. EQE curves of samples with high amounts of RbF, with low and high CGI. A clear improvement is visible in the near infrared region, indicating increased optical absorption and improved collection.
**Figure S5.** EQE curves (log scale) and Urbach energy for samples with increasing amount of Cu (low amount of RbF during PDT). The Urbach energy decreases with increasing Cu concentration until it saturates at around 16 mV with a CGI of approximately 0.95.

**Table S1.** [Cu]/([Ga]+[In]) ratio as measured by XRF and by inductively coupled plasma optical emission spectrometry (ICP-OES) for improved precision. The offset found is within ±0.01.

|          | Low RbF series | High RbF series |
|----------|----------------|-----------------|
| XRF      | 0.88           | 0.95            |
| ICP-OES  | 0.87           | 0.95            |
|          | 0.96           | 0.96            |